国际工程科技发展战略高端论坛
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中国工程院
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膜技术在水和气体净化中的应用

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MEMBRANE TECHNOLOGY FOR GAS AND LIQUID SEPARATIONS AND PURIFICATIONS

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内容提要

膜技术在水和气体净化领域的应用已成为全球环境保护的重要措施之一。根据2013年中国工程院举办的国际工程科技发展战略高端论坛——“膜技术在水和气体净化中的应用”，十余位来自美国、欧洲、新加坡及我国顶级膜技术领域的专家就膜技术在污水回用领域的应用、海水淡化采用膜技术的经济性、气体膜在石化领域的应用以及未来膜技术的发展趋势等议题进行了深入的研讨。其中，欧洲膜材料协会主席 Enrico Drioli 和新加坡膜技术中心教授 Tony Fane 针对新型膜过程如膜蒸馏、正渗透、膜乳化、膜冷凝、膜结晶等的最新研究进展进行了深入讲解；美国工程院院士 William J. Koros 针对气体分离膜材料和气体分离膜应用等进行了全面介绍。全书重点介绍了膜过程、膜材料、膜应用等研究领域的最新进展。书中既有概括性的论坛综述，也提供了各位专家的报告内容。

本书是中国工程院国际工程科技发展战略高端论坛系列丛书之一，具有较为重要的参考价值，可供国内外相关科研院所从事膜技术领域研究的人员及高校师生参阅。

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一、引　言

2013 年 10 月 16 - 17 日，由中国工程院主办的“膜技术在水和气体净化中的应用”国际高端论坛在中国科学院过程工程研究所举行。中国工程院院士高从堦、侯立安、曹湘洪参加论坛，来自海外以及全国相关科研院所及高校的 160 多名代表参加了这一膜技术领域的高端盛会。

本次论坛特邀了美国工程院院士 Norman Li、美国膜材料协会主席及美国工程院院士 William J. Koros、欧洲膜材料协会主席 Enrico Drioli 等在膜技术研究领域有影响力的知名专家学者到会作主旨报告，以膜技术在水和气体净化中的应用为主题，重点就膜过程、膜材料、膜应用等研究领域的最新进展进行专题报告。欧洲膜材料协会主席 Enrico Drioli 和新加坡膜技术中心教授 Tony Fane 针对新型膜过程，如膜蒸馏、正渗透、膜乳化、膜冷凝、膜结晶等的最新研究进展进行了深入讲解；美国工程院院士 William J. Koros 针对气体分离膜材料和气体分离膜应用等进行了全面介绍。

与会中外专家学者就膜技术在污水回用领域的应用、海水淡化采用膜技术的经济性、气体膜在石化领域的应用以及未来膜技术的发展趋势等问题进行了深入研讨。

膜技术在水和气体净化领域的应用是全球的发展趋势。各种耦合技术，如反渗透与正渗透耦合以降低能耗和产水成本、反渗透与膜蒸馏技术的耦合以实现零排放为目标将是未来膜技术在污水回用领域的发展趋势。未来对膜过程的研究主要是如何降低膜过程的能耗。

二、报告内容

（一）膜过程——创新的过程工程

1. 膜技术在过程强化中的应用

目前，膜工程对各个领域的影响不断增加。海水和苦咸水脱盐、工业水的回

用、废水处理、气体分离、膜生物反应器（MBR）、人工合成有机物工业均为膜过程成功的典型案例。其他膜过程，如 MBR 被认为是最可行的技术。膜成功应用的动力在很大程度上源自膜的基本特性，如节能、环境影响小、无化学试剂及易于自动化等。这与过程强化战略紧密相关。

目前，全球所面临的关键问题是如何维持工业的稳定增长，过程强化是可行的解决方案，膜在过程强化中起到重要作用。它具有替代传统能量强化技术的潜力，实现特种组分的选择性和高效传递，提高反应过程性能。在膜的运行系统中，反渗透（RO）膜系统的脱盐效率是热法的 10 倍；MBR 的紧凑程度是传统淤泥法的 5 倍多；燃料电池与 RO 单元组合的效率是热法的 16 倍。

海水脱盐所用膜的产能为430 亿 t/d，占整个脱盐市场的63%，脱盐市场不断增长，其中海水反渗透脱盐将占到反渗透脱盐技术的80%。

2. 绿色、环境友好的溶剂/稀释剂

在过去的30 年中，聚偏氟乙烯（PVDF）作为制备膜的合适材料，已广泛用于制备 MF/UF 膜。PVDF 膜的制备方法为相转化法。相转化包括非溶剂诱导相转化（NIPS）和热致相分离（TIPS）。近年来，通常采用 TIPS 法制备 PVDF 膜。

在用 TIPS 法制备 PVDF 膜的过程中，稀释剂非常重要，其影响 PVDF 膜的形态、结构和性能。在高温下用 TIPS 法制备膜的合适稀释剂，应该与聚合物有相容性、具低挥发性和良好的热稳定性。另外，稀释剂相对分子质量较低、低毒及环境友好。Enrico Drioli 教授在报告中总结了 1990—2012 年相关文献用 TIPS 法制备膜的稀释剂，如邻苯二甲酸酯、邻苯二甲酸二辛酯（DOP）、人造的酞酸二丁酯、二苯（甲）酮、碳酸二苯酯等。

意大利国家研究理事会膜技术研究所的 Enrico Drioli 教授带领他的课题组用广泛接触食物类聚合物（聚乳酸）的增塑剂乙酰基柠檬酸三丁酯（ATBC）作为制备 PVDF 的稀释剂。ATBC 为水性和油性聚合的增塑剂，这些聚合物包括丙烯酸、甲基丙烯酸等聚合物体系。与 DOP 相比，制备硝酸纤维素薄膜时，它有许多改进，如低毒、寿命长。

3. 膜技术发展的新型膜过程

膜蒸馏：膜技术与蒸馏过程相结合的膜分离过程，它以疏水微孔膜为介质，在膜两侧蒸气压差的作用下，料液中挥发性组分以蒸气形式透过膜孔，从而实现分离的目的。膜蒸馏的优势有：理论上的 100% 截留率；占地面积小、结构紧凑、建设费用低；操作温度低、可利用废热、操作压力低，设备投资少，过程更安全、更容易操作等。

膜结晶：由膜蒸馏发展而来。与传统结晶技术相比，膜结晶的优势主要有：传

质面积大、诱导周期短、能够优化控制过饱和程度、异相成核的表面效应、由于聚合物膜表面导致成核自由能的降低、可控制低过饱和程度下的晶体成长速率、可控制晶型、晶体尺寸均一、晶体尺寸分布窄。膜结晶过程主要用于生产催化剂晶体以及无机、有机或生物材料的结晶,用于耐溶剂结晶过程、选择性的多晶形物结晶等。

膜乳化:膜乳化技术是1988年由日本科学家提出的新型乳化方法,该法是在一定的压力下,将分散相通过微孔膜分散到连续相中,其显著特点是乳状液液滴大小主要由微孔膜孔径来控制而呈单分散性。与传统乳化技术相比,膜乳化的优势有:能耗低、制备条件温和、可形成单分散胶团/微粒、胶团/微粒尺寸和形状均匀、通过改变膜孔尺寸和操作条件可以调控胶团/微粒的大小等。膜乳化作为一种新型的乳状液制备技术,可以制备各种类型粒径的单分散乳状液。膜乳化过程在食品乳状液、药物控释系统、单分散微球(囊)的制备等诸多领域有着广泛的应用前景。

膜冷凝:作为一种清洁的单元操作,膜冷凝可以作为废气的一种预处理手段,如作为CO_2废气进入另一个膜单元之前的预处理手段。与致密膜相比,膜冷凝操作压力低;与常规冷凝相比,膜冷凝没有腐蚀现象。

目前,耦合膜过程优势明显,其中,FO-RO耦合脱盐过程备受关注,该过程的分离原理是,待处理废水经过适当预处理后,泵入FO单元的进料液侧,将经过适当预处理的海水泵入FO单元的驱动液侧,通过FO膜,进料液侧待处理废水中的水通过FO膜进入到驱动液侧的海水中,进料液侧的废水被浓缩,而海水被不断稀释,被稀释后的海水再泵入反渗透系统进行处理,通过RO,获得产品水和RO浓水。该过程的技术目标是实现电耗低于2.5 kW·h/m^3,主要通过三方面实现:① 将水回收率再提高30%;② 浓水再减少30%;③ 产水的价格实现0.6美元/t。该耦合过程的研究重点主要集中在:① FO-RO耦合过程的研究(包括原理、系统设计、系统结构等);② 新型FO/RO膜材料的研究;③ 污染控制技术研究;④ 预处理技术研究。

此外,MD/PRO耦合脱盐过程也是一个研究热点,常规海水脱盐系统的回收率小于40%~50%,通过这一耦合过程,可以处理反渗透海水淡化后的高含盐水,可将高含盐水排放量减少到30%,能量回收5 W/m^2,实现水和能量资源的高效利用。

目前,GE正在开展采用膜蒸馏技术浓缩高盐度废水(TDS 150~230 g/L)项目,膜蒸馏过程中没有膜性能的下降和膜结垢现象,目前GE正在寻找合适的试验地点,预计2014年膜蒸馏有可能会实现商业化模式运行。

4. 未来努力方向

为了适应主体和环境的变化，开发一系列新的、不同性能的膜。巧妙的质量/热传递规律；对危险环境（如军事、极限运动、空间站等）的自我维护及适应性；抗污染性、可冲洗性及自清洁性；对有害液体、辐射热、紫外及化学和生物试剂有更高的防护性；膜保护层的自修复；在极端环境和运行条件中具有更好的力学性能和耐化学性；膜用于长距离通信、数据存储和检测的传感器；开发预测材料的性能的模型。

（二）中国膜科学技术发展的概况

1. 膜技术在中国的发展历史

中国膜技术始于20世纪50年代，在90年代后期得到迅速发展，90年代RO/NF膜技术已经由实验室研究转向中试化研究，此时开始进行气体分离膜方面的研发，对于氮气、氢气的分离已取得较好的效果，还有一些专家进行了渗透蒸发、膜蒸馏、膜反应器等方面的研究，从2000年到目前，膜科技在中国取得了显著进步，出现了一些新的膜材料（PVDF、PES、PP等）、制备方法（NIPS、TIPS等）、新的膜过程（MD/MBR）等。

2. 中国膜科学技术的现状

最近几年，膜分离技术的发展得到了国家相关部门的高度重视，国家重点基础研究计划（“973”、“863”）和国家自然科学基金项目均对膜研究给予专项资金支持，从而使得我国的膜分离技术取得很好的成就。目前，中国膜研究机构及公司有1000多家，约有300多家公司可以生产膜，如膜天、赛诺等；研发成果也已经在工业处理、海水淡化等领域得到应用。

3. 典型膜技术

（1）MF/UF

主要介绍了两种材质的膜，即PVDF和PVC，PVC膜由于具有优良的化学稳定性、成本低，且具有较高的性能，被广泛应用，此膜材料主要采用NIPS方法进行制备。台湾高雄自来水厂采用海南立昇公司生产的PVC超滤膜建成亚洲最大的超滤自来水生产厂，规模达到30 m^3/d。结合膜天公司采用TIPS法生产的PVDF超滤膜，介绍了TIPS膜制备方法的发展。TIPS膜制备方法的关键是选择合适的溶液完成PVDF膜的液液分离。

（2）NF/RO

由均苯三酰氯与芳香二胺通过界面聚合形成聚酰胺复合膜是目前海水淡化反渗透膜的主要制备方法。我国长春应用化学研究所自行设计制备的基于联苯

四酰氯（BTEC）、联苯三酰氯（BTRC）、芳香三胺（TAM）等新型单体的新的聚酰胺膜材料，突破了由均苯三酰氯（TMC）与芳香二胺制备反渗透复合膜的限制，研究结果表明基于三胺单体的反渗透复合膜，TMC 膜比 MPD 膜水通量提高近 30%，为进一步优化成膜工艺制备提供可产业化的新型反渗透复合膜奠定基础。目前我国生产的反渗透膜元件达到国外先进水平，市场的占有率也在逐步增长，初步具备与国际抗衡的水平。

（3）气体分离膜

已应用于气体分离领域的高分子材料有 PDMS，PI，PMP，PPO，PT 等，中国科学院大连化学物理研究所与中海油合作，将膜分离技术用于低品位天然气中回收甲烷、轻质油及液化气，总投资近 500 万，年处理量为 1360 万 Nm^3，解决了单井气田气源不稳定、CO_2 含量高（80% 以上）等技术难点。

（4）其他一些典型的膜材料

A. 沸石分子筛膜

沸石分子筛膜是将沸石制备成厚度为微米级的薄膜，实现分子的分离，重点介绍了 NaA 型和 MFI 型沸石膜。国内不少大学都在研究沸石膜的制备，不过目前尚未有工业应用实例，到目前为止，仅日本某企业在 20 世纪 90 年代成功建成并投产了一套 NaA 沸石膜的工业装置，该装置用于醇/水分离。

B. 金属膜

金属膜具有良好的塑形、韧性和强度以及对环境和物料的适应性，因此得到关注。主要是钯膜、多孔 Ti－Al、Fe－Al 复合膜等。

4. 在中国膜技术发展趋势及其面临的挑战

国家“十二五”计划将重点扶持膜科技发展，膜产值到 2015 年要达到 1000 亿元，所以中国膜技术发展空间很大，极具潜力。

提到膜科技发展基础研究方面的三个问题：

1）如何通过环境与分离性能关系提升膜过程的工艺设计水平；

2）如何通过分离性能与材料结构关系将膜过程的设计从工艺设计推进到微观结构的设计；

3）在应用过程中膜的浓差极化。

（三）膜和水的发展现状

目前新加坡获取淡水资源的途径主要有以下三方面：雨水收集、海水淡化和废水回收。其中，雨水收集系统主要处理的是地表水资源，采用微滤膜（MF）和超滤膜（UF）过滤技术；海水淡化采用的是反渗透（RO）脱盐技术，过滤成本较大；工

业和生活废水的回收采用反渗透或是纳滤技术(NF)过滤二级处理水,以节约成本。这三种水处理技术均是通过膜技术来实现。膜技术已经成为新加坡获取淡水资源的中坚力量。从 Tony Fane 教授提供的数据可以看到,2010 年新加坡通过海水淡化技术为其国内提供了 10% 的水资源,而 2060 年这一数字将提高到 30%;另外,在 2010 年新加坡通过废水回收技术为其国内提供了 30% 的水资源,而 2060 年这一数字将提高到 50%。现在,每天通过膜技术处理的水量已经达到了 1 Mt,对于新加坡如此小的国土面积,这样的处理能力可谓相当可观。

1. 新型膜和膜过程

(1) 反渗透

反渗透(RO)技术是目前海水淡化工厂最常采用的工艺。近年来建造的海水淡化工厂规模越来越大。更多的处理量要求意味着更大的膜组件,对膜通量的要求也更高,这些方向也是膜科学中心的研究热点。目前提高膜通量的一种研究方向是在膜片中添加带有孔道的纳米物质,比如碳纳米管、沸石、石墨筛等无机材料。另外一种是根据仿生学原理,在反渗透薄膜中添加水通道蛋白,这种方法对膜通量性能的提高非常明显,从而减少水处理工厂的能源浪费。但是由于浓差极化(CP)的影响,膜片通量的提高并不意味着膜组件通量的提高。为了降低浓差极化的影响,需要改进膜组件的设计,比如对导流网的重新设计、膜组件之间连接方式的改进等。

(2) 正渗透

正渗透(FO)的低能耗和能量回收优势,使其成为一个热点问题,它是一种依靠渗透压驱动的膜分离过程,即水通过选择性半透膜从较高水化学势区域(低渗透压侧)自发地扩散到较低水化学势区域(高渗透压侧)的过程。正渗透过程的驱动力是驱动液与原料液的渗透压差,不需要外加压力作为驱动力。与反渗透过程相比,正渗透具有如下优点:膜污染较轻、无需外加压力、能耗低、回收率高、浓水排放量少、污染小、环境友好。在 FO 过程中,膜是一个关键因素。近来,SMTC 已经制备出用于 FO 过程的平板膜和中空纤维膜。

(3) 膜蒸馏

膜蒸馏(MD)凭借其高水回收率、高脱盐率而备受关注,它能处理反渗透不能处理的高盐水,并且可利用工业废热。膜蒸馏是采用微孔疏水膜,以膜两侧蒸汽压差为驱动力的一种新型膜分离过程。它可以算是迄今为止脱盐效率最高的膜技术。膜蒸馏所用的膜为不被待处理溶液润湿的疏水微孔膜,即只有蒸汽能够进入膜孔,液体不能透过膜孔。用于膜蒸馏过程的膜需要有强疏水性和高孔隙率,目前 SMTC 已开发了超疏水膜蒸馏膜的制备技术。

（4）延迟渗透

将正渗透膜稍微改进,就可用于延迟渗透(PRO)膜过程。PRO 过程可以根据盐梯度产生能量,如根据海水/河水的含盐量梯度,用于海水/河水处理。近来,SMTC 已经制备出用于 PRO 过程的平板膜和中空纤维膜。

（5）膜蒸馏结晶

膜蒸馏结晶(MDC)是由膜蒸馏演变而来,对于经过反渗透海水淡化后的浓水以及其他的浓缩盐类,可以通过膜蒸馏结晶处理来分别回收水分和盐类固体。膜蒸馏结晶过程的两个难点是需要将结晶过程控制在膜组件外部结晶,并且需要优化整个过程的能量利用。过程的权衡以及优化控制可以采用 Aspen 模拟软件模型模拟。

（6）新型膜生物反应器(MBRS)

SMTC 在常规膜生物反应器的基础上,正在致力于开发新型膜生物反应器,如膜蒸馏生物反应器(MDBR)和正渗透生物反应器(FOBR)。MDBR 和 FOBR 均是具有高截留率的膜生物反应器(HRMBR),它们采用特种膜,都可以在ORT >> HRT 下运行,为难降解物质的处理提供充分时间。这两种膜生物反应器的优势是都可以利用低温热、产水水质更好。HRMBR 的特点是盐类可以大量累积,这样就需要适盐菌。此外,MDBR 也需要最低能耐 55℃的嗜热菌。MBR 也改进为流化床厌氧膜生物反应器,流化床厌氧膜生物反应器的优势是污染少、沼气量小。另外,萃取膜生物反应器可用于进料废水里有机溶剂的萃取过程。接下来几年内,MBR + RO 将成为污水处理回用的发展趋势。

2. 未来的展望

膜法污水回用是全球的发展趋势,膜法污水回用过程中,RO 仍是主导,但是在反渗透膜、膜组件以及操作模式上尚需改进和提高。FO 和 MD 凭借其能量再生优势,在水回用方面的作用越来越突出。

未来对膜过程的研究主要是如何降低膜过程的能耗。未来的主要研究方向主要集中在:① 低能量消耗的预处理工艺;② 高通量反渗透膜的制备;③ 耦合工艺,如 FO - RO - PRO 的发展;④ 新型污染控制技术的开发;⑤ 厌氧工艺的使用;⑥ 苦咸水浓缩。上述问题的解决,可有效提高膜技术在水回用领域的优势。

（四）我国饮用水安全及膜法水处理应用现状

1. 饮用水安全概述

世界卫生组织(WHO)调查资料显示,全世界约 80% 的疾病和 50% 的癌症与饮用不洁的水有关。当今,中国工业高速发展,人民享受经济发展的成果,然而,

我国的环境日益成为最重要的问题,特别是水资源安全。没有安全的水资源社会的可持续发展无法实现。在中国,饮用水安全包括两个方面:一个是在特定时间和区域因为大雨从而导致洪水泛滥;另一个是由于污染或干旱导致水资源短缺。

在过去的20年里,中国的洪水灾害不断增加,如何使用雨水作为饮用水,特别是在雨期,是一个热点问题。在干旱地区,地下水是最重要的饮用水来源,但一些二价离子如砷和溴等将造成严重的健康危害,需要除去这些有害物质。在中国的东部和南部,虽然有很多河流和湖泊,但水污染很严重,污水处理和减少排放被认为是保护水资源的两个有用的方法。

2. 饮用水安全面临的挑战

1)我国水资源总体现状堪忧:① 水资源匮乏;② 水资源分布不均;③ 地下水水质恶化;④ 湖泊水质堪忧。

2)污染物种类多元化:① 悬浮物污染;② 氮磷有机物污染;③ 重金属污染;④ 酸碱污染;⑤ 难降解有机物污染;⑥ 放射性物质污染;⑦ 热污染;⑧ 特种污染物。

3)传统净水工艺面临新挑战:① 新污染物不断出现,污染日趋复杂,饮用水呈现污染物复合、污染过程复合以及污染效应复合的复合污染特征;②《生活饮用水卫生标准》(GB5749—2006)全面实施,指标由35项增加到106项;③ 传统水处理工艺以去除水中悬浮物、胶体颗粒物为主,对小尺寸污染物,去除能力有限。

3. 膜法水处理技术的发展及应用现状

基于上述现状和需求,许多膜技术用于水处理以保证饮用水的安全。在中国,超滤过程被安装在超过数百个水处理厂中。例如,从2009年起,10 000 m^3/d的超滤膜组件装置在太湖运行,50 000 m^3/d的超滤装置在佛山市设计并建成。反渗透是另一种用于脱盐的膜技术,但水处理的成本较高,在中国很少有水厂使用。一些有机物不能被超滤脱除,反渗透可以将所有离子脱除,而纳滤可以脱除大多数有机物和二价离子,其通量高于反渗透。因此,纳滤过程被用于制备饮用水,一些小型的水厂也在北京、杭州等城市建成。将来,膜技术会更多的应用在非饮用水供应和污水处理过程中,如果一些非技术因素可以被消除,如膜技术处理的水允许进入管网系统,将缓解中国的水压力。

针对不同尺寸的污染物,可以使用不同类型的膜分离技术,特别适合于解决当前我国饮用水污染物多元化的难题。膜法处理饮用水的热点问题主要包括:① 增强膜的抗污染能力,延长使用寿命;② 膜法处理饮用水时,有益离子的保留问题;③ 基于膜过程的组合工艺设计及应用。

由于饮用水中可能含有多种污染物,单一的膜法处理饮用水可能难以完全保

证水的安全性，组合工艺处理法仍是饮用水处理的常用方式，膜组合工艺应用的实例——天津杨柳青水厂膜处理示范工程、曹妃甸 RO 海水淡化示范工程、太阳能动力膜过程系统、美国远途救援净水系统等。

4. 研究展望与建议

（1）新型膜工艺流程设计与优化

研发先进的膜处理组合工艺，优化协同不同工艺、方法，探索联合净化方法，实现多种技术优势互补。

（2）膜与组件及过程的研发

① 研发抗污染、抗氧化、高通量、机械强度高、寿命长、价格低廉的新型膜材料，如沸石分子筛、杂化材料、纳米材料、仿生材料、抑菌材料等；② 研发新型大单元膜组件及新型膜组件组合方式，推动膜用于水净化及深度处理过程；③ 研究水在膜内的传输机制和离子的截留机制等分离机制，反馈膜材料的设计。

（3）非传统水源的综合利用

非传统水资源的开发利用主要包括雨水利用、污水资源化及“海水开源”三方面，传统水资源和非传统水资源的耦合互补利用，有利于解决饮用水供水矛盾。

（4）加快推进制度建设

加快推进制度建设包括用水总量控制制度、用水效率控制制度、水功能区限制纳污制度、管理责任与考核制度等。

（5）建设膜产业科技强国

我国膜产业虽已进入了快速增长期，但与国际水平相比尚有较大差距，高性能膜材料、膜组件等仍需进口，因此需要加大政策扶持力度、提升自主创新能力、深化国际交流合作、加强人才队伍和平台建设。

（五）大型气体分离膜

膜技术在气体分离纯化领域中得以应用。论坛重点介绍了以膜技术作为主要手段，实现高回报、高效分离的技术实例，其中包括天然气中高浓度酸性气体的去除；膜诱导吸附法脱除烟道气中二氧化碳；丙烯和丙烷这两种难分离气体的分离；以及页岩气中脱水工艺这一极有意义的研究方向。通过几个大规模使用膜技术的实例来说明膜技术的成果，阐述气体膜应用未来的展望。

1. 膜的发展过程

20 世纪 60 年代以来，以超滤和微滤为代表的第一代膜过程。多孔结构膜如超滤和微滤的应用奠定了膜过程在工业领域应用的重要基础。

第二代膜过程催生的反渗透工艺，于 20 世纪 60 和 70 年代开始兴起。反渗

透设施能源效率比蒸馏过程提高一个数量级。如今，其提供着 100 亿 gal/d 的淡水，大约占据全球海水淡化市场份额的 60%（其市场份额还在提升，并将逐渐取代热法）。之后，这些更先进的第二代膜可以区分自由水和水合的阳离子和阴离子，在埃米级别的分子尺度上是实现分离。其能够识别的特征尺寸大约 6 Å，也就是说可以截留大于该尺寸的所有物质。

第三代膜产品是在 70 年代曾一度被忽视的气体分离膜技术。然而现在第三代膜的应用也已非常广阔：① 超过 95% 的钻井平台所用氮气；② 5% ~15% 的分离埃米及大小的气体物质（0. 18 ~0. 5 Å）；③ 脱除天然气中的 CO_2 等工艺都是以第三代膜为核心技术的。

第四代必须大幅度地提高膜性能，实现在高能耗的能源、化工、食品和纯水领域的大规模应用。其关键就要突破聚合物的扩散极限并实现全分子尺寸上的高效膜分离，需要考虑在第四代膜中添加更高效的先进材料，如沸石、陶瓷、金属和金属有机骨架材料（MOF）。

2. 能源、环保、制造业领域的应用

膜分离工程作为能源的解决方案，通过提供更高的能量利用率和回收率缓解能源紧张的局面。作为一个能源密集型产业，在上游实现化学能的高效利用和回收，能够使化工产业将风险最小化、效益最大化。

（1）天然气净化领域

天然气净化领域中先进的膜的应用：① 管道中甲烷气运输前的预处理；② 降低在甲烷气中掺杂二氧化碳时造成的气体燃烧值的降低。这一领域应用的主要问题是：膜的溶胀和塑化现象，乙酸纤维素膜对 CH_4 和 CO_2 的渗透性增加，CO_2/CH_4 选择性下降。如何避免溶胀和塑化现象，或者在该过程后成功地恢复膜的性能是一个必须解决的问题。

（2）乙烯、丙烯以及乙烷、丙烷的分离

传统化工中，这样的过程是典型的能源密集型产业。其原因是，分离纯化过程需化学状态的转变，其相变热和热驱动力巨大，需要消耗极大能量。化工厂区 2/3 的面积和 80% 的能量在这一过程中消耗。然而利用膜技术进行分离，无需化学状态的转变（气相与液相的转变），也就减少了分离过程的相变热和热驱动的消耗，其节能效果十分客观。

3. 高性能材料在气体分离膜中的添加与应用

（1）高性能碳材料在气体分离膜中的添加与应用

碳分子筛（CMS）可以有效提高调整 CO_2/CH_4 的分离系数。芳香族聚合物复杂的聚合途径以及如何在这个过程中掺入 CMS 以提高膜的性能，是一个非常有

前景的课题。CMS 具有“超薄”的杂化石墨烯片状材质。

碳分子筛（CMS）可以调整 CO_2/CH_4 结合性能，从而获得不同的分离效果。当前，从线性芳香族聚合物中均匀添加 CMS 仍然是较复杂的过程。它包含的关键控制因素有：制膜料与 CMS 的分散；热解温度；“放热”；热解气的释放。

（2）MOF（金属 - 有机骨架）材料在气体分离膜中的添加

MOF 材料是一个非常新颖的分子级别的框架结构，其具有极大的比表面积和规整的结构，被成功地用于聚合物混合动力汽车的发电中，不需要分散和裂解，就可以制备纳米复合中空纤维膜。其制成的具有 0.1 μmol/L ZIF - 8 聚合物的混合涂料涂覆或功能层使膜的性能产生了质的飞跃。其可控的结构也能够使膜材料获得对不同分子的高选择渗透性。能够提供克服聚合物扩散上限的能力。扩散选择性达到更高的标准（其实例就是实现丙烯/丙烷分离）。

总之，新的大型气体膜过程已经得到广泛应用。例如，天然气中的 CO_2/CH_4 分离的应用；更先进的 N_2/CH_4 和 $(N_2+CO_2)/CH_4$ 案例需要碳分子筛的添加与应用；石化工业“下游”的分离，如丙烯/丙烷的分离。但仍然期待出现潜在的主要的节能应用和竞争优势应用领域。先进制膜材料的研发和膜结构形态的控制至关重要，同时制造出高比表面体积的膜组件，提供相应的生产实用设备，也是重要的技术关键。

（六）渗透汽化用沸石分子筛膜的制备和应用

沸石分子筛膜是由沸石分子筛颗粒在多孔支撑体上紧密堆积而成的一层薄膜，利用其规则的分子筛孔道结构可实现物质分子水平的分离。亲水性的 NaA 型分子筛渗透汽化膜具有规则的孔道结构，孔径为 0.42 nm，大于水的分子直径 0.29 nm，而小于绝大多数有机溶剂的分子直径，且其本身具有极强的亲水性，因而特别适合于有机溶剂脱水。

基于亲水沸石膜的渗透汽化（蒸汽渗透）分离被认为是一个经济有效的从有机溶剂中脱水的技术，研究人员做了大量工作以改善膜性能、降低设备成本。报告展示了课题组最近在制备沸石膜和在工业有机溶剂脱水方面的应用情况。

1）擦涂和浸渍相结合的引晶方法，可制备重现性好、高品质的 NaA 型沸石膜；纳米尺寸的球磨晶种也被用于诱导制备 NaA 型沸石膜，这可显著降低合成时间；使用二甲基二甲氧基硅烷（DMDS）作为硅烷前体，通过水解反应可进行分子筛膜晶间孔道的修补。

2）采用晶种擦涂和浸渍相结合的晶种涂覆方式用于分子筛膜合成。先将支撑体用砂纸打磨后烘干，采用晶种糊状物擦涂支撑体表面，以消除支撑体表面可

能存在的缺陷，再用提拉浸渍法预涂晶种，最后采用水热合成法合成 NaA 分子筛膜，所合成的 NaA 分子筛膜表面连续致密、分离性能优良、重复性好，适合规模化生产。

3）采用球磨机对具有较大粒径的 NaA 分子筛颗粒进行破碎，获得纳米级分子筛颗粒作为晶种，然后在载体表面涂覆一层晶种层，采用水热合成法诱导制备 NaA 分子筛膜。所合成的 NaA 分子筛膜同时具有高的分离性能和渗透通量，合成周期短、成膜重复性高，适合规模化放大生产。

4）分子筛膜晶间孔道的修补方法：利用分子筛膜侧室的有机硅烷修饰液，通过晶间孔道与滞留在孔道上的水发生水解反应，产生 SiO_2 基团，进而有效减小分子筛膜晶间孔道。本方法修饰后的分子筛膜的分离选择性可得到显著增加，成品率高、重复性好。

目前，项目与江苏九天高科有限公司合作，建成了一条年产 10 000 m^2、长 800 mm 的单通道膜的生产线。很多基于 NaA 型沸石膜的工业脱水过程的工作已经开展。为稳定运行，进料要求控制 pH 值在 6.5 ~ 8.5，已建成的甲醇、乙醇、异丙醇、乙腈等溶剂的工业脱水装置超过 10 个，这些溶剂可被脱水至水含量低于 0.1%（质量分数）。

此外，在制备中空纤维分子筛膜也进行了广泛研究，经测定 NaA 型中空纤维结构的沸石膜具有超过 9 kg/(m^2 · h)的高渗透通量，表现出良好耐酸性的 T 型中空纤维沸石膜也已制备完成，可用于 pH 4 条件下丙醛溶液的脱水。开发出了中空纤维沸石膜组件。

（七）纳滤处理和回收废水中低浓度持久性污染物全氟辛酸铵

近年来，全氟辛酸铵（APFO）作为一种稳定性强的有机污染物，越来越引起全世界的关注。由于 APFO 分子链中较强的 C—F 以及其良好的水溶性，很难通过物理和化学方法降解，因而该有机污染物将长期存在于环境中，对环境造成污染。报告主要介绍了纳滤膜 NF90 和 NF270 对 APFO 的脱除以及浓缩回收情况，以及在大生产过程中通过纳滤装置完成对工业废水中 APFO 的浓缩再利用。

1）通过合适的纳滤膜实现废水中 APFO 的回收和脱除。NF90 对 APFO 的脱出率达到了 99%，高于 NF270 对 APFO 的脱出率（92%），因此选择 NF90 纳滤膜处理含有 APFO 的工业废水最合适。

2）通过 NF90 纳滤膜，在适当的工艺条件下，可以完成 APFO 的浓缩，从而得到高浓度的 APFO。

3）通过 NF90 纳滤膜可以从生产含氟聚合物产生的废水中，处理以及回收

APFO,其回收率达到99%以上,因而大幅度地降低了APFO的排放,解决了其环境污染问题。

4）一套每天处理200 m^3 具有较低含量APFO废水的纳滤装置已经成功投入生产,该体系能够在生产PVDF的工厂中完成废水中APFO的回收以及浓缩再利用。

从实验室小试实验,选择了合适的纳滤膜,经过完善工艺,最终在工厂建立了纳滤水处理装置,完成了其对APFO的浓缩。降低了工业废水中APFO对环境的污染,而且浓缩的APFO可以进行回收再利用。不但产生经济效益,还具有一定的环境效益。

（八）纳米粒子膜在液体和气体分离中应用的回顾

在膜中加入小颗粒用于分离最早出现在1965年由通用电气制备的包含硅颗粒的硅橡胶膜。含有无机颗粒、沸石晶体的混合基质膜（MMM）在20世纪80年代开始出现,并对新型吸收剂的发展产生了影响。高纵横比薄片的出现又进一步促进了膜的发展,这些研究往往针对气体分离。随后出现的碳纳米管引起了人们对碳纳米管－聚合物混合基质膜的研究兴趣,加入合成的碳纳米管或改性的碳纳米管,液体分离膜的性能受到显著影响。此外,还有许多有关碳纳米管或碳纳米管/沸石杂化膜用于反渗透膜、纳滤膜领域的研究,其中包括在膜中加入包括石墨薄片、金属有机骨架在内的纳米粒子制备出耐溶剂的纳滤膜。报告主要从以下三个方面对纳米粒子膜在液体和气体分离中的研究进行了回顾:① 混合基质膜在气体分离中的研究;② 混合基质膜在液体分离中的研究;③ 混合基质膜在渗透汽化中的研究。

1. 混合基质膜在气体分离中的研究

首先以He和甲烷气体为例,介绍了其在25℃,在硅橡胶、天然橡胶、低密度聚乙烯、高密度聚乙烯等聚合物中的传输、溶解、选择性等特征,从基于最小的沸石界面的各种气体的动力学筛分直径,到提出气体分离膜的理论机制,介绍了混合基质膜用于气体分离的研究起源,最后以橡胶和玻璃态聚合物膜分离 H_2/N_2 气体的渗透性和选择性之间的“upper－bound”上限Robeson关系（1991年）为例,阐明了渗透性和选择性之间互为制约的关系。对于气体和液体分离来说,传统有机聚合物膜的渗透性和选择性存在trade－off效应,很难同时提高,与之相比,混合基质膜能够突破trade－off效应的制约,使得渗透性和选择性同时提高,并兼具有机高分子材料和无机材料的优点。然后列举了早期有关混合物基质膜的相关研究。

混合基质膜中填充的添加剂有沸石纳米晶体、气相二氧化硅、纳米二氧化硅、碳分子筛、单壁碳纳米管、石墨薄片、石墨烯、枝状大分子。以填充沸石晶体为例，认为制备气体混合基质膜面临以下挑战：① 在沸石相和有机膜相之间的界面相容性成为造成膜的选择性损失的一个主要问题，尤其是玻璃态聚合物；② 膜皮层厚度低（小于等于 50 nm），需要至少 10 层填充材料获得一个渗透阈值，并要求沸石晶体有甚少的团聚；③ 含有尖锐晶体的纺丝溶液可能会破坏或损伤纺丝模具表面，导致中空纤维膜表面出现缺陷；④ 膜组件制备时填充的固相物影响了膜的刚性。

2. 混合基质膜在液体分离中的研究

作为第二相，用于混合基质膜中的材料有沸石晶体（制备薄层纳米复合膜）、硅纳米颗粒、硅纳米凝胶（可避免纳米颗粒的团聚）、TiO_2 纳米颗粒、银纳米颗粒、多壁碳纳米管（MWCNT）、单壁碳纳米管（SWCNT）、金属有机骨架（MOF）、水通道蛋白、Noria 超级分子（充当固体质子载体）。

Jeong 等 2007 年介绍了采用界面聚合法分别制备 RO 薄层纳米复合膜（TFN）和薄层复合膜（TFC）的结构，区别是 TFN 膜聚酰胺功能层中含有纳米粒子。US 专利（020/0062156A）提出了在功能层上添加纳米颗粒的四种方法来制备 RO 膜，分别为：① 将纳米颗粒添加到水相；② 将纳米颗粒添加到有机相；③ 将纳米颗粒添加到有机相和水相；④ 将纳米颗粒添加到含有水溶液的水相中。Mary L. Lind 等 2009 年试验研究了沸石晶体尺寸对沸石 - 聚酰胺反渗透纳米复合膜的纯水通量和 NaCl 脱盐率的影响。Mary 等对沸石 - 聚酰胺纳米复合膜用于正渗透进行了改进，对膜的渗透系数、盐截留率、盐渗透系数等性能进行了研究。另一个材料是有机金属骨架（MOF），Sorribas 等 2013 年发现，与相同截留率时的 TFC 膜相比，MOF - TFN 膜渗透能力得到大大提高。

报告还介绍了采用 CNT 制备选择性分离膜的两种方法：一种是通过化学气相沉积（CVD）法制作整齐排列的 CNT 基膜；另一种为在聚合基体中或预先存在的膜孔中分散/引入改性的 CNT。这种 CNT 基混合膜可用于 UF，选择性地截留 20 kDa 和 100 kDa 的分子质量。这种膜的水通量可达传统 UF 膜的 5 ~ 6 倍。利用这种膜作为基体，采用界面聚合法制备了含有 CNT 的聚酰胺 FO 膜。制备的 FO 膜通量提高 3 倍，盐透过率降低了 3 倍。更高的通量也对控制浓差极化提出更高的要求。

Roy 等 2011 年对 CNT 在膜分离中的应用进行了研究报道，通过采用多孔膜作为基体，在水相溶液中加入 CNT 制备亲水性 PP - CNT 膜、亲水性 PES - CNT 膜，认为 CNT 基混合膜有非常好的应用前景。

总之，采用界面聚合法制备随机排列的碳纳米管－薄层复合膜相对容易；为了提高溶质截留率，必须提高表面功能层的密度，如果目的是RO脱盐，那么功能层聚合物的特点、水簇的特点则非常关键；采用CVD法制备垂直排列的CNT混合基质膜既困难又昂贵；垂直排列的CNT混合基质膜可控制溶剂通量和溶质分离。

3. 混合基质膜在渗透汽化中的研究

Vane等2008年研究了混合基质膜用于乙醇/水的渗透汽化分离，通过在硅橡胶上负载65%（质量分数）的沸石ZSM－5（疏水的），制备的ZSM－5/硅橡胶混合基质膜，在50℃时分离含有5%（质量分数）的乙醇水溶液，乙醇/水的分离系数最高为3.0。Lin等2013年报道了采用制备的PTFPMS/沸石4A（亲水的）混合基质膜用于分离乙醇/水溶液，乙醇/水的分离系数高达11.5。渗透通量高达23.210 12 kmol·m/(m^2·s·kPa)，是PTFPMS膜的6倍。

用于液体分离的含有纳米晶体的混合基质膜正在被商品化。现有改进主要对溶剂通量有所提高，而对溶质截留率没有影响。在FO和UF方面，碳纳米管混合基质膜和碳纳米管支撑膜取得一定的进展。除化学气相沉积法，还需要研究更简便的制备碳纳米管垂直排列膜的方法。用于气体分离的混合基质膜还没有实现商品化，距离商品化的实现还有很艰难的路要走。

（九）CO_2分离用膜的研制和应用

CO_2分离主要包括烟道气和天然气中CO_2的分离去除，它直接与人类在新世纪面临的环境和能源两个关键问题相关，CO_2是温室气体的重要组成部分，需要从烟道气中分离去除CO_2以减少温室效应；天然气中含有CO_2和H_2S等酸性气体，这些酸性气体会腐蚀运输管道，因此必须控制其含量以提升天然气的品质。报告主要从三个方面进行了介绍。

1. 聚酰亚胺材料的合成及中空纤维膜的制备

1）开发了几种新型聚酰亚胺材料的合成方法，显示了较好的CO_2渗透性和分离能力，已进行了20 kg规模的聚酰亚胺生产过程的实施。

为调节膜的选择性、提高抗塑化性，使所制备的膜兼具好的气体渗透性和选择性，向膜材料的主链6FDA－mPDA中添加PEO成分，使共聚物既包含软段成分，又有硬段成分。

2）经过优化具有较好膜孔结构形态的、高CO_2通量和满意分离效果的中空纤维膜及工业规模的膜组件已经制备出来，一旦条件具备就可以进行真实工况条件下的运行。

中国科学院大连化学物理研究所成功地设计了包括高效气/液分离、多级预

过滤和膜组件装配成串联或并联模式的组合分离过程,借助化工软件的优化使整套膜设备在最佳状态下将 CO_2 从天然气中分离出来,该套设备已在2006年年底投入运营。

2. MOF/聚酰亚胺混合膜

无机/有机杂化膜是膜技术的重要研究领域,合成了两种可控颗粒尺寸的MOF(金属有机骨架,是由含氧、氮等的多齿有机配体与过渡金属离子自组装而成的配位聚合物)材料,实验证明,以聚酰亚胺作为基膜材料、添加MOF后可在没有明显的选择性损失情况下提高气体的渗透性、具有良好膜孔形态的中空纤维杂化膜的制备正在进行中。

目前用已合成的两种MOF即Micro-ZIF-8和Micro-CuBTC作为添加剂所制备的无缺陷的混合基质膜的气体选择性几乎没有变化,而渗透性均高于麦克斯韦模型(Maxwell model)的结果,其中Micro-ZIF-8还要高于Micro-CuBTC。

3. PTFE多孔膜吸收过程

PTFE是具有非常好的化学稳定性和机械强度的聚合物膜材料,中国科学院大连化学物理研究所开发了具有自主知识产权的、孔结构可控的PTFE中空纤维生产线,设计开发了用于从天然气中去除 CO_2 的膜接触器,目前与一家国际公司合作的膜接触器系统正在安装调试,将在2013年年底试运行。

(十)新型通用离子交换膜的研究和实践

1. 阴离子交换膜研究进展

对于膜的性能,主要通过膜的选择性、渗透性和稳定性三方面来考察。其面临的主要问题是:① 如何避免使用有害的材料——氯甲基甲醚(CME)?② 如何单独控制离子交换容量(IEC)和水含量(WC)?③ 如何使得制备的膜具有全面性?④ 如何提高膜的稳定性?

以上问题的解决方案包括使用溴化来替代氯甲基化以避免使用CME,同时通过控制溴化比例和溴化度来控制离子交换容量和水含量。采用定量设计,如氨基化,使得采用同种聚合物制备不同用途的离子交换膜成为可能。利用仿生交联剂制备具有高强度和良好热稳定性的有机-无机杂化膜。

2. 离子化单体的离子交换膜研究进展

离子交换膜在燃料电池中得到广泛应用,这种应用也对离子交换膜提出了多种性能上的要求,如高的 H^+/OH^- 导率、低的燃料融合性、优良的机械强度以及长期稳定性等。

研究人员从Nafion膜材料的结构中得到启发,选择侧链型离子化芳香族聚合

物作为制备离子交换膜的材料,而侧链型离子化芳香族聚合物又可以通过芳香族聚合物后接枝离子化侧基和离子化侧基单体聚合两种方式得到,从而可以精确控制离子化基团的位置和含量。例如,直接酰化聚酮或者先对离子化的单体进行酰化后再进行聚合都是立足于此研究思路。

3. 以离子交换膜为基础的膜过程的发展及应用

目前离子交换膜的应用主要集中在生物医药、水处理以及石化领域三大方面。生物医药的应用主要包括:氨基丁酸、药物氨基酸、赖氨酸以及发酵有机酸的处理方面;水处理的应用主要包括:电镀废水、丁腈橡胶废水等废水处理方面;石化领域的应用主要用于脱硫剂再生以及石化废水处理方面。

目前,中国科技大学的新型离子交换膜已经开始商业化生产,并被用于有机酸生产、净化分离等领域。

三、交流与讨论

与会中外专家学者就膜技术在污水回用领域的应用、在海水淡化领域的应用成本、气体膜在石化领域的应用以及未来膜技术的发展趋势等问题进行了深入的交流与讨论。

膜技术在水和空气净化领域的应用是全球的发展趋势。在膜法污水回用以及海水淡化过程中,RO 膜仍是主导。在 RO 膜片的研发方面仍是以聚酰胺薄层复合膜的改性为主,最新的技术包括已经商业化的采用纳米沸石分子筛粒子改性以提高膜片的水通量以及采用仿生学原理在反渗透薄膜中添加水通道蛋白以提高膜的水通量;在膜组件方面的开发趋势是不断追求膜组件的大型化以提高产水效率;在整个脱盐工艺流程的设计上更加注重水和能源的综合利用,各种耦合技术,如反渗透与正渗透耦合以降低能耗和产水成本、反渗透与膜蒸馏技术的耦合以实现零排放为目标,将是未来的发展趋势。

针对海水淡化领域的膜技术成本问题,与会专家认为目前海水淡化成本已有大幅度下降,但因材料成本上升,所以总体上海水淡化成本降低了一些,但是短期内很难有大幅降低或突破。海水淡化的两大技术主要是蒸馏和反渗透,目前的海水淡化应用以反渗透为主,新加坡第一座海水淡化工厂——新泉海水淡化厂,是目前全球最大型的采用反渗透技术的海水淡化厂,海水淡化成本在 0.7 美元左右。未来的发展趋势是将蒸馏和反渗透技术结合起来,可大大降低海水淡化的成本,3 年后每立方米海水淡化的成本将从目前的约 70 美分降到 50 美分。

气体分离膜在天然气净化领域,乙烯、丙烯以及乙烷、丙烷的分离回收领域得

到了广泛应用，但先进制膜材料的研发和膜结构形态的控制至关重要，同时制造出高比表面体积的膜组件、提供相应的生产实用设备，也是重要的技术关键。未来对膜过程的研究主要是如何降低膜过程的能耗。

第二部分

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第三部分

主题报告及报告人简介

Membrane Engineering for an Innovative Process Engineering

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Abstract: Our modern society has to solve and overcome various severe problems for maintaining and increasing the quality of our lives, such as: global water stress, energy production, environmental pollution, CO_2 capture, etc. Process intensification in process engineering, new advanced smart materials and molecular engineering are all disciplines which might contribute to find solutions. Membrane Engineering is covering all aspects of process engineering, from molecular separation to chemical transformations (membrane reactors), to mass and energy transfer between different phases (membrane contactors).

In the last years, the impact of membrane operations in various areas has grown fast. Seawater and brackish water desalination, industrial water reuse, wastewater treatment, gases separations, membrane bioreactors, hybrid artificial organs and agro-industry (such as dairy industry, juices and wine productions, etc.) are typical examples of membrane engineering success. The motivation for this success is in large part related to their basic properties in term of energy consumption, low environmental impacts, no use of chemicals, easy to automatization, etc. All these aspects are very well related to the strategy of Process Intensification.

Integrated membrane operations are also growing in interest and in industrial utilization. Integrated membrane operations might be considered today in various production lines, based in the utilization of existing membrane systems from the downstream processing to the final product formulations.

This work critically reviews the current status and emerging applications of (integrated) membrane operations with a special focus on water, energy and raw materials production.

1 Introduction

The growing population along with industrialization and development caused severe issues which have to be faced to ensure and improve the living standard of the future generations. In particular, the lack of fresh water and the growing need of energy and raw materials are current problems which have to be addressed to ensure the progress of the future society. To meet the requirements of sustainable development, the Process Intensification (PI) strategy can be used. It entails to: ① maximize the effectiveness of intra- and intermolecular events; ② give each molecule the same processing experience; ③ optimize the driving forces at every scale and maximize the specific surface area to which these forces apply; ④ maximize the synergistic effects from partial processes[1,2]. Membrane engineering is a technology in which all the requirements of PI can be realized[1,3] due to its intrinsic characteristics of advanced molecular separation, improved efficiency, ease of operation and scale-up, and aptitude to integrate different but complementary membrane operations. Membrane engineering, including pressure driven membrane operations, membrane contactors, gas separation, fuel cell applications etc., brings chemical engineering to a new and highly improved level. Today membrane processes have in several cases left behind the conventional chemical unit operations. Membrane bioreactors (MBR) in municipal water treatments, pressure driven membrane operations and integrated membrane systems in seawater and brackish water desalination are some important examples where conventional plants have been turned into membrane processes due to their high energetic efficiency, compactness, extraordinary level of physical disinfection and reduced sludge production.

Membrane engineering with its various operations can address the growing problems not only of water stress but also of mineral depletion and energy consumptions.

Potable water shortage is one of the most serious problem for future generations. It has been estimated that, in the year 2000, 3. 1 billon people lived under moderate water stress and 2. 6 billion were exposed to high levels of water stress[4]. Access to fresh and clean water is strongly linked to the health of the population[5], therefore in many developing countries water resources are the main requisite for the improvement of the living standards. Moreover, water resources are not only consumed in domestic activities but also in agriculture, industrial and touristic uses thus influencing food production and industrial growth. Water stress is predicted to increase in the future years. The same is happening in energy consumption. The latter grew rapidly in the last decades and is projected to increase further in the following years (Fig. 1)[6]. As a consequence, efficient technologies able to minimize energy intensity (i. e., energy consumption per unit GDP) have been developed and will be further researched in future (Fig. 1).

In the last decades mineral deficiency is also becoming quite common all over the world. For example, the demand for lithium has already doubled over the past decade and it is expected to more than double over the next 10 years (Fig. 2). Lithium growing consumption was largely driven from its use in small format lithium-ion battery (i. e., rechargeable batteries used in consumer devices such as cell phones, laptops, digital cameras and hand held power tools). Future increase in lithium demand is expected to come from continued growth in the small format lithium-ion battery, as well as new demand from the large format lithium-ion battery used in applications such as the hybrid, plug-in-hybrid and full electric vehicle – as well as for battery applications within the utility grid storage industry. Until now lithium has been mainly recovered from

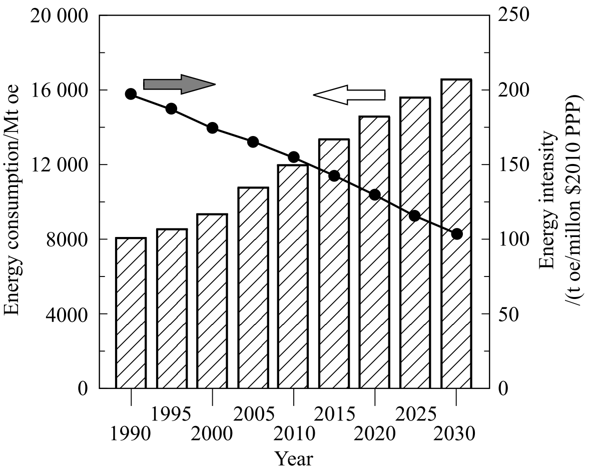

Fig. 1 Outlook of energy consumption (left axis) and energy intensity (right axis) (adapted from [6])

minerals in the mining industry or from high content lithium waters such as salt lake brines. The main drawbacks of the lithium production processes are the low lithium grades and recovery factors, the complications in having available new production sites or in enlarging the existing salt lake brines areas (in particular because they are associated with high level of pollution[7]).

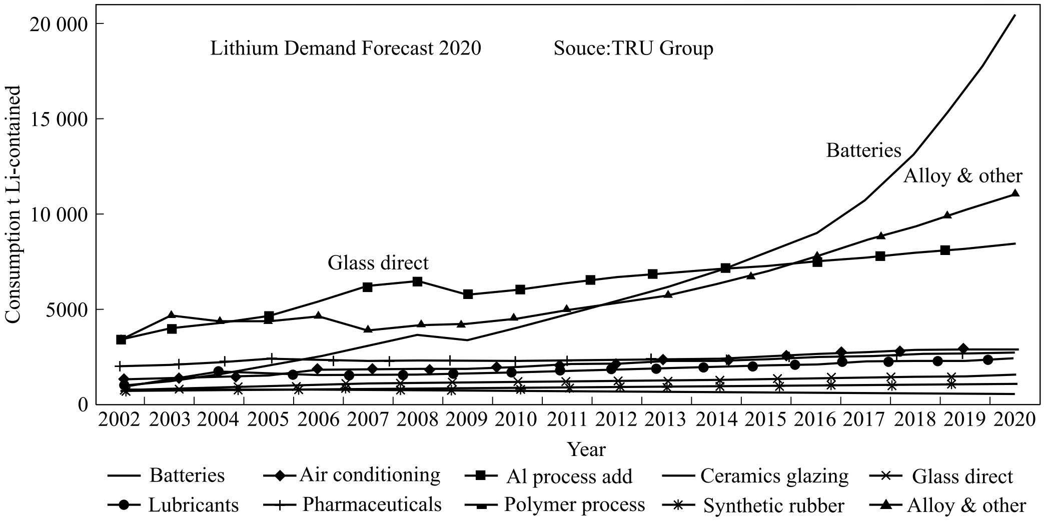

Fig. 2 Lithium demand forecast (http://www.globalprofitsalert.com/global-investment-news/kelley-damiani/an-element-for-lithium-batteries-set-to-flourish-117211)

Another example of mineral depletion can be found in the increasing uranium demand (as energy source) which has already exceeded the global production[8] and which are projected to increase from 61 500 tons in 1997 to 75 000 tons in 2020 (Fig. 3).

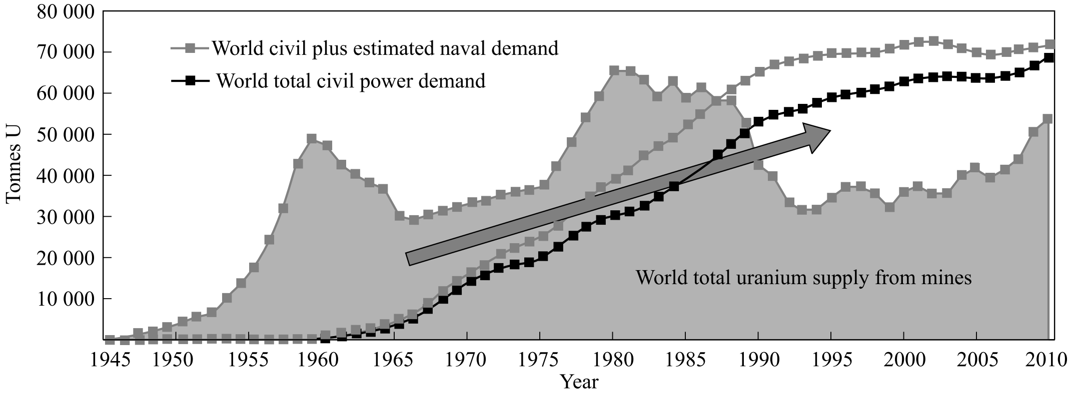

Fig. 3 World uranium production and demand

(http://moneyformoney.wordpress.com/tag/cco/)

Membrane engineering offers comprehensive prospects to the solution of future water, energy and raw materials demands.

This work gives a critical evaluation of the current status and emerging applications of membrane operations, with a special focus on water/energy/mineral production from salty waters. It highlights some of the latest advances in membrane processes and provides a look at the major challenges for further development of membrane technology.

2 Membrane operations for water, energy and raw materials production from salty waters

The importance of potable water, clean energy and sustainable raw material sources is evident considering the drawbacks of water shortage, fossil fuels emissions and finite resources depletion. An alternative source of water, energy and materials is salty water. Membrane engineering has already shown its potentialities in water desalination where, today, the most particular accomplishment of membrane technology is the replacement of conventional distillation methodologies for fresh water production (such as conventional multi-stage flash (MSF) and multi-effect desalination (MED)) with membrane based desalination processes (mainly reverse osmosis (RO)).

For what concerns clean energy, it can be produced by salinity gradient power(SGP). SGP is based on the chemical potential difference between concentrated and dilute salt solutions. The conversion of the osmotic energy of salt solutions into mechanical or electrical energy can be realized by osmotically driven membrane operations such as forward osmosis (FO), pressure retarded osmosis(PRO)and reverse electro-dialysis(RED).

Salt waters can be exploited also for the production of those raw materials currently in strong demand and dangerous depletion trough membrane distillation(MD)and membrane crystallization(MCr).

2.1 Potable water production through membrane processes

Membrane technology is today recognized as the dominant technology for water desalination because thermal options are approximately 10 times less energy efficient[9] and it is expected to further consolidate in future its leadership through the design of integrated membrane processes.

The global installed desalination capacity around the world is 65.2 million m^3/d and membrane installations account for around 60% of the desalination market today and have been forecasted to increase to 80% in 2016. 90% of membrane desalination installations use RO technology whose capacity is increasing rapidly. Only in countries with abundant oil reserves, thermal MSF and MED plants are built. The growing number of RO desalination plants is in large part due to several advances in technology that occurred during the 1990s, which include:

- new low energy RO membranes with improved salt rejection and lower price,
- high efficiency pumps and motors,
- more efficient energy recovery devices(ERDs).

The progresses in SWRO desalination caused a decreasing in the cost of the reclaimed water from membrane plants and an increasing use of membrane technology for water desalination.

Currently, RO desalination plants with capacities of more than 500 000 m^3/d are in operation[10,11] and the goal of reaching a capacity of megatons per day is now emerging. Examples can be found in the Megaton project in Japan and in the SEAHERO project in South Korea[12-14]. However, the massive capacity increment also promotes some serious concerns such as the disposal of the produced brine. Other aspects that need improvements for a further spreading of membrane-based desalination systems are the cost reduction and the improvement of water quantity and quality. All these issues can be addressed in an integrated approach in which different membrane operations can be used in the RO pre-treatment and post-treatment. For example, in the RO pre-treatment some other pressure-driven membrane processes can be utilized as an interesting alternative to conventional processes(i. e., chemicals and mechanical filtration units). In particular, MF (a low-pressure membrane process for the removal of colloidal and suspended micrometer-size particles), UF(another low-pressure membrane process typically used to retain macromolecules, colloids, and solutes with molecular weights greater than few thousand) and NF (a high pressure membrane process for the removal of turbidity, microorganisms, hardness, and most part of multivalent ions) are becoming standard and efficient pretreatment options for sea- and brackish-water desalination.

For wastewater treatment, MF/UF pretreatment technology can also efficiently reduce the highly fouling nature of the feed.

Other benefits arising from the utilization of pressure driven membrane processes in the pre-treatment steps are the possibility to handle a large variation in raw water quality, the smaller footprint and the opportunity to increase RO flux and water recovery. Proof of the benefits in the adoption of membrane over conventional pre-treatment is their recent proliferation.

Another pretreatment option to reduce natural organic matter is the utilization of a membrane bioreactor (MBR). This has a great potential to provide disinfected effluents of high quality, especially suitable for reuse and recycling in wastewater treatment or for RO pre-treatment in sea- and brackish-water desalination[19]. Use of an MBR as RO pretreatment is also being investigated in the MEDINA research project(http://medina. unical. it).

As it will be described in the following sections, also the dangerous effects of the brine discharged from the RO desalination plants on the environment can be minimized through an integrated system in which the desalination process is re-designed introducing membrane operations also in the RO post-treatment transforming the traditional brine disposal cost in a potential new profitable market. In particular, ① membrane distillation (MD) and membrane crystallization (MCr) can be utilized for producing solid materials of high quality and controlled properties (as specific polymorph of salts), ② pressure retarded osmosis (PRO) and reverse electrodialysis (RED) can be used to generate energy from RO brine.

Other examples of integrated membrane based processes for desalination are the above mentioned MEGATON and SEAHERO projects. In the first part of the projects the emphasis has mainly been on increasing the desalination capacity. However, in the second part of the projects the brine disposal issues and the energy consumptions are addressed. Hybrid systems with membrane distillation (MD) and pressure retarded osmosis (PRO) units are proposed for the minimization of the environmental impact of the brine, the recovery of energy (see section 2.5) and the extraction of valuable resources from the brine. Moreover, the SEAHERO project (http://www.seahero.org/eng/) has suggested a hybrid system forward osmosis/reverse osmosis for increasing the recovery factor by 30% and hereby reducing the brine volume in the same extend. This hybrid desalination process can minimize the energy consumption to less than 2.5 kW · h/m^3 and water price to 0.6 $/t.

2.2 Membrane contactors in water treatment and water purification

Membrane contactors (MCs) are systems utilizing a hydrophobic membrane with appropriate pore structure as a fixed interface between two different phases without dispersing one phase into another. In these processes the membrane does not act as a selective barrier but rather sustains the interfaces. The separation process is based on the principles of phase equilibrium.

With respect to conventional systems, MCs have some important advantages such as high interfacial area per volume unit, low operating temperatures and pressure, high rejection, modular design, easy scale-up, less membrane fouling and low sensitivity to concentration polarization phenomenon. Drawbacks are related to the presence of an additional mass transport resistance (the membrane itself) and to the rather limited range of the operating pressures below the breakthrough threshold. The performance of MCs strongly depends on the properties of the membranes used. In general, a high hydrophobicity (for aqueous applications) is required to prevent wetting and mixing between the different phases in contact; elevated permeability leads to high fluxes; high chemical and thermal stability are necessary to improve the membrane resistance to chemical attack and its resistance to degradation and decomposition.

MD and MCr are two examples of MCs that can be used for mitigating the impact of concentrates on the environment and for the recovery of the valuable contained components.

1) **Membrane distillation (MD)** is a membrane process which combines both membrane technology and evaporation processing in one unit. It involves the transport of water vapor through the pores of hydrophobic membranes via a partial pressure difference across the membrane. With respect to conventional desalination technologies such as multistage-flash distillation and RO (techniques involving high thermal energy and high operating pressure respectively, finally resulting in excessive operating costs), MD offers the attractiveness of operation at atmosphere pressure and low temperatures (30 ~ 90℃), with the theoretical ability to achieve 100% salt rejection. Moreover, MD is not limited by concentration polarization phenomena as it is the case in RO. Previous work[15] showed that no concentration polarisation occurs with membrane distillation at concentrations up to 300 g/L. A relatively small flux decline is observed when concentration and viscosity increase, but this is only due to thermodynamic effects: when the salt concentration increases, the activity coefficient is modified and this can explain the water flux decrease. However, this flux decline is low in comparison with the one observed (of about 70% of the initial flux) with RO, which is due to both osmotic pressure and concentration polarisation.

2) **Membrane crystallization (MCr)** is conceived as an alternative technology for producing crystals and pure water from supersatured solutions; the use of the membrane distillation technique in the concentration of a solution by solvent removal in the vapor phase is utilized in this application.

MCr is able to promote crystals nucleation and growth in a well-controlled pathway, starting from undersaturated solutions. In a membrane crystallizer the membrane matrix acts as a selective gate for solvent evaporation, modulating the final degree and the rate for the generation of the supersaturation. Hence, the possibility to act on the trans-membrane flow rate, by changing the driving force of the process, allows to modulate the final properties of the crystals produced both in terms of structure (polymorphism) and morphology (habit, shape, size, and size distribution). The experimental evidences that can be found in several published articles[16-18] validate the effectiveness of MCr as an advanced method for performing well-behaved crystallization processes.

MD and MCr are both efficient tools to improve seawater desalination processes:

1) integration of a MD unit to process RO retentate could ① increase the amount of recovered water and ② reduce the amount of discharged brine;

2) integration of a MCr unit to process RO retentate could ① enhance the water recovery factor, ② minimize the discharged brine and ③ produce valuable crystalline products.

The studies carried out by Drioli and co-workers[16,20,21] showed that the introduction of a MCr unit on NF and RO retentate streams of an integrated membrane-based desalination system constituted by MF/NF/RO increases plant recovery factor so much to reach 92.8%. Moreover, it has been experimentally shown that the presence of organic compound (i.e., humic acid) in the retentate inhibits crystals growth rate[22]. This proved the necessity to optimize the NF/RO pre-treatment steps, in order not only to reduce the NF/RO membrane fouling but also to control the crystallization kinetics that are linked with the nature and the amount of the foreign species existing in the highly concentrated brines emerging from the NF and RO stages.

In some studies on MCr[23] a rapid decrease in trans-membrane flux has been observed due to crystal deposition on the membrane which reduced the membrane permeability. This problem can be minimized through a right design of the process and a proper control of the operative conditions. With respect to the best control of operative conditions, temperature polarization is an important factor depressing the driving force and hereby the process performance. Ali et al.[24] explored the effect of temperature polarization on membrane distillation performance by means of a specially designed cell. In particular, a cell with sixteen sensors located at specific locations within its body was built to measure the bulk and membrane surface temperatures on both feed and permeate sides. They found that temperature polarization phenomenon decreases with increasing the feed flow rate, and decreasing the feed inlet temperature and concentration. Moreover, they proved that solution concentration has very less role in flux reduction as compared to thermal polarization at low feed concentration, whereas the flux reduction due to concentration becomes important at high feed concentration where a coupling of heat and mass transfer exists.

Finally, the additional advantage of membrane distillation and membrane crystallization of low working temperature provides the possibilities to utilize waste heat or other sustainable energy resources(such as geothermal or solar energy).

2.3 Membrane distillation applications

Even though membrane distillation was patented in the 1960s[25], it is has not been commercialized because of the success of competing technologies. However in the last few years, MD has emerged with numerous commercially devices and novel applications besides desalination.

An increasing industrial application for MD is the treatment of wastewater resulting from the textile industry, including the purification of dye solutions[26, 27]. Membrane distillation has also found applications in metallurgical processes for which no other membrane-based systems apply. Some applications include concentrating waste acid, caustic and salt solutions with concentrations as high as 1 mol/L[28].

A novel application for MD has been proposed by Cath et al.[29] who incorporated MD into a combined direct osmosis/osmotic distillation(DO/OD) process to treat hygiene and metabolic wastewater.

MD has been also explored in food industry for juice applications (for example, for the concentration of fruit juices at temperatures lower than other thermal methods for the preservation of the organoleptic traits and flavours[30, 31]) or to increase the alcoholic potential of the must[30] or to recover ethyl 2, 4-decadienoate (i. e., the main pear aroma compound from a solution containing an ethanol-water mixture)[32].

The separation of methanol-water mixtures and of benzene-toluene mixtures are other novel applications for MD[33].

Despite the potential for MD in all the above described systems, its wide commercial implementation has not yet taken place. However, the recent concerns emerging from greenhouse-gas emissions and energy consumption have prompted the industrial world to consider the use of renewable energy as a key factor for new technologies that are being developed. This aspect can be particularly exploited in water treatment systems where obtained waters are frequently warm and their thermal energy can be used to drive the MD separation process. Therefore, the MD treatment of waste brine streams becomes sustainable and useful to enlarge existing water supplies or reduce brine disposal volumes. An example can be found in the waste water produced by oil and gas industry referred as oilfield water or produced water. Produced water leaving the oil and gas production process is in general at a high temperature making the treatment with membrane distillation ideal[34, 35]. Nevertheless, volatile components containing in the produced water, such as small organic molecules and dissolved gases might be transported across the membrane, causing contamination of the permeate[35]. Different polyvinylidene fluoride (PVDF) and polypropylene (PP) hollow fiber membranes were tested in direct contact MD for desalting real high saline oilfield produced[36] and the analysis of the collected permeates indicated that salt rejection factors greater than 99% and total carbon rejection higher than 90% can be achieved. Alkhudhiri et al.[37] have tested air gap membrane distillation for the treatment of produced water. They found that salt and organic rejection are as high as 99. 99% and 98. 6%, respectively.

2. 4 Membrane condenser for water capturing

Another novel membrane contactor application with the vision of water separation and recovery from industrial gaseous waste steams is membrane condenser[38-40]. In this membrane technology, hydrophobic membranes are utilized for water condensation and recovery in the retentate side of the membrane module, whereas the dehydrated stream is recovered on the permeate side of the membrane. Experiments have been carried out to evaluate the membrane module performance in terms of amount of recovered water, in function of various operating parameters (i. e., membrane characteristics, temperature, pressure and relative humidity of the inlet flue gas). The experimental results were validated through the simulation analysis of the process. The achieved results indicate that high amount(>20%) of the water vapor initially contained in the flue gas stream can be recovered as liquid with very low ΔT(<5℃) between inlet flue gas and membrane module.

The water obtained by condensation assisted by membranes represents a new and promising source of water. Membrane condenser, moreover, might be considered of interest in various gas streams treatments, with membrane as an appropriate pre-treatment for dehumidification or reduction of ion concentration.

2. 5 Membrane technology for energy production

Membrane engineering is contributing in a positive way not only to minimize water shortage and raw materials depletion, but it also provides the possibility to produce energy from clean and sustainable sources. Attention towards *green energy resources*, such as solar or wind, is growing and more and more these energy sources are being implemented not only in industries but also for household consumption. However, most of these energy sources are dependent upon weather conditions and frequently not applicable continuously. A sustainable form of energy source independent from solar radiation or wind power is the salinity-gradient energy, also called blue energy. The latter is the energy that can be obtained from mixing water streams with different salt concentrations. Blue energy is available where fresh water streams flow into the sea or it can be made available from natural or industrial salt brines.

In general, all techniques currently available for salty water treatment could be used to generate power from salinity gradients when operated in the reversed mode, such as: pressure-retarded osmosis (PRO) and reverse electrodialysis(RED).

PRO is an osmotically driven membrane process that uses a membrane to separate two solutions with different salinity (for example fresh water and seawater). If hydrostatic pressure is applied to the concentrated solution, the water transport will be partly retarded, which results in a pressurization of the volume of transported water. This pressurized volume can be used to generate electrical power in a turbine.

In RED a concentrated solution (e. g. , seawater) and a dilute solution (e. g. , river water) flow through a stack of alternating cation and anion exchange membranes (CEMs and AEMs) between a cathode and an anode. The chemical potential difference between the two solutions induces a voltage over each membrane (membrane potential), and the total potential of the system is the sum of the potential differences over all membranes. The chemical potential difference activates ion transport through the membranes from the concentrated solution to the dilute solution. The potential difference over the electrodes can be used to generate electrical power when an external load or energy consumer is connected to the circuit.

PRO and RED have their own field of application: PRO seems to be more adapt to generate power from concentrated saline brines because of the higher power density combined with higher energy recovery. For the same reason, RED seems to be more attractive for power generation using seawater and river water[41].

Although the salinity gradient power was recognized more than 50 years ago, many research and development issues, especially those related to membrane properties and costs, still need to be resolved before PRO and RED are available for large-scale commercial application. However, a reconsideration of these membrane processes is worthwhile due to the declining membrane costs, to the increasing prices of fossil fuels and to the possibility to re-design desalination plants for water and energy production via the integration of RO (as desalination technology) and RED (as energy production technology).

A hybrid RED system using highly concentrated solutions recovered from a seawater desalination plant (based on RO or evaporation) and further concentrated by solar evaporation, and seawater (or brackish water) as the dilute solution, has been proposed by Brouns[42]. Model simulations of this system indicate that the development of thin membranes with specific characteristics in terms of resistivity and permselectivity in an adequate RED stack design is necessary for producing a high RED output. A FP7 European funded project "*Reverse Electrodialysis Alternative Power Production* (acronym: *REAPower*)" launched in 2010 is utilizing RED for energy production from the brine of the desalination plants. The vision of the project is to gain a power output of 53.6 kW/m^3 by mixing brine and seawater. By this an expected power density of 21.5 W/m^2 can be obtained[43]. Furthermore, extensive research is devoted to materials and component development for the commercialization of this particular procedure.

Post et al.[41] estimated that the global energy output from estuaries is 2.6×10^{12} W, which is approximately 20% of the present worldwide energy demand. Skilhagen[44] estimated that the cost of energy from osmotic power is 50 ~ 100 €/(MW · h), which is comparable and competitive with other new renewable energy sources such as wave and wind[44].

A Norwegian company currently commercializing PRO is Statkraft. The first prototype was operational in 2009[44] and an agreement has been signed with IDE technologies for the design and construction of a 2 MW pilot plant[45, 46]. In the next, a plant of 25 MW will be realized[47, 48]. If the energy output from all Norwegian salinity gradient sources (around 12 TW · h/a) will be recovered, 10% of the Norwegian power consumption will be saved[49].

3 Membrane materials for membrane contactor applications

Membrane development is an essential key-factor for the commercialization of membrane operations. An example has been the development of the asymmetric cellulose acetate membrane for reverse osmosis (RO) which made RO desalination a commercial opportunity in the 1960s. Until now membrane improvement has mainly been focused on making the membrane more hydrophilic for the needs of pressure driven membrane operations. The development of novel polymeric membranes is now evolving for the use in the new membrane operations such as membrane distillation and membrane crystallization. In the past, membrane distillation has been mainly carried out with commercial membranes properly manufactured for microfiltration, however research activities on preparation of membranes specific developed for MD are emerging rapidly[50]. Fluoropolymers (such as PVDF, PTFE and ECTFE) provide the possibility to manufacture hydrophobic membranes with superior thermal stability, improved chemical resistance and low surface tension[51]. PVDF is widely used for contactor applications because of the easy processability with phase separation methods along with good hydrophobicity and chemical resistance[51]. Several PVDF membranes have been prepared by changing the processing conditions, such as additives, solvents, air gab, bore fluids etc. [52]. The prepared membranes have shown good performance both in direct contact membrane distillation and vacuum membrane distillation[52]. Superior hydrophobic membranes can be obtained by coating the PVDF membranes with e. g. HYFLON in order to improve the mechanical resistance, the micro-structure and the liquid entry pressure[53].

Recent approaches are also considering the performance of microporous hydrophobic/hydrophilic composite membrane, with a top hydrophobic thin layer responsible for the mass transport, and a hydrophilic sub-layer able to reduce the conductive heat loss through the whole membrane matrix[50].

Although membrane operations are highly affiliated with sustainable development, in the membrane preparation procedures some toxic solvents are used. In order to ensure the overall sustainability of the membrane technology, from membrane/module fabrication to end-product utilization, Cui et al. have investigated an environmental friendly solvent, acetyl tributyl citrate (ATBC), for the preparation of PVDF membranes[54]. This solvent can also be used in medical application, beverage industry, toys, etc. The carried out study indicated that the prepared PVDF membranes exhibited good mechanical properties, promising for water treatment applications.

4 Conclusions

High water stress, increasing energy consumptions and mineral depletion are all already critical issues. Process engineering is one of the disciplines more involved in the technological innovations necessary to face these strongly inter-connected problems. As a matter of fact, water is also needed for energy generation(e. g., cooling component); energy is also needed in desalination and for raw material production (especially in mining where large amount of energy and water are necessary).

Recently, process engineering has suggested the logic of Process Intensification (PI) to resolve these problems. Membrane technology, whose basic aspects satisfy the requirements of the PI strategy, can represent a problem-solver with inter-correlated solutions. In the last years membranes operations have been already assigned a key role in water reclamation schemes that are aimed at higher water quality reuse applications (i. e., reverse osmosis is considered one of the most promising technologies for desalting salty waters). Moreover, the traditional membrane separation operations (e. g., MF, UF, NF, RO), widely used in many different applications, are today combined with new membrane systems such as MD, MCr, PRO RED. At present, redesign of important industrial production cycles by combining various membrane operations suitable for separation and conversion units, and thus realizing highly integrated membrane processes, is an attractive opportunity because of the synergistic effects that can be attained.

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Survey on the Development of Membrane Science and Technology in China

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Research on membrane and membrane processes was started from 1950s in China. In 1958, the membrane research in China was started in Institute of Chemistry. The first membrane was ion exchange membranes based on PVA[1]. In 1965, exploring research on reverse osmosis(RO) membranes was begun. This work was pioneered by Prof. Gao in Ocean University of China. First RO membrane is cellulose acetate(CA) membrane. This work laid a good foundation for the progress of membrane science and technology in China. In 1970s, Chinese membrane entered the developing stage. The membranes and related modules are most developed, such as electrodialysis (ED), RO, ultrafiltration(UF) and microfiltration(MF). In 1980s, membrane technologies stepped into application stage, and also some new membrane processes were developed. Water treatments by membrane technology were put into application, such as seawater desalination, pure water production, purification and concentration of various liquids; and some of applications were in large scale. Meanwhile, gas separation (GS) membranes developed very quickly. The membrane processes for oxygen enrichment and separation of N_2/H_2 entered pilot period. Studies on pervaporation (PV), membrane distillation (MD), inorganic membranes (IM) and membrane reactors (MR) were also carried out. In 1990s, membrane research got into a rapid developing period. Various membrane and membranes processes were investigated extensively. Especially, preparation of inorganic membrane entered commercialization, and inorganic membranes were applied in chemical industry. In addition, membrane application in bioengineering was launched. From the beginning of this century, Chinese membrane researchers made a great progress. In the aspect of membrane preparation, many new types of membrane materials were studied, such as RO TFC membrane, PVDF membrane prepared by TIPS, zeolite membranes for pervaporation. In the aspect of membrane processes, MD process in pilot scale for sea water desalination and MBR process in large scale for water reuse were carried out. Some new membranes and new membrane processes are being investigated.

At present, there are over 100 membrane research teams in China and they are located in Chinese universities and research institutes. Among them, about 30 research groups contribute important work to membrane research of China. In fact, in these years the development of membrane technology in a large extent benefited from the Chinese government's strong support. One important financial support for most researchers is from National Natural Science Foundation of China(NSFC). Another very important financial support is from the Ministry of Science and Technology of China. There are three main types of supports from it. One is national basic research program, named "973", which is the biggest grant to support fundamental research in China. The second program is "863" plan, and it promotes lab's technology to pilot or commercial scale. The third program is the National Key Technology R&D Program, and this program supports the pilot technology to industrial scale. From 2003 to now, we are granted two phases "973" plan, and obtained about 60 million RMB. The "973" plan greatly promoted the fundamental studies of membrane science and technology in China. Under of the great support from Chinese government, Chinese membrane research made a great progress. The number of the Chinese patents in membrane field increases year by year, and more and more papers about membrane research were published by Chinese researchers. Furthermore, a large membrane market has been formed in China because the foreign membrane companies entered and China itself has a lot of enterprises. There are nearly 1000 membrane companies, and among them over 300 are membrane manufacturers. Some big membrane manufacturers have played a significant role in membrane production and membrane processes in China. They shorten the gap of membrane technology between China and some advanced countries in some membranes.

MF/UF membranes are the biggest membrane production in China. As for preparing porous polymer MF/UF membranes, there are two main methods, NIPS and TIPS. Generally, the MF/UF membranes via NIPS method have big finger-like pore, but their pore sizes are not uniform. The membranes via TIPS have uniform pore size and good mechanical strength. A patented technique from Zhejiang University prepared low cost and high performance of capillary PVC(polyvinyl chloride)blending membranes[2]. The membranes can be used for ultrafiltration or nanofiltration processes. One of the biggest UF membrane manufacturers is Litree Company. It can produce 3 million m^2 PVC membranes per year, and have over 500 000 residential customers. For examples, the PVC membranes were applied for water treatment at Kaohsiung of Taiwan with capacity of 300 thousand ton per day, and membranes based water system provided direct drinking water for visitors from 260 countries for Shanghai World EXPO2010. The PVC membranes are also applied for municipal water treatment.

The PVDF hollow fiber membranes have been widely applied in different areas. This most used field is the membrane bioreactor(MBR) system based on the membrane. PVDF membranes can be prepared by TIPS method. The key point of TIPS method for PVDF membranes is to select a suitable diluent to undergo the liquid-liquid phase separation with PVDF polymer. Tsinghua University has successfully developed a series of diluents with different polarities to broad the liquid-liquid phase separation region for PVDF membranes[3]. They obtained suitable diluents such as DPK and DPC and got bicontinous microstructure of PVDF membranes. Furthermore, they recently have realized the industrial production of PDVF membranes via TIPS by Scinor Corporation with the yield of 300 thousand m^2 per year. Some PVDF membranes have been applied in water treatment, for example in Solar and Steel industry, with the capacity of 30 thousand tons per day.

During the application of MF/UF membranes in water treatment, one of the critical problems is the membrane fouling. For example, in the MBR system, there is always formation of bio-fouling film on the membrane surface, resulting in reduced separation performance and short lifetime of membranes. In order to improve the hydrophilicity and anti-fouling properties of the porous membranes, a series of surface modifications of polymer membranes, such as polymer grafting, plasma treatment, copolymerization and macromolecule immobilization have developed by Zhejiang University[4-6]. These developed approaches are very effective to avoid bio-fouling.

Recently, RO membranes have been made dramatic progress in China. Several new monomers for RO membranes with high flux and antifouling properties have developed[7,8]. These work made the performance of domestic RO membranes closer to the world advanced products. RO manufacturer Vontron Company increased the Chinese RO market share. The application of RO membranes in China mainly includes drinking water production, pure water industry and desalination of seawater. Take water desalination for example, the numbers of RO equipment with capacity over 100 ton per day are about 40.

For pervaporation process, there are many groups focused on polymeric membranes in China. Group-contribution method calculating the solubility parameters of the membrane materials and the components of the target separation system has been developed by Tsinghua University[9]. They obtained a series of high performance pervaporation membrane, including PVA and PDMS. The PVA pervaporation membrane has been commercialized. One of the typical PVA applications of pervaporation membranes in China is for solvent dehydration. Until now, there are over 60 solvent dehydration plants using PVA membranes in China, such as for ethanol, isopropanol system dehydration.

From 1980s, the main membrane materials developed in China for gas separation are PDMS, PI, PMP, PPO and PTMSP. The applications of these membranes are over 26 provinces and districts in China. The applying fields cover many gas-related industries. One of the widest applications of gas separation membranes is hydrogen recovery and purification. The application fields include synthesis ammonia process, methanol production, and refinery gas. Furthermore, gas separation membranes are also applied for VOCs recovery, such as application in gas station, olefin purge gas and oil production process. In order to obtain CO_2 gas separation membrane, several groups devoted to develop several new membrane materials for CO_2 gas separation. For example, Dalian Institute of Chemical Physics and Tianjin

University recently have developed many kinds of high performance gas separation membrane materials with good anti-plasticization and antioxidizability properties, such as crosslinked polyimide, multi-permselective materials and novel fixed carrier membrane materials[10-12].

China has the world biggest chlorine alkali industry with the capacity of 35 million ton per year. Developing domestic ion exchange membranes are critical for Chinese researchers. In 2010, Dongyue Group successfully developed the production line of domestic perfluorinated ion exchange membranes, and they applied in chlorine alkali plants with the capacity of 10 thousand tons per year. Another kind of ion exchange membrane is bipolar ion exchange membranes. Domestic bipolar ion exchange membranes have been developed by University of Science and Technology of China and realized their industrial production and application[13]. For example, the bipolar ion exchange membranes can be applied for acid recovery from aluminum foil production feeds. The treatment amount of feed acidic solutions reached 59 thousand m^3 per year.

Besides organic membranes, there are many institutions in China devoted to the research of inorganic membranes, and they are mainly located in the eastern coastal cities. Among them, the research group from Nanjing University of Technology is the biggest, which is led by Prof. Nanping Xu. From 1990 to now, inorganic membranes have a great development and impressively from the laboratory to the market. There are several important milestones. The most important milepost is Prof. Xu's Group made the ceramic membrane technology from the laboratory to the market in 1997.

Ceramic microfiltration and ultrafiltration membranes have been large-scale produced and applied for more than ten years in China. At present, commercialized MF and UF ceramic membranes are main alumina, zirconia and titania. Jiangsu Jiuwu High-Tech Co., Ltd. is the biggest manufacturer for ceramic membranes in China. It supplies tubular and multichannel membrane elements. UF ceramic membranes were used to deal with the wastewater such as banknote printing wastewater and rolling emulsion. When the membrane technology used in banknote printing wastewater, it can reuse of the treated water and recovery of valued dyes. Steel factory can produce large amount of oil-water emulsion. When we used the ZrO_2 membrane, the rejection of oil reached 99.9%, and recovery of water larger than 90%. This process is running for over 10 years. The technique is used in more than 20 steel factories. One important application of porous ceramic membranes is in the biotechnology industries, such as for inosine refinement. Compared with the traditional technology, ceramic membrane technology improves inosine recovery from 85% to more than 90%, reduces the consumption of acid and base, reduces 70% waste water and decreases 60% of COD in waste water. Because of chemical resistance and thermal stability, ceramic membranes can be applied in chemical industry. One example is porous ceramic membrane reactor. The membrane reactor technology can be used in heterogeneous catalytic reaction, which can couple the catalytic reaction with the membrane separation in one process and realize the product and catalyst in-suit separation. It can be applied in the production of important medicine intermediate p-aminophenol and chemical intermediate cyclohexanone oxime. Ceramic microfiltration membranes were successfully employed to remove ultrafine catalysts from the reacted slurry. The recovered catalysts were recycled continuously back to the reactor and reused in the next batch of reaction.

In the last decade, zeolite membranes have attracted much attention because of their potential applications as selective separation membranes, catalytic membrane reactor, chemical sensors and microelectronics. Most work of this field has focused on the synthesis and applications of NaA and MFI zeolite membranes. For preparing NaA zeolite membrane, the wiping and dip-coating method was applied to seed support to low the influence of defect of mullite and raise the permeation flux[14]. What's more, using polymer-NaA zeolite composite hollow fiber as support of NaA membranes, PV dehydration results shows that the flux increases to 9.3 kg/($m^2 \cdot h$) and separation factor is still larger than 10 000[15]. MFI zeolite membrane prepared on YSZ hollow fibers support shows higher alcohol separation performance from alcohol/H_2O systems than the other inorganic supported MFI membrane. NaA membranes have been large-scale produced by Nanjing University of Technology and industrial applied for isopropanol, methanol, and ethanol dehydration.

Mixed ionic-electronic conducting (MIEC) materials are widely investigated in China since 1990s. The challenges of MIEC are developing new membrane materials with high oxygen permeability and high chemical stability, new methods for the preparation of materials and membranes and new dense membrane reactors. Many kinds of MIEC materials have been developed in recent years. For preparation of asymmetric mixed-conducting membrane, especially of supported tubular membrane, a combination of spin-spraying and co-sintering method has been developed. It provides a new path for the preparation of asymmetric tubular membrane. This simple and cost-effective fabrication technique can be readily used for mass production. On the aspect of the applications of MIEC membranes, they can be used for partial oxidation of methane(POM), CO_2 decomposition coupled with POM, water splitting and NO decomposition etc.

Porous metals are of great interest as a potential engineering material in various industrial fields because of their unique properties such as their impact energy absorption capacity, their gas and liquid permeability, thermal conductivity, and electrical insulating properties. Porous Ti – Al & Fe – Al alloys membranes have been prepared by Central South University. The membranes have been applied for production of $TiCl_4$ and $ZnSO_4$.

In the past decade, new membrane materials and membranes have also a great development in China. Various bio-inspired smart gating membranes of thermo-responsive, pH-responsive, glucose-responsive, molecular-recognizable have been successfully developed by Sichuan University[16 – 18]. For example, a positively K^+ – responsive membrane with functional gates driven by host-guest molecular recognition is prepared by grafting poly (NIPAM-co-AAB15C5) copolymer chains in the pores of porous nylon-6 membranes[19]. The grafted gates in the membrane pores could spontaneously switch from “closed” state to “open” state by recognizing K^+ ions in the environment and vice versa. The positively K^+ – responsive gating action of the membrane is rapid, reversible, and reproducible.

Membranes with highly uniform pore size are important in various fields. Zhejiang University reported the preparation and performance of ordered membranes templated by breath figures, and the pore diameter of the membrane is on the micrometer scale[20]. The ordered membranes (pore diameter of 3 μm) fabricated at two-phase interfaces enable a high-resolution and energy-saving separation process. Nanjing University of Technology prepared uniform membranes characterized by easily accessible, continuous nanopore systems with well-defined, uniform pore sizes by nondestructive replication of nanoporous polymeric membranes with likewise bicontinuous morphologies[21]. The nanoporous polymeric membranes consisted of recoverable asymmetric BCPs and were generated by selectively swelling the minority component of the BCP accompanied by reconstruction of the domains consisting of the glassy majority component[22].

Metal-organic frameworks are constructed from metal ions or ion clusters acting as "joints" and the organic ligands (imidazolates for ZIF) as "linkers" to produce the porous coordination polymer with the highly regular structure. This material has many advantages with high surface areas, tailor-made pores, designable structures, preferential adsorption. Because of the advantages, MOF has been regarded as a new type of membrane material. The first MOF (HKUST-1) membrane was prepared on copper net via in situ hydrothermal growth, which shows excellent H_2 separation performance[23]. The MOF-based mixed matrix membrane (ZIF-8/PMPS) was synthesized. It shows a very promising performance for recovering bio-alcohols from dilute aqueous solution[24]. Nanjing University of Technology developed a facile reactive seeding method for the preparation of continuous MOF membranes, in which the porous support acted as the inorganic source reacting with the organic precursor to grow a seeding layer[25]. The as-prepared MIL-53 membrane shows high selectivity for dehydration of the azeotrope of ethyl acetate (EAC) aqueous solution by pervaporation. A new generation of a chiral separation membrane composed of homochiral $Zn_2(bdc)(l\text{-}lac)(dmf)$ (Zn-BLD) was successfully fabricated on a porous zinc oxide substrate by a reactive seeding technique[26]. An *ee* value of 33.0% for *R*-methyl phenyl sulfoxide (MPS) over S-MPS was obtained at the feed concentration of 5 mmol/L. In addition, step-by-step seeding method was developed to prepare HKUST-1 (known as $Cu_3(btc)_2$) membranes on porous α-alumina supports.

Recently, in order to promote the development of membrane materials industry, "12th five-year plan" (2011-2015) in membrane field has listed the “membrane materials with high performance” as major project by the Ministry of Science and Technology of China. The key directions include water treatment, gas separation, special membranes and new membranes and membrane processes. These researches will provide theory foundation of design and preparation for application-oriented membrane materials.

In summary, membrane science and technology has been made great progress since 1990s in China. Next, much attention should be paid to the research through the efforts of ourselves, and the international exchange and cooperation. The development of membrane science and technology in China has been internationally recognized. Chinese researchers are being expected to make a greater contribution to the development of membrane science and technology in near future.

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Membranes and Water—Recent Developments

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1 Introduction

Membrane technology is playing an increasingly important role in the water industry. This includes membranes for surface water treatment, for desalination (both brackish and seawater), for waste treatment in bioreactors and for water reclamation and reuse (see Fig. 1). The available membrane technologies range from low pressure microporous membranes (MF and UF) to higher pressure membranes (NF and RO), as well as electrodialysis and the emerging techniques of forward osmosis (FO) and membrane distillation (MD).

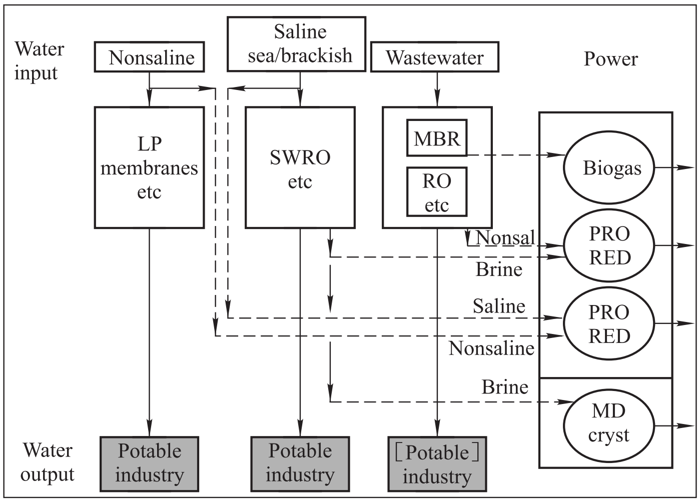

Fig. 1 The membranes and water domain

Recent developments have focused on novel membranes and operations and assessing novel processes. The drivers have been improved efficiency and energy issues, in response to the need to reduce GHG emissions. In this presentation the status of membranes and water is reviewed. In addition, examples are provided by the development of membrane technology in Singapore and research at the Singapore Membrane Technology Centre.

2 Singapore & SMTC

Singapore is a world leader in the application of membrane technology to water supply. Currently more than 1. 2 megatons per day of water pass through membranes in Singapore. This comprises about 274 MLd(million liter per day) surface water treatment, 455 MLd desalination and 500 MLd NeWater reclamation. Not surprisingly this membrane-dependent environment supports R&D in membrane technology. A recent report (Lux (2013)) highlights the success of this approach with the top 2 universities being from Singapore. The research in the SMTC reflects many of Singapore's priorities and the latest trends in membranes and water.

The Singapore Membrane Technology Centre was established in early 2008 with the primary objective to do fundamental and applied research in membrane technology for environment and water industries. The SMTC has more than 40 projects in the thematic areas:

- water production,
- water reclamation,
- membrane bioreactors,
- energy issues,
- sensors and monitoring,
- membranes for special needs.

Underlying objectives are to improve efficiency and reduce energy usage in membranes in water. There are major efforts in (i) novel membranes, (ii) module design and operation, (iii) fouling and its control, (iv) novel and improved membrane applications. The following highlights our activities.

3 Novel membranes

1) Reverse osmosis. Although desalination is constrained by minimum

energy and osmotic pressure considerations there is the potential to reduce seawater desalination energy by 25% to 30% with superpermeability membranes. As a result there is an ongoing quest for such membranes. One approach may be biomimetic membranes, incorporating aquaporins which are natural protein-based water channels with high water and low salt permeability. Aquaporins can be combined with liposomes to form spherical vesicles, and we have shown that these can be incorporated into thin film composite (TFC) membranes (Zhao et al., 2012) with fluxes enhanced by 50% or more. Both flat sheet and hollow fibre composites are possible.

2) Low pressure NF. Several methods have been evaluated to produce NF membranes capable of water softening at modest pressures ($\leqslant 2$ bar). Methods include layer-by-layer deposition of polyelectrolytes and dual layer hollow fibres. Using the latter process membranes have been prepared with water permeabilities of 15 lmh/bar ($L/(m^2 \cdot h \cdot bar)$, 1 bar $= 10^5$ Pa) and rejections of mono and divalent ions of about 10% and >90% respectively. Numerous applications of these membranes are envisaged.

3) Forward osmosis (FO). FO is a hot topic due to its potential for low energy processing or in energy recovery (see below). SMTC has produced both flat sheet and hollow fibre membranes with outstanding properties. Membrane structure is a key issue with a required RO-like skin layer and a thin and highly porous support layer. We can produce TFC hollow fibre membranes with high water permeability and low salt transmission (Chou, 2010). A dual skin hollow fibre has been prepared to help control internal fouling of the membrane. A development of our FO membrane is very suitable for Pressure Retarded Osmosis (PRO, see below).

4) Membrane distillation (MD). MD has the attraction that it can process salty water to high recoveries and extract water from SWRO brine. It is also amenable to use of waste heat with low GHG emissions. MD membranes need to be hydrophobic and highly porous, and we have developed techniques to increase contact angles into the superhydrophobic range (Liao et al., 2013). This property allows MD operation without wetting out and loss of separation. We are using MD membranes in MD crystallization and the MD bioreactor (see below).

4 Modules, hydrodynamics, systems

Advances in membranes need to be matched to enhanced techniques to control concentration polarization and fouling. SMTC has been examining various strategies to enhance polarization control.

1) Vibrations. Vibrations can be readily applied to submerged hollow fibres, both axially and laterally, to control polarization and fouling. We have observed better enhancement with lateral movement and a small degree of fibre looseness (Li et al., 2013). Theoretical analysis suggests improved control for small diameter fibres (Zamani et al., 2013). It is more challenging to apply vibrations to RO modules. However we have shown that rotational vibrations of a spiral wound module can significantly delay the onset of scaling.

2) Bubbling. Although bubbling is widely used for polarization and fouling control in MBRs there is a need for optimization (Xia et al., 2013). The benefit of two phase flow has also been demonstrated in a hollow fibre MD module where bubbling has improved shell-side flow distribution and increased flux by over 100% (Chen et al., 2013).

3) RO cascade design. There are novel ways to modify polarization and osmotic effects in RO. In an RO process plant there are combinations of membrane modules and pressure vessels in multistage cascades. SMTC has developed novel arrangements based on the 'reflux-recycle' concept familiar to chemical engineering. As an example, our analysis shows that the process can be operated at lower pressures, or can achieve higher recovery (75%) at the typical pressure for 50% recovery operation (Chong et al., 2013).

5 Operational and fouling issues

Fouling is a significant source of inefficiency in all membrane processes. SMTC has been investigating fouling across the spectrum from low pressure pretreatment, RO, MBRs, MD and FO applications. One of the most challenging issues is biofouling.

1) Biofouling in RO. Using well-controlled feed and operating conditions we have shown how biofouling in RO is mitigated by flux, crossflow, the

presence of spacers, nutrient level etc(Suwarno et al., 2012). The rate of fouling correlates with the estimated concentration of nutrient at the membrane surface. Confocal microscopy of autopsied samples reveals the development of the biofilm components. A novel biomimicry strategy is being evaluated that uses NO donors to trigger biofilm dispersion, with encouraging results(Barnes et al., 2013).

2) Biofouling in MD. The MD bioreactor (see below) experiences biofouling that manifests as a fouling resistance. In addition the biofilm also influences the magnitude of the vapour pressure in MD through the Kelvin effect(Goh et al., 2013). Interestingly the biofouling appears to protect the membrane from early wetting out.

6 Applications and processes

The following describes examples of novel membrane applications in the water domain.

1) Pressure retarded osmosis (PRO). PRO provides a means of generating power from salinity gradients, such as seawater/river water or SWRO brine/NeWater brine. The most effective PRO membranes are modified FO membranes that can maximise the osmotic pressure difference. SMTC has developed both flat sheet and hollow fibre PRO membranes (Chou et al., 2012); our most recent membranes can achieve 20 W/m^2 at 15 bar and this is competitive with any other reported PRO membranes. There are also new flow sheet options involving the combination of PRO with RO. Energy savings and increased water recovery are feasible.

2) Forward osmosis draw solutes. Some applications of FO can take advantage of available draw solutes, as in the PRO example above. Other applications may become feasible if an effective draw solute is developed. The requirement is for a material with high osmotic pressure that is readily regenerated. One approach being developed at SMTC is the use of thermo-sensitive hydrogels(Cai et al., 2013).

3) MD crystallization(MDC). Seawater RO brine, and other concentrated salts can be processed by MDC to recover water and solids. The challenge is control of the crystallization process external to the MD module and also to

optimise the energy usage of the process. The trade off between membrane area and energy usage has been analysed by an Aspen-based model (Guan et al., 2012).

4) Novel membrane bioreactors (MBRs). In addition to a comprehensive study of conventional MBRs, including fouling (Zhang et al., 2006), SMTC is developing a range of novel MBRs. The MDBR (Phattaranawik et al., 2008) and the FOMBR (Yap et al., 2012) are 'high retention' (HR) MBRs using membranes that allow operation with ORT>>HRT, providing time for treatment of recalcitrants. Both MBRs have the potential to use low grade heat and to produce high quality water. A feature of the HRMBRs is that salts also accumulate. This means that halophilic biomass is required; the MDBR also needs thermophiles for operation at ca 55℃. Additional MBR applications involve the Fluidized Bed Anaerobic MBR for low fouling and biogas production and the Extractive MBR with organic (membrane) extraction into a bioreactor for organics in difficult feed waters (salty, pH extremes).

5) Membranes for special needs. Water supply is usually jeopardised after tsunami or earthquake events. SMTC has an interest in membranes for these situations, as well as in third-world water supply. We have proposed a decision tool for emergency water supply technologies (Loo et al., 2012) and have developed an 'integral membrane' based on cryogels that can achieve good water recovery from turbid streams (Loo et al., 2013).

6) Life cycle assessment (LCA). Decision tools are useful in the identification of preferred process options. The widely used LCA technique has only recently been used for membrane technology applications. SMTC has applied LCA to assess the ecotoxic impact of brine discharge the improved approach (Zhou et al., 2013) reduces reliance on chemical analysis and ecotoxicology tests.

7 Sensors and monitoring

The efficiency of membrane processes can be improved by effective monitoring to provide early warning of problems. SMTC is evaluating and developing a number of sensors for low pressure and high pressure membrane processes.

1) Integrity sensor (IS). This device can detect changes in permeate quality from a low pressure membrane due to membrane or fibre damage. The IS responds to small changes in transmembrane pressure when a sample passes over the IS ‘collection’ membrane (Krantz et al., 2011), and can detect 1 damaged fibre in 10^5 fibres. The IS is commercialized by a start-up company (MINT P/L).

2) Ultrasonic time domain reflectometry (UTDR). The UTDR has been used for several years to detect membrane fouling. SMTC has extended the UTDR applicability to detection of colloidal and bio-fouling. The latter is a particularly challenge as biofilms have similar acoustic impedance to water and this has been overcome using an acoustic enhancement technique (Sim et al., 2013). Application involves a ‘canary cell’ concept where a side stream passes through a flat sheet simulator (operating at similar conditions to the plant) with a UTDR detector. The canary cell signal preempts the problems on the plant, providing an early warning.

3) Electrical impedance spectrometry (EIS). The canary cell can also be fitted with EIS detectors. Using electrodes in the feed and permeate streams the EIS uses a wide range of AC frequencies and detects the impedance spectra that can then be interpreted in terms of fouling layers. SMTC, in collaboration with Inphaze Pty Ltd., has shown that EIS signals provide a ‘finger print’ associated with different types of foulant (Sim et al., 2013).

8 Future prospects

Fig. 1 depicts the various membrane activities in water and related power and brine issues. There will inevitably be renewed efforts to reduce net power consumption in the membranes and water domain. In this section we speculate on trends for future developments.

(1) Desalination

Current state of the art membrane desalination demands about 3.0 to 3.5 kW · h/m^3 water produced. Of this about 2.5 kW · h/m^3 is used for the membrane processes of pretreatment (ca 0.3 kW · h/m^3) and reverse osmosis (ca 2.2 kW · h/m^3), as depicted in Fig. 2. The RO stage, including energy recovery, typically operates at about 2x the minimum energy of separation (1.06 kW · h/m^3 at 50% recovery for 35 g/L seawater (Elimelech and Philip, 2011)). There are some opportunities to reduce the membrane process energy demand for desalination and these are summarized at the bottom of Fig. 2. Firstly the pretreatment, to reduce turbidity and assimiliable organic carbon, could potentially be achieved in a biologically stabilized, gravity-driven, UF process (similar to Peter-Varbanets et al., 2010). The energy demand for this could be negligibly small. For RO the next generation of super-permeability membranes, configured in a multistage cascade, could potentially shave 30% off the RO energy demand giving a value around 1.5 kW · h/m^3 (Fig. 2). Finally the osmotic power embedded in the RO brine could be recovered by PRO, if a low salinity stream is available, to yield up to 0.3 kW · h/m^3 brine. The lower salinity stream could be concentrate from a wastewater reclamation plant. A spin-off from this PRO stage would be a diluted seawater brine for discharge. Overall the energy for membrane desalination could drop from about 2.5 to a value in the range 1.5 to 1.2 kW · h/m^3. This would represent a significant drop of 40% to 50% in desalination energy demand. The trade off would be a larger footprint for pretreatment and for the PRO process, and additional capital cost for the PRO.

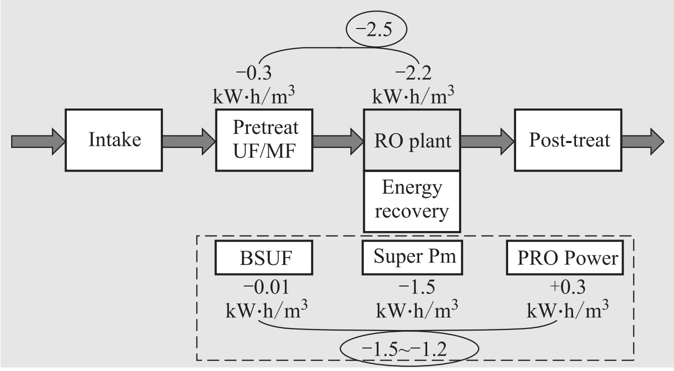

Fig. 2 Membrane desalination and energy demand

(2) Other FO opportunities

Direct desalination by FO is limited by the availability of a suitable 'engineered' draw solution that is readily regenerated; the development of such a draw solute is a long term challenge. However FO can be attractive when high salinity streams are available. Two examples could have application in the short term, as follows:

1) Seawater pretreatment. In this case seawater provides the draw and impaired water(low salinity wastewater) is the diluting stream. This approach delivers lower osmotic pressure feed to RO, with potential energy savings(Sim et al., 2013a). The trade off is a product water derived partially from waste water.

2) Fertigation. In this process the draw solution is a concentrated fertilizer and the dilution water could be brackish ground water. The FO process provides a means of ground water desalination with modest energy demand (Phuntso et al., 2011).

(3) MD opportunities

The attractions of MD, namely processing at high salinity and the ability to use waste heat(as a low GHG option), provide significant incentives for more applications of this technology. Of interest are opportunities to increase seawater recovery by brine processing, possibly combined with recovery of valuable minerals, and a coupled process with FO, where MD achieves regeneration of draw solute. In addition MD is being considered for concentration of 'produced water', for example in a process combining MD with vapour compression(globenewswire, 2013).

(4) Anaerobic MBRs

Energy, as biogas, from municipal wastewater should have a big future. The membrane bioreactor has potential benefits in providing control of SRT, some control of ORT, and yielding a high quality water. However membrane fouling may be an issue. The anaerobic fluidized bed MBR appears to control fouling at modest energy demand without gas scouring(Kim et al., 2011). SMTC is helping to optimize this approach with Korean and US partners. Another option for future AnMBRs may be the use of vibrating membranes(Li et al., 2013).

(5) Fouling monitors

Developments at SMTC point to the use of novel sensors to detect incipient fouling in membrane plant, allowing for corrective action. Cost benefit analysis should be able to confirm the suitability in a given application. The noninvasive detection methods based on various electromagnetic and optical properties can be incorporated into ‘canary cells’ located in a process sidestream to monitor the ‘state of the process’ (Sim et al., 2012), or in sensors measuring the ‘state (fouling propensity) of the feed’. Fig. 3 depicts the approach that could use telemetric communication of data.

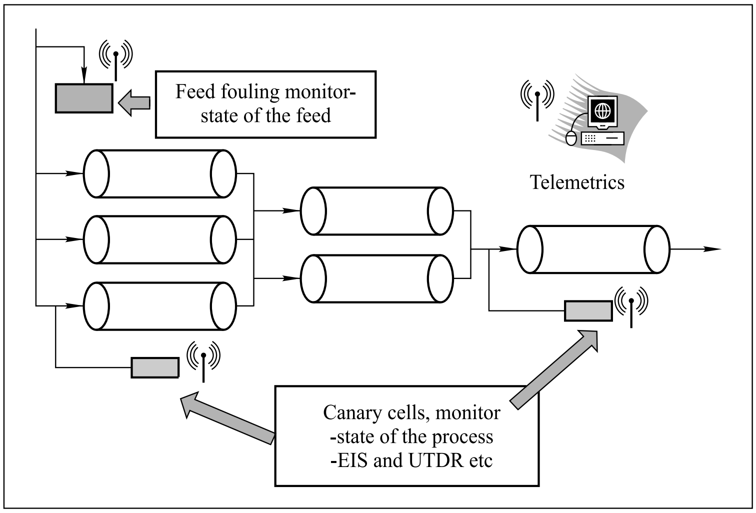

Fig. 3 Sensors for fouling control in RO

9 Conclusions

Membranes are vital to water supply. Reflecting global interests, research at the SMTC covers the spectrum of membrane-water activities, from non-saline to saline to wastewater. There are many opportunities to increase efficiency and reduce net energy requirements.

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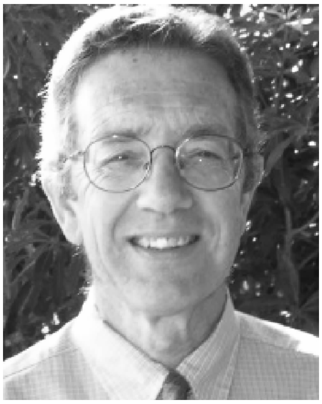

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饮用水安全问题与膜法水处理技术进展

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摘要:针对日益严重的水源污染和水资源短缺问题,研发高效的饮用水净化技术是亟待解决的民生问题之一。膜分离技术因其高效、低耗等优点在饮用水安全保障方面备受关注。本文针对饮用水安全面临的难题和挑战,介绍了膜法饮用水净化技术的发展沿革,论述了膜组合工艺在饮用水安全保障方面的应用现状,对未来膜法饮用水净化技术的发展提出了建议。

关键词:膜技术;水处理;饮用水;安全

一、引　言

饮用水安全问题主要包括两个方面:饮用水资源短缺和饮用水质保障。其中,饮用水质量直接关乎人类健康,因而受到人们的广泛关注。随着工业和经济的发展以及城镇化速度的加快,饮用水污染问题已呈日益恶化的趋势。世界卫生组织(WHO)调查资料显示,目前水中已见报道的污染物高达2221种,其中供人们饮用的自来水中可能含有近750种对人体有害的物质,全世界已发现的约80%的疾病和50%的癌症与饮用不洁净的水有关[1]。

由于中国近年来经济的快速发展,环境问题日益显著,一些地区的饮用水源受到污染。另外,突发性的非传统安全事件对饮用水安全同样造成一定威胁。因此,开发实用的饮用水净化和应急技术,构建完善的安全保障体系具有重大意义。

近年来,膜技术在分离纯化方面表现出的明显优势使其在饮用水安全保障方面得到了很好的应用[2,3],相对于传统的水处理技术,膜分离技术净化饮用水更为绿色、高效。

二、饮用水安全面临的挑战

（一）中国饮用水资源总体现状堪忧

中国的饮用水面临着淡水资源匮乏，水资源分布不均，地下水质恶化与过度开发，湖泊水量与水质急剧降低等诸多安全问题。而且中国 80% 的饮用水净化方法还停留在传统的混凝、沉淀、过滤、消毒四步工艺，而传统的净化工艺已难以应对近年水体中越来越多的有机污染物，使得安全合格的饮用水更难得到保障。

（二）污染物种类多元化

由于中国工农业发展较为迅速，产业发展模式不够完善，造成环境污染比较严重，从而导致饮用水源呈现复合污染趋势，大大增加了饮用水处理的难度和成本。常见的饮用水污染种类及其危害见表 1。

表 1　饮用水污染类型及危害

污染类型	危害
悬浮物污染	水体变得浑浊，吸附有毒物质、重金属、农药等
氮磷有机物污染	为水中微生物生长提供营养，导致水体微生物污染
重金属污染	重金属使蛋白质变性，对人、畜有直接的生理毒性
酸碱污染	饮用水 pH 值的过高或过低，都影响人的体液环境
难降解有机物污染	难以生物降解，容易在生物体内累积
放射性物质污染	导致生物畸变、破坏生物的基因结构及致癌等
热污染	水温升高使水中某些毒物的毒性升高
特种污染物	含有各类病毒、细菌、寄生虫等病原微生物，流入水体会传播各种疾病；生物毒剂或化学毒剂破坏人体内的新陈代谢过程

（三）传统净水工艺面临新挑战

尽管中国饮用水安全保障力度持续加大，法律法规和标准体系日益健全，饮用水安全状况得到显著改善。但由于中国经济发展方式尚未得到根本改变，加之受全球气候变化和工业化、城镇化快速推进的影响，饮用水安全形势仍然不容乐观：相当部分的淡水资源难以直接饮用，需要初级或深度处理，以华北地区地下水为例，可直接饮用的仅占 22.2%，需要专门处理的高达 56.55%[4]。另外，污染问题日益突出，新污染物不断出现，污染日趋复杂，饮用水呈现污染物复合、污染过

程复合以及污染效应复合的复合污染特征。而传统水处理工艺以去除水中悬浮物、胶体颗粒物为主,对小尺度污染物去除能力有限,因此,严格的水质标准和严重的污染问题直接挑战着传统净水工艺,使之面临巨大的挑战,膜法水处理技术被认为是保障饮用水安全的重要方法之一。

三、膜法饮用水净化技术的发展及应用现状

(一)膜法饮用水净化技术的发展沿革

针对日益复杂的饮用水安全问题,越来越多的研究者将目光投向膜技术。20世纪末研究者开始尝试将微滤(MF)技术应用于饮用水净化研究,并于2005年在美国康涅狄格州的Foxwoods Casino厂采用调节pH值后加曝气预氧化和压力式柱状微滤膜工艺,饮用水净化处理的效果均良好[6]。随着对MF净水工艺研究的深入,发现MF产水不够洁净,分离尺度更小的超滤(UF)过程的用于饮用水净化处理,研究发现,UF的产水较MF更为纯净,对常规的自然水源,经UF处理后便可达到饮用水安全标准,典型案例是对美国明尼苏达州规模为26万m^3/d的Minneapolis净水厂进行改造:原工艺为投加石灰软化—铁盐混凝—沉淀—滤池过滤,改造后的过程则采用压力式柱状超滤膜替换滤池,产水水质得到明显提高[6]。

随着膜法饮用水净化技术的发展,发现对于盐度较高或小分子有机物较多的水源,UF往往难以奏效,特别是UF对TOC、COD_{Mn}、UV_{254}的去除率偏低[7]。于是开始尝试将纳滤(NF)和反渗透(RO)技术应用于饮用水净化处理,发现RO和NF具有非常良好的有机物和盐去除性能[8]。Gaid等[9]对法国Mery-Sur-Oise水厂NF工艺做了详细的研究,结果表明该工艺对有机物有着很好的去除效果:对溶解性有机碳(DOC)平均去除率为60%,对农药莠去津(Atrazine)和西玛津(Simazine)去除率达90%以上,出水中残留的微污染物绝大部分低于分析检测限度。

近年来,随着部分地区饮用水源呈现复合污染的趋势,以及对膜法饮用水净化技术研究的不断深入,逐渐形成了以膜技术为核心的组合工艺,并将饮用水净化从常规处理逐步推向以膜组合工艺为主的深度处理。

(二)膜组合工艺在饮用水安全保障中的应用进展

由于饮用水中可能含有多种污染物,单一的膜法饮用水净化过程往往难以保证水质安全。膜组合技术将多个分离过程相结合,可以发挥不同过程的分离特点,达到处理复杂污染的效果,是饮用水深度处理的常用方式。膜集成工艺通常包括图1所示的三个主要部分:预处理、主处理及精处理。其中,预处理工艺主要

用于去除原水中的胶体、颗粒物、细菌等，一般选择去污因数低、适用范围广的处理技术，如絮凝沉淀、吸附、过滤、超滤、微滤等；主处理工艺主要使用能大幅降低原水中重金属、放射性元素和有机物的技术，如蒸发、纳滤、反渗透等；精处理工艺：选择能够深度去除水中污染物的工艺，如离子交换等。

图1　膜组合工艺流程示意图

1. 膜过程与其他技术的组合工艺应用进展

机械过滤是最简单的预处理工艺，将机械过滤的产水加药杀菌后进入膜系统构成组合工艺，可以大幅度提高产水水质。典型的应用实例是如图2所示基于此组合工艺的天津杨柳青水厂，该膜组合工艺处理示范工程建成于2008年5月，以微污染的滦河原水为水源，系统产水规模为5000 m^3/d，总产水率为98%，运行结果表明[10]：出水浊度主要集中在0.07～0.08 NTU，除浊效果理想；粒径大于2 μm的颗粒数稳定在10个/mL以下，大大提高了去除两虫的保障率；常规工艺出水和膜出水的耗氧量接近，都满足标准要求，但总体趋势膜出水更好；另外，与传统工艺相比，膜工艺的加氯量和三氯化铁投加量较少，对铁、亚硝酸盐、细菌、藻类等水质指标的去除效果更好。

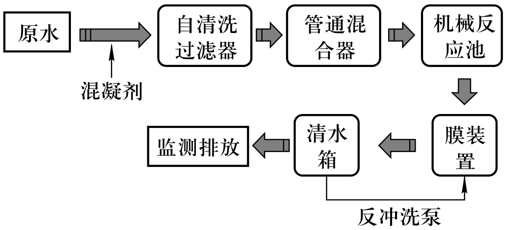

图2　天津杨柳青水厂膜处理示范工程流程示意图

混凝是饮用水处理过程中最常用的工艺之一，直接将混凝与微滤（MF）或超滤（UF）组合的工艺较为简单，但混凝过程对膜的影响颇有争议，一些学者认为金属离子与水中的天然有机物发生结合之后，容易在膜表面沉积，从而加重膜的污染[11]。因此，简单地絮凝与膜组合工艺较少被采用。

活性炭吸附可以有效地去除水中大部分低浓度有机物和色度，20世纪70年代后期开始被应用于饮用水处理，但对有机物等的去除不够彻底，并且活性炭中容易滋生微生物，因此活性炭吸附后再经膜处理可以确保水质安全。Tomaszewska等[12]将UF和活性炭吸附相耦合，该组合工艺对色度、腐殖酸、酚的

去除率分别为96%、89%、97%。另外,也有人发现使用活性炭和UF的组合工艺对合成有机物(SOC)、嗅和味的去除效果均有很大的改善[13]。Tsujimoto[14]则对颗粒活性炭(GAC)吸附与UF组合工艺进行研究,发现GAC的吸附作用和生物酶解作用,可以有效提高水中有机物的去除率、提高出水水质、降低膜污染。

臭氧具有非常良好的灭菌效果,Tanaka等[15]进行了臭氧预氧化和UF组合的工艺探究,他们发现臭氧可以将水中的有机物分解成不易污染膜的小分子物质,既提高产水安全性,又降低膜污染。

2. 多膜过程组合工艺应用进展

不同类型的膜孔径尺度差异较大,可用于去除不同尺度的污染物,该特点特别适合解决饮用水污染物多元化的难题。因此,多膜组合工艺成为目前饮用水深度处理的重要研究和应用方向。在多膜过程组合工艺中,设计者常将MF或UF作为系统预处理部分,而将纳滤和反渗透作为主处理工艺。最常用的工艺为利用MF去除大颗粒或者藻类,UF去除细菌和浊度,纳滤和反渗透则用于去除盐分和有机物。

多膜组合工艺最典型的代表为海水淡化过程。根据膜的孔径大小MF膜可用于去除藻类,因此,早期或部分水质较好的海水淡化过程中,MF被作为RO的预处理过程并简化系统工艺。例如,2005年建成的世界上最大的以色列Ashkelon海水淡化厂主要设施由五个部分组成,其中,最核心部分即由MF和RO过程组成,作为最终预处理的MF产水进入RO脱盐,整个产水能力达到33万m^3/d。然而,很多地区海水浊度较高,直接使用MF很难奏效,又有设计者开发出连续MF为代表的新型MF技术,并被广泛使用,它们可以更好地降低水体中胶体颗粒和细菌数量,产水水质更为优异[16]。

由于RO膜表面为致密的分离薄层,对进水的SDI等有较高的要求,MF并不能完全保证RO的进水要求。UF作为RO的预处理技术是近期发展起来的很有潜力的膜工艺,特别适合于高浊度海水原水:UF出水SDI值一般为0.2~1,浊度在1 NTU以下,且水质非常稳定,基本不受原水水质变化的影响。例如,中国首个自主设计并由国内企业总承包的最大膜法海水淡化工程于2011年在河北曹妃甸建成投产[17],日产淡水5万m^3,该工程便是采用“气浮-UF-RO”的联合工艺(图3)。

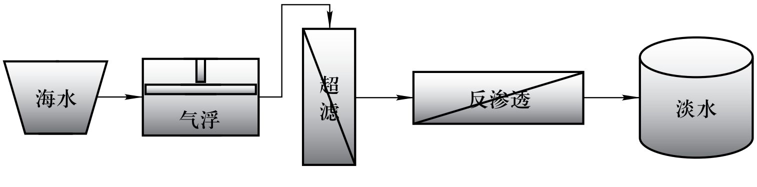

图3 曹妃甸多膜组合海水淡化工艺流程图

多膜组合工艺不仅能有效地保障饮用水水质，而且还具有非常好的操作灵活性，可以根据水质的不同调节所使用到的膜过程，因而特别适合水质动态变化的地区使用。例如，周志军等[18, 19]利用 UF 和 RO 组合工艺建立了一个海岛饮用水处理示范装置，该装置可以根据沿海池塘水在季节变换时产生的淡咸水交替的问题，控制单独使用 UF 或者组合工艺，既保证供水质量，也降低了运行成本。类似地，印度 Dasari 等[20]最近在安得拉邦 Prakasam 建立了一个 UF 和低压 RO 的组合工艺示范装置用于处理地表和地下水，并进行了经济性评价，发现地表水需要采用组合工艺进行处理，水回收率达到 60%；而地下水采用 UF 装置处理后即可达到饮用标准，水回收率为 80%，因此，从经济性考虑针对不同水源应采用相应的处理工艺。

合理的组合工艺设计还可以获得高产水回收率。例如，将低压 RO 与 UF 组合，UF 的浓缩水作为低压 RO 进水，则可大幅度减少浓水的排放，提高系统产水效率。陈欢林等[21, 22]以钱塘江潮汐咸水为研究对象，将超滤、纳滤和反渗透三膜过程组合用于处理周期性变化的潮汐水。其中，超滤作为整个系统的核心工艺，在淡水期作为主产水单元；纳滤则在咸水期使用，可以除去咸水中的大部分盐；低压 RO 作为最后一个环节，用于 UF 和 NF 的浓水脱盐，进一步回收淡水，在保证产水达标的情况下，整个系统的回收率可达 90%～95%。

表 5 列出了几种典型的膜组合工艺用于处理饮用水的结果，从表中可以看出，以膜过程为主的组合工艺在饮用水安全保障方面效果非常明显。

表 5　针对不同处理对象的膜集成工艺对比

膜集成工艺	处理对象	处理结果	参考文献
UF + RO	地表水（印度）	去除几乎所有的盐分和有机物，水回收率达到 60% 以上	[20]
UF + NF + RO	钱塘江水	去除水体盐分、有机物，大大提高系统水回收率	[21, 22]
MF + RO	地下水	产水达到国家饮用水标准，口感大大改善	[23]
混凝 + MF + RO	低浊度海水	产水达到国家饮用水标准	[24]
UF + RO	高浊度海水	COD_{Mn}、总硬度、Cl^- 的去除率分别达到了 95%、98%、97% 以上，脱盐率也达到 97%	[25]
MF + RO	高污染海水（西西里岛）	产水达标，多年来运行稳定，耐生物污染	[26]
NF－RO	海水	降低操作压力，提高回收率	[27]
UF + RO	波斯湾海水（阿联酋）	产水效果好，回收率高	[28]
MF + RO	地中海海水（以色列）	产水达标，产水量大，是世界最大的海水淡化工厂之一	[29]

3. 新能源膜组合工艺研究进展

反渗透和纳滤等均属于压力驱动膜过程，产水过程需要克服渗透压，能耗相对较高，因此开发利用太阳能、风能和核能等新能源的膜组合工艺具有重要的意义。

辽宁红沿河核电站利用核能驱动，采用 UF + RO 组合工艺建立了中国首个核电海水淡化项目，出水水质达到生产和直接饮用的标准[30]。

太阳能是最可再生能源，邵卫云等[19]在舟山岛建立的以雨水为水源、以太阳能为动力的屋顶接水与超滤供水组合示范系统，是膜组合工艺的崭新形式。另外，为了弥补阴雨天太阳能无法工作的不足，还开发了如图 4(b)所示的太阳能加风能发电系统，为膜过程提供能源，大大提高了紧急电力保证度，供水能力可达到 15 m^3/d。

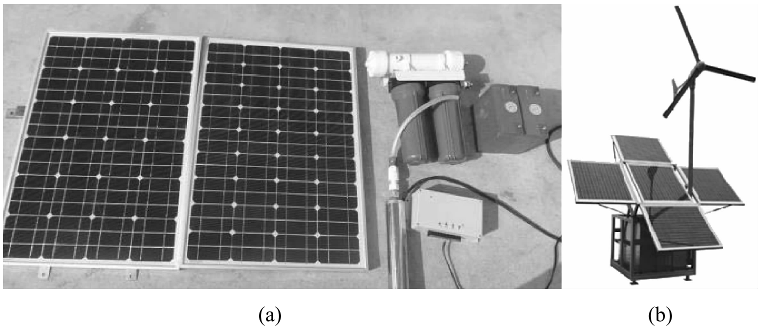
(a) (b)

图 4　太阳能动力屋顶接水供水系统示范和太阳能加风能发电系统

El - Shaarawi 等[31]搭建了一个太阳能光伏泵驱动海水淡化反渗透组合系统，并建立了一个数学模型来描述不同操作参数、地区和天气条件下太阳能 - RO 系统海水淡化的性能和投资成本，模拟结果对建立独立的小型太阳能驱动 RO 海水淡化具有重要的参考意义。

4. 膜法应急供水组合工艺研究进展

当发生强降雨等较大自然灾害时，供水系统容易受到水源污染、管道破裂、污水渗漏等损害，水中各种有机物、重金属、微生物等严重超标，使得水源中各组分异常复杂、水质变差，严重影响饮用水安全。采用常规的饮用水制备工艺来处理雨水，难以保证产水水质，结合应急供水的特征，对雨洪等进行适当的预处理后，使其满足 RO 等膜技术的要求，经低压 RO 处理后即可获得符合国家标准的饮用水。

根据已有的研究工作，基于 UF 和低压 RO 膜过程的双膜组合工艺可以在雨

洪应急供水安全中发挥重要的作用[32]。针对多变、污染的水源,经双膜处理后的产水水质稳定、达标。除此之外,膜集成应急净水装置还具有适合多途径运输、多方位组装、复杂的环境和气候,可长短期切换运行等特点。

王世昌等[33]报道了国际上近几年才开发出的膜法紧急供水淡化与净化系统(图5),装置主要技术包括UF或UF+RO,装置易于运送与安装。该系统可适应于高浊度水、海水、核污染水、生物与化学污染水等。该装置具有除浊能力强,可从3000 NTU除到0.5 NTU,可除重金属铅、钙、汞、砷等,产水稳定,不易堵塞,快速净化(只需3~5 s)等优点。


(a) (b)

图5 美国开发的远途救援净水系统

随着核能的开发和国际形势日趋复杂,发生放射性污染的可能性正在逐渐增大,一旦发生日本福岛核电站泄漏等类似紧急状况,高性能的应急供水装置就显得非常重要。据报道采用以纳滤为核心技术的特殊污染水处理膜组合系统,可将比活度为5488 Bq/L的原水净化成比活度为0.3289 Bq/L的净水(表4),对放射性核素的去除率大于99.99%[2,34,35]。

表4 特殊污染水处理膜组合系统对放射性物质的去除

核素	水比活度/(Bq/L)	出水比活度/(Bq/L)
铯-137	794	0.069
钚-239	120	0.0179
锆-95	1640	<0.095
铌-95	2470	<0.065
钌-103	464	<0.082
合计	5488	0.3289

四、膜法饮用水安全保障的展望与建议

（一）未来膜法饮用水安全保障的研究重点

随着膜法饮用水净化技术发展逐渐成熟，以及水安全问题的日趋严峻，对膜法饮用水安全保障体系也提出了更高的要求，因此，可以预见以下几个方面可能会成为膜法饮用水安全保障的研究重点。① 耐污染膜与工艺的开发：膜法饮用水净化的成本较传统工艺偏高，延长膜的使用寿命可以适当降低制水成本，所以深入开展膜污染机制研究，开发耐污染膜和基于“临界污染点”设计抗污染的工艺显得尤为重要；② 膜法处理饮用水时，有益离子的保留问题：尽管可以通过膜组合工艺得到水质非常稳定的去离子纯净水，但纯净水作为长期饮用水源是否健康一直是个有争议的话题，大多数研究者认为，选择性地保留一部分有益离子是非常有必要的，如何充分发挥分离膜的选择性，有效或选择性地保留有益离子将成为未来的研究方向之一；③ 反渗透浓海水的处理：随着海水淡化产能的增加，排放到近海的浓海水量逐渐增加，对环境造成了严重的污染，浓海水中含有大量有价值的物质，同时高盐水也具有高的化学能，利用正渗透、反电渗析等技术进行盐差发电可能会成为未来的一个研究热点。

（二）膜法饮用水安全保障发展建议

膜法水处理技术是目前最有效的饮用水安全保障手段，其去除效率与膜的类型、进水水质、运行条件等因素息息相关，在实际应用中，应针对不同的水质和运行条件来研发最适合的膜处理组合工艺，实现多种技术优势互补；同时还需继续研发新型的膜材料与膜组件，如具备抗污染、抗氧化、高通量、机械强度高、寿命长、价格低廉的新型膜材料，以及新型大单元膜组件和新型膜组件组合方式，推动膜用于水净化和深度处理过程；此外，由于目前膜技术应用方面的研究较多，膜分离机制方面的研究还不够系统，还不能科学合理地解析膜的分离过程，对工程实践也缺乏指导作用，因此探讨膜分离过程的解析表达是膜科学研究的重点之一。

利用好雨水与海水这类非传统饮用水源，同样可以有效地缓解用水供水矛盾，对雨水资源进行收集、储存和净化后可以直接利用；而以海水为原水，通过海水脱盐处理生产淡水，将在中国饮用水供应中发挥越来越大的作用。鉴于膜法饮用水净化技术的优势，应加快推进膜法处理饮用水的管网准入制度建设。

五、结　　语

饮用水安全是保障社会发展、维护公众健康的关键物质基础，而膜技术是水处理领域的新技术，随着国家政策扶持力度的不断加大，膜分离技术的创新发展，相信未来膜技术在水安全保障领域的应用将更广阔。

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Status of Potable Water Security and Progress of Membrane Water Treatment Processes

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Abstract: As to the increasingly serious water pollution and shortage, developing effective process to assure the security of potable water is one of the urgent livelihood issues. Membrane-based water treatment has attracted attention and been studied to purify drinking water due to its high efficiency and low consumption. In this paper, the difficulty and challenge of the safety in the potable water have been introduced, and the developing history of the membrane process for potable water treatment has been presented. The application progress of membrane integrated process for assuring the security of potable water has been reviewed. Finally, several suggestions are listed for the development of membrane-based water treatment in potable water supply.

Keywords: membrane process; water treatment; potable water; safety

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纳滤膜法处理和回收废水中低浓度全氟辛酸铵

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摘要：采用纳滤膜考察了从废水中回收全氟辛酸铵的可行性，先用全氟辛酸铵模拟溶液考察了纳滤膜 NF270 和 NF90 对全氟辛酸铵的截留效果，在全氟辛酸铵浓度为 100 mg/L 时，纳滤膜 NF270 的截留率为 92.0%，而纳滤膜 NF90 的截留率大于 99.0%。选用 NF90 进一步考察了操作条件对纳滤膜回收全氟辛酸铵效果的影响，在过膜通量为 66.4 L/(m^2·h)、搅拌速度为 2400 r/min、温度为 25℃ 时可以将起始浓度为 10 000 mg/L 的全氟辛酸铵浓缩至 117 073 mg/L，浓缩结束时跨膜压力为 14.9 bar，表明采用纳滤膜能够从废水中回收全氟辛酸铵。在小试实验工作的基础上，对该工艺进行了工业化放大，设计建造了一套日处理量为 200 t 废水的全氟辛酸铵回收装置，在某聚偏氟乙烯生产企业中用于处理和回收废水中低浓度全氟辛酸铵，取得了良好的效果。

关键词：纳滤；全氟辛酸铵；废水处理；回收

一、引　言

全氟辛酸（perfluorooctanoic acid，PFOA）是一种有机全氟化合物（perfluorinated chemicals，PFCS），在自然界中并不是天然存在，是由人工合成的物质，其制造和使用历史已经超过 60 年[1]。全氟辛酸较碳氢链表面活性剂具有更低的表面张力，润湿性能更好，具有良好的热稳定性以及化学稳定性，应用范围非常广泛。在含氟聚合物生产中，全氟辛酸的铵盐还被用作乳化剂，用于乳液法含氟聚合物的聚合反应中，生产的聚合物主要有聚四氟乙烯、聚偏氟乙烯、聚全氟乙丙烯等，全氟辛酸铵用于含氟聚合物的生产已经有 50 多年的历史。与其他典型的持久性有机污染物不同，全氟辛酸的水溶性较好，不易吸附至固体表面，排放到自然界中的全

氟辛酸都会迁移至水体中，且在迁移过程中不易被土壤、活性污泥吸附，非常容易在水体中累积。由于碳氟键的稳定性，全氟辛酸不易被降解，在不同国家和地区的地表水、地下水、海洋，甚至是自来水中都能检测到全氟辛酸的存在[2,3]，在人迹罕至的偏远区域，也能在自然环境中检测到全氟辛酸的存在[4]。全氟辛酸在生物体内和环境中不易降解，会在生物食物链和环境中累积，在人体内的半衰期在3.5年左右[5]，其对健康和环境的危害逐渐为众多研究所证实。因此，水体中的全氟辛酸污染急需引起重视。

工业废水排放被认为是全氟辛酸排放至自然界中的主要途径之一，许多文献报道生活在排放源附近的居民体内的全氟辛酸浓度较高[6,7]。由于全氟辛酸化学稳定性非常好，传统的污水处理工艺无法将其从水体中去除干净，需要采用如光化学降解法[8]、超声降解法[9]等方法才能将其部分降解，一般采用吸附[10]、絮凝[11]等方法将其从水体中去除。但由于全氟辛酸生产成本较高、价格非常昂贵，如果能够从废水中回收利用，还可取得显著的经济效益。目前，从废水中回收全氟辛酸铵的工艺主要有蒸馏浓缩法、泡沫分离法、离子交换法等方法，但都存在着回收效率低、成本高、造成二次污染等问题。纳滤膜的分离性能独特，尤其对低相对分子质量的有机物截留率高，用于处理含有低浓度有机物废水效果良好，可用做从废水中回收全氟辛酸。本研究采用纳滤膜回收废水中的低浓度全氟辛酸铵，并在实验研究的基础上在某化工厂进行了工业化运行，取得了良好效果，可为含有低浓度全氟辛酸铵废水的处理工艺提供一种新的方法。

二、实验

（一）实验材料

本实验考察了两种纳滤膜对全氟辛酸铵的浓缩效果，这两种纳滤膜分别是NF270和NF90，根据各制造厂商提供的资料以及实验测定的数据，这两种纳滤膜的基本性能参数如表1所示。

表1　实验用膜的基本性能参数

性能参数	NF270	NF90
膜材料	聚酰胺	聚酰胺
截留分子质量(MWCO)/Da	200	150
纯水透过系数(25℃)/[L/(m^2·h·bar)]	15.6	10.1
NaCl稳定脱盐率/%		85~95

续表

性能参数	NF270	NF90
$MgSO_4$ 稳定脱盐率/%	>97	>97
$CaCl_2$ 稳定脱盐率/%	40～60	
最高操作温度/℃	45	45
最高操作压力/bar	41	41
连续运行 pH 范围	3～10	3～10
短时清洗 pH 范围	1～11	1～11
最大给水污染指数(SDI)	5	5

脱盐率测试条件:500 mg/L $CaCl_2$,70 psi (4.8 bar),25℃;2000 mg/L $MgSO_4$,70 psi (4.8 bar),25℃;2000 mg/L NaCl,70 psi (4.8 bar),25℃。

实验所用全氟辛酸铵(ammonium perfluorooctanoate,APFO)由日本东洋纺化学生产,纯度大于98.0%,购于北京百灵威化学技术有限公司。溶液均用去离子水配制,所有溶液在进行纳滤实验前先经过0.45 μm的微滤膜预过滤。

(二)实验装置

纳滤实验装置如图1所示,带磁力搅拌的终端膜过滤装置为实验室自制,容积为13.0 mL,有效膜面积为4.52×10^{-4} m^2。实验操作温度保持在25℃,所有的实验都在恒定通量(constant permeate flux)条件下操作。纳滤实验装置(图1)主要由高压泵、进样柱(50 mL)和进样阀、带磁力搅拌的终端膜过滤装置、压力传感器及采集系统组成。在测试膜片纯水通量时,将进样阀切换至“load”状态,这时料液槽中的纯水直接进入膜过滤装置。在浓缩实验时,先将进样阀切换至“load”状态,将所需要的料液注入进样柱中,然后将门切换至“injection”状态,这时,进入纳滤实验装置的是进样柱中的溶液。所用进样阀和进样环与高压活塞泵配套,最高能承受40 bar的压力。

(三)分析方法及仪器

全氟辛酸铵溶液的浓度采用紫外分光光度计在210 nm处测定,所用仪器为上海精密仪器厂UV757CRT分光光度计。但紫外分光光度法在测定浓度小于50 mg/L的全氟辛酸铵溶液时偏差较大,不能用于定量。

参照文献[12],低浓度的全氟辛酸铵采用高效液相色谱和质谱联用测定,但操作条件与文献[12]有些不同。实验所用设备由美国Agilent公司HPLC1100和美国Thermo Fisher公司LCQ Deca XP电喷雾质谱组成,色谱柱为Zorbax SB C18

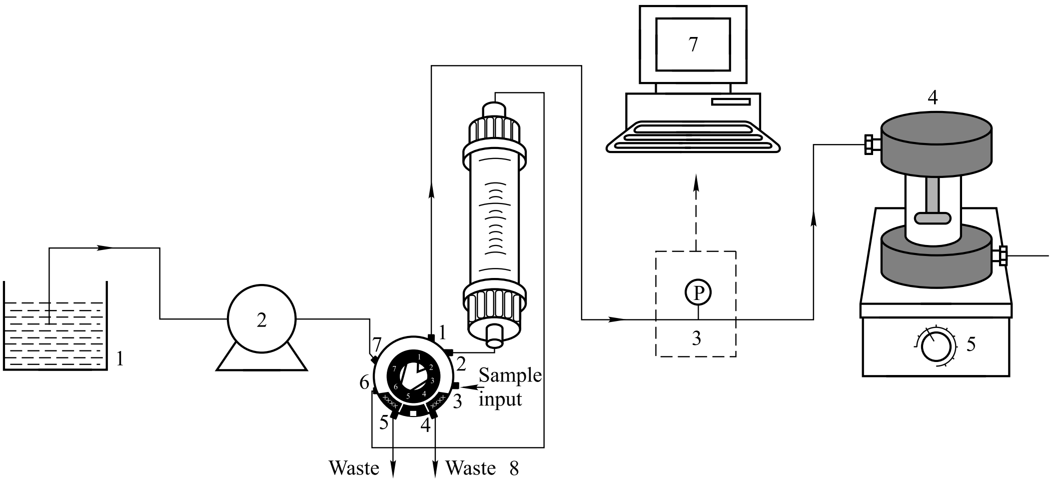


图 1　带进样装置的纳滤实验装置示意图

1. 料液槽；2. 高压泵；3. 压力传感器；4. 带磁力搅拌的终端膜过滤装置；5. 磁力搅拌器；6. 渗透液收集槽；7. 计算机数据采集系统；8. 进样阀和进样柱

(150 mm × 2.1 mm i. d.，5 μm)；流动相 A：水(含 0.1% TFA)，B：乙腈(含 0.1% TFA)；梯度：0 ~ 13 min，B：30% ~ 90%，13 ~ 20 min，B：90%，20 ~ 25 min，B：90% ~ 30%，25 ~ 30 min，B：30%；流速：0.2 mL/min，进样量为 50 μL。

质谱条件：ESI 电喷雾离子源，喷雾电压为 4.5 kV，加热电压为 25 V，离子导入电压(skimmer 电压)为 20 V，离子传输毛细管温度为 300℃，采用负离子监测模式。

(四) 实验步骤及理论部分

1. 实验步骤

实验用膜在使用前先在去离子水中浸泡过夜，在进行纳滤实验前用去离子水在 20 bar 下压实 30 min 以上，待纯水通量稳定后再使用。实验采用浓缩操作模式，不断将料液由进料柱注入搅拌槽中，恒定过膜通量，检测并记录过膜压力，收集透过液，待达到一定的浓缩倍数后停止实验，收集浓缩液，分别测定透过液及浓缩液的全氟辛酸铵含量。

2. 计算方法

溶质的截留率用表观截留率(R_{obs})来表示，其计算公式为

$$R_{\mathrm{obs}} = \left(1 - \frac{C_{\mathrm{p}}}{C_{\mathrm{b}}}\right) \times 100\%$$

式中，C_{p} 为透过液中溶质的浓度，mg/L；C_{b} 为截留液侧溶质的浓度，mg/L。

由于实验采用终端过滤，截留液侧溶质的浓度是变化的，其浓度由下式计算：

式中，C_b 为截留液侧溶质的浓度，mg/L；C_{b0} 为截留液侧溶质的初始浓度，mg/L；C_p 为透过液中溶质的浓度，mg/L；V_0 为搅拌槽的容积；V_P 为渗透液的体积。

溶液浓缩倍数（volume reduction rate，VRR）用下式计算：

$$\mathrm{VRR} = \frac{V_0 + V_P}{V_0}$$

式中，V_0 为起始料液的体积；V_P 为浓缩液的体积，在本实验中，浓缩液的体积是恒定不变的，即为 13.0 mL。

三、实验结果及分析

（一）纳滤膜的评测与筛选

1. 纳滤膜的纯水通量测定

膜的纯水通量是膜性能的一个基本参数，与膜的孔径大小及孔隙率相关，在一定程度上与膜的截留率相关。在不同通量下测定膜的跨膜压力，考察其跨膜压力随过膜通量的变化情况，可以确定膜的稳定性。由图 2 所示，NF270 和 NF90 这两种的纳滤膜的跨膜压力随着过膜通量的增加而不断增加，且线性较好，表明在实验操作条件下，这两种膜的透水性能均非常稳定。

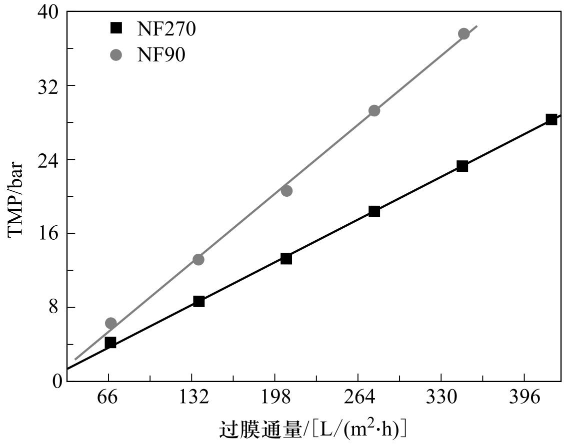


图 2　两种纳滤膜的跨膜压力随过膜通量的变化情况

在相同的过膜通量条件下，NF270 的跨膜压力要比 NF90 的小，根据公式 $J = L_p \cdot \Delta p$（J 为透过通量，Δp 为压差）可以计算两种膜的纯水透过系数，NF270 和 NF90 在 25℃时的平均膜纯水透过系数分别为 10.1 L/(m^2·h·bar) 和 15.6 L/(m^2·h·bar)，NF270 的纯水通量要比 NF90 大 50% 左右。

2. 两种纳滤膜对低浓度全氟辛酸铵的截留浓缩效果对比

将浓度为 100 mg/L 的全氟辛酸铵溶液注入搅拌槽中，分别用 NF270 膜和 NF90 膜对其进行浓缩，通量为 132.7 L/(m^2 · h)，搅拌速度为 600 r/min，温度为 25℃，每浓缩一倍时(透过 13 mL)收集透过液，记录跨膜压力，透过 143 mL 后停止浓缩(图 3)。

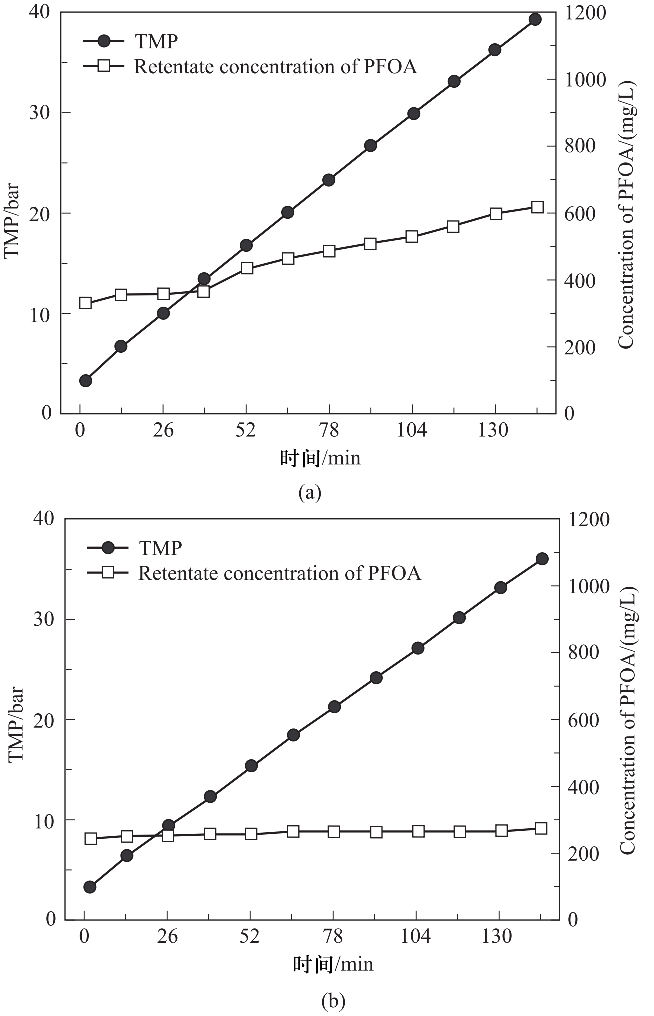
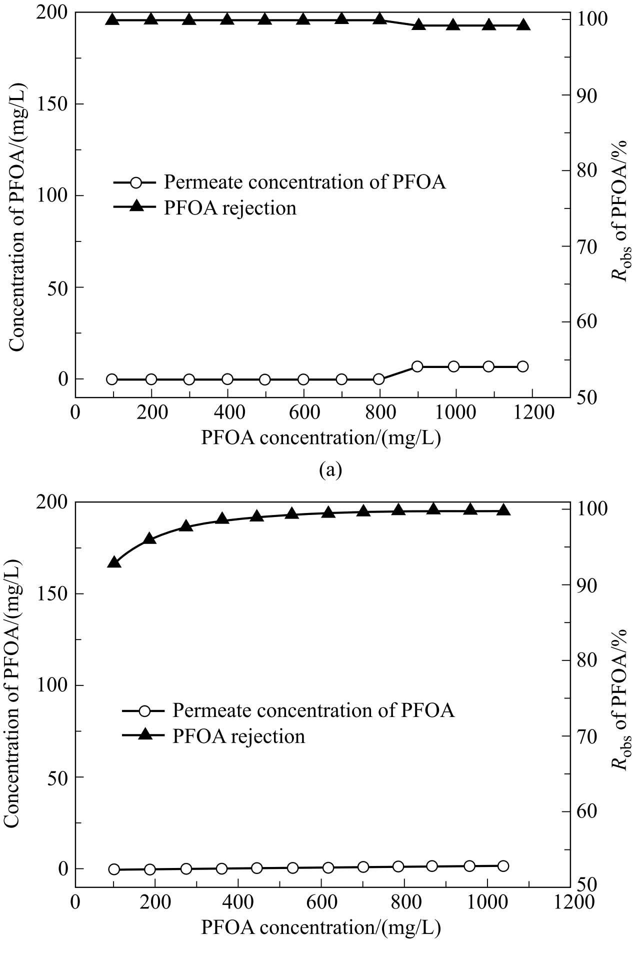


图 3　浓缩过程中跨膜压力(TMP)和浓缩液侧全氟辛酸铵浓度随时间的变化：(a) NF90；(b) NF270

在浓缩过程中，NF90 的起始跨膜压力约为 12 bar，要比 NF270 的起始压力 8.3 bar 高，但都与这两种膜在相同通量时过纯水的跨膜压力相似，说明在全氟辛酸铵浓度较低时，对膜的影响较小。随着浓缩的进行，NF90 的跨膜压力上升明显，当浓缩 12 倍时，NF90 的跨膜压力达到 20.6 bar，这时浓缩液侧的全氟辛酸铵浓度为 1178 mg/L。而 NF270 膜在浓缩过程中跨膜压力上升并不明显，在浓缩 12 倍时，NF270 的跨膜压力为 9.2 bar，这时浓缩液侧全氟辛酸铵的浓度为1105 mg/L。

这表明 NF90 对 PFOA 的截留率要高于 NF270，由图 4 可知，NF90 在全氟辛酸铵浓度较低时，膜的截留率接近 100%，而 NF270 的截留率在最低时仅有 92% 左右，但会随着截留液侧全氟辛酸铵浓度的升高而不断升高。虽然 NF90 的跨膜压力要比 NF270 高些，但在处理低浓度全氟辛酸铵时的截留率更高，所以更加适合用于含有低浓度全氟辛酸铵废水的处理。



(a)

(b)

图 4　浓缩过程中透过液中全氟辛酸铵浓度以及膜表观截留率随截留液侧浓度的变化：（a）NF90；（b）NF270

（二）纳滤膜操作条件对全氟辛酸铵回收效果的影响

在纳滤膜的使用过程中，膜的操作条件，如膜面流速、过膜通量、温度等对膜的分离、浓缩效果也会产生较大的影响。而过膜通量是其中较为关键的参数，增加过膜通量可以提高膜的处理效率，也可以增加膜的截留率，但是过高的膜通量会加剧膜表面的浓差极化，导致跨膜压力的升高，浓差极化导致的膜表面溶质浓度的升高还会导致膜表观截留率的下降以及透过液中溶质浓度的升高。

将10 000 mg/L的全氟辛酸铵溶液注入搅拌槽中，用NF90膜对其进行浓缩，搅拌速度为2400 r/min，考察不同通量66.4 L/(m^2·h)、132.7 L/(m^2·h)、199.7 L/(m^2·h)对浓缩效果的影响，温度为25℃，每浓缩一倍时(透过13 mL)收集透过液，记录跨膜压力。

在过膜通量为199.7 L/(m^2·h)时，起始的跨膜压力即为28.4 bar，后迅速上升至37.3 bar，只能浓缩三倍。降低过膜通量能降低跨膜压力，在过膜通量为66.4 L/(m^2·h)时起始跨膜压力为8.7 bar，至浓缩12倍时，跨膜压力也只有14.9 bar，还能继续浓缩(图5)。

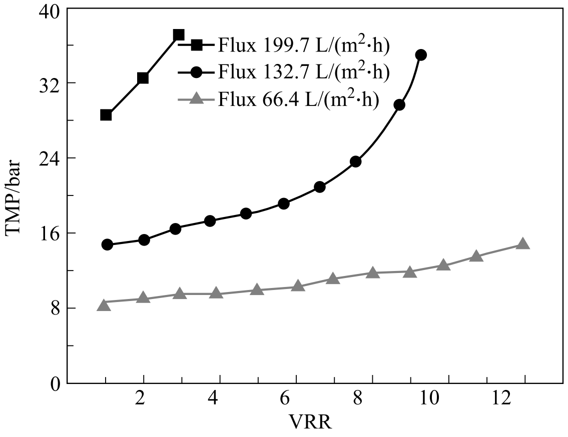


图5　不同过膜通量下跨膜压力随浓缩倍数的变化

从图6中可以看出，在较低的过膜通量时，透过液中的全氟辛酸铵浓度要高，提高过膜通量可以降低透过液中全氟辛酸铵的含量，这是由于增加过膜通量，提高了水的过膜速度，而水要比溶质更易透过膜，因此透过液中的溶质浓度会降低。但将过膜通量提高至一定程度时，会加剧浓差极化，导致膜表面的溶质浓度大大高于本体液中的浓度，透过液中溶质浓度升高，膜表观截留率降低。

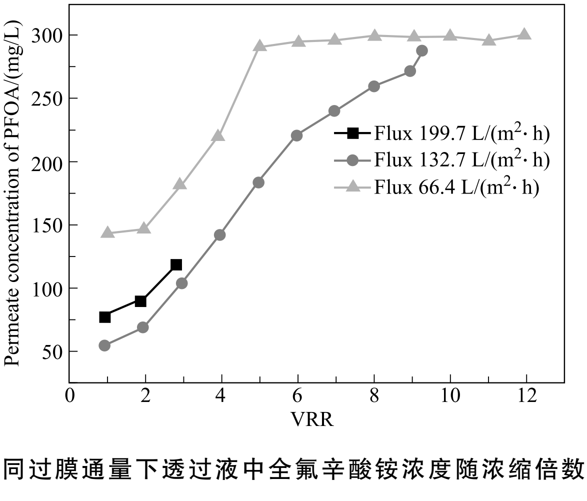


图6　不同过膜通量下透过液中全氟辛酸铵浓度随浓缩倍数的变化

在较低的过膜通量条件下，由于膜表面的浓差极化现象并不严重，可以将全氟辛酸铵溶液浓缩到较高的浓度，在过膜通量为 66.4 L/(m^2 · h)时，可以将起始浓度为 10 000 mg/L 的全氟辛酸铵浓缩至 117 073 mg/L(图 7)，而跨膜压力也只有 14.9 bar，浓缩效果较好。

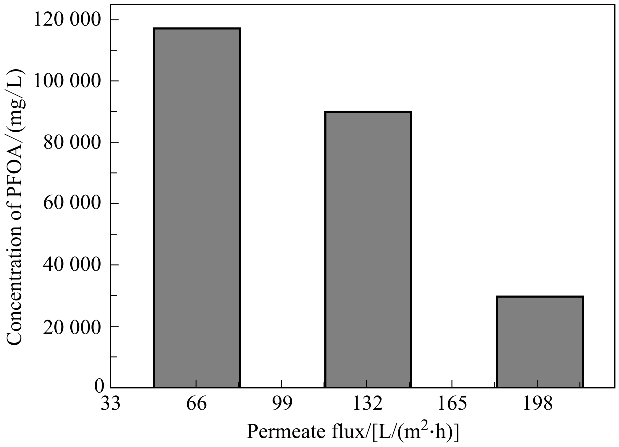


图 7　不同过膜通量下所能浓缩到的最高的全氟辛酸铵浓度

四、工业化应用及效益

实验研究表明，纳滤膜能够用于浓缩废水中低浓度的全氟辛酸铵，可将废水中浓度为 100 mg/L 的全氟辛酸铵浓缩至 100 000 mg/L 以上，得到的浓缩液可以重新用于生产过程中，经过处理后的水也可以用于其他生产工艺中，在进行废水处理的同时实现了有用物质的回收，具有明显的经济和环境效益。因此，进一步将纳滤膜法处理低浓度全氟辛酸铵废水工艺进行工业化应用，实施单位是一家生产聚偏氟乙烯聚合物的企业，排放的废水中不仅含有全氟辛酸铵，还有残留的聚合物。根据工厂的实际工况，工业化设计时在纳滤系统前面设计了一套超滤系统，用于废水的澄清，澄清后的废水再用纳滤膜浓缩全氟辛酸铵。

（一）设计概要

系统设计处理含低浓度全氟辛酸铵废水能力为 200 t/d，按照每天工作 20 h、2 h 清洗设备、2 h 机动设计，设备设计废水处理能力为 10 t/h。由于废水中的全氟辛酸铵含量较低，约为 100 mg/L，如需将其回用，需要尽可能将其浓缩，设计将废水浓缩 100 倍以上，且处理后的废水中含氟化合物含量低于 10 mg/L，满足国家相关排放标准。

（二）工艺流程

为了保证废水水量能够持续供应且废水水质的稳定，将含氟树脂生产过程中产生的废水统一收集起来放入原水储罐中，由于废水中含有较多的残留树脂，首先采用超滤系统将废水中的悬浮树脂去除，澄清后的废水放入超滤缓冲罐中，再用纳滤系统对澄清后的废水进行浓缩，浓缩液进入浓缩液储罐中，透过液一部分进入系统清洗用水储罐中（CIP 系统），一部分回用至其他工艺，具体的工艺流程如图 8 所示。

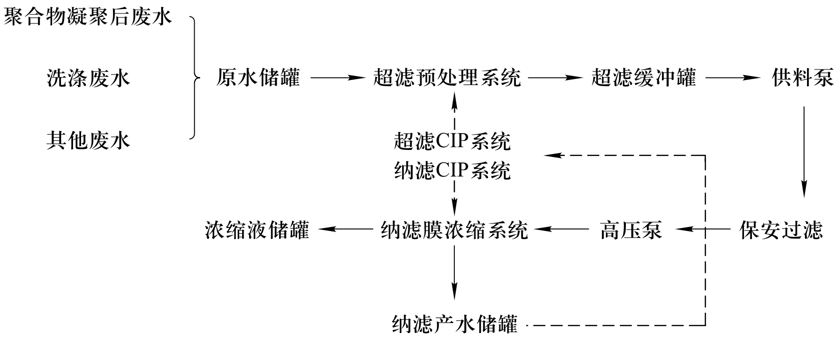


图 8　全氟辛酸铵回收系统工艺流程示意图

该系统主要由超滤预处理系统、纳滤浓缩系统和控制系统组成，超滤和纳滤系统通过控制系统都能实现远程和现场控制。

（三）经济效益

投入实际运行的全膜法回收废水中全氟辛酸铵示范工程的废水处理量为 10 t/h，系统可以回收废水中 99% 以上的全氟辛酸铵，系统已经在某氟化工企业正常运行 4 年多，每天可以回收全氟辛酸 20 kg 左右，平均每年可以回收 6 t 左右的全氟辛酸，按照全氟辛酸每吨售价 120 万元左右，每年回收的全氟辛酸价值达到 720 万元左右，运行成本（包括电费、耗材、设备折旧、人工等）约 86 万元/年，具有明显的经济和社会效益。

纳滤膜法回收全氟辛酸铵具有能耗低、操作简单、易于放大、不需要任何辅助设备、不产生二次污染等优点。废水中的全氟辛酸铵的回收率在 99% 以上，经过处理后的废水中含氟化物浓度低于 10 mg/L，完全满足国家相关排放标准，且该方法对类似的含低浓度氟化物废水具有通用性，具有很高的经济和环保效益。

五、结　　论

1）小试实验表明，在合适的操作条件下，纳滤膜可以将废水中浓度为

100 mg/L左右的全氟辛酸铵浓缩100倍以上，对全氟辛酸铵的截留率始终保持在99.0%以上，得到的浓缩液可以回收并用于生产过程中，经过处理的废水也能重复利用。因此，采用纳滤膜技术可以实现全氟辛酸铵废水的零排放。

2)根据聚偏氟乙烯生产废水的排放情况，建立了超滤预处理，回收废水中的全氟辛酸铵工艺。该工艺能够将废水中的全氟辛酸铵回收99.0%以上，具有明显的经济和环境效益。

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Treatment and Recovery of Low Concentration Persistent Organic Pollutant of Ammonium Perfluorooctanoate from Wastewater by Nanofiltration

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Abstract: The feasibility of recovery of low concentration ammonium perfluorooctanoate (APFO) from wastewater was studied. Two nanofiltration membranes, i. e., NF270 and NF90, were tested with an APFO model solution. The rejection of APFO for the NF270 was 92.0%, and for the NF90 was > 99.0% at a feed concentration of 100 mg/L APFO. The effects of operating conditions were also examined. With increasing membrane flux, the concentration factor and APFO rejection decreased. At a stirred speed of 2400 r/min, a membrane flux of 66.4 L/($m^2 \cdot h$), the concentration of APFO of 117 073 mg/L was obtained with the NF90 membrane and the final transmembrane pressure was 14.9 bar. Based on the results, a nanofiltration system with the treating capacity of 200 t/d low concentration APFO containing wastewater was built up and successfully put into operation in a PVDF production plant.

Keywords: nanofiltration; ammonium perfluorooctanoate; wastewater treatment; recovery

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Large Scale Gas and Vapor Separations Using Membranes—A Pragmatic Perspective

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Abstract: Large scale separation and purification processes are integral parts of commodity production complexes. While reactors correctly receive a great deal of attention, roughly 40% of the energy consumption in the chemical and refining and petrochemical industries is associated with separation processes. Most current large scale separation processes have been developed with a focus on efficacy, rather than a concern about energy efficiency, per se. Gas and vapor separation processes are particularly energy-intensive and offer high payoff opportunities to reduce both energy consumption and CO_2 emissions in commodity production processes. Recent developments in membrane materials have set the stage for the emergence of a new generation of much more energy efficient gas and vapor separations; however, identifying new materials is only a necessary first step. In advanced separation devices such as membranes, module manufacturing, *rather than special materials* per se are usually the limiting cost factor. This fact can help guide pragmatic consideration of strategies to enable the emergence of a new generation of membranes to reduce energy intensity within upstream natural gas and downstream chemical processing industries. Beginning with a high level view, elements of such a strategy are developed in this paper and used to define a path to the next generation of successful membrane processes for gas separations. Specific examples of this strategy and implementation paths are provided to outline how the approach can be implemented with mutual benefit to industry and society.

1 Introduction

Large scale separation and purification processes transform low value resources into more useful fuels, basic chemicals, food and clean water; however, they also consume a great deal of energy. Growing global population, increased competition for natural resources and the desire for better worldwide standards of living will intensify demands upon such processes. These trends will place a burden on available energy resources and lead to large increases in carbon dioxide emissions under a "business as usual" scenario. Approaches that minimize energy intensive thermally-driven separations can allow as much as an order of magnitude reduction in energy intensity per unit of product purified[1, 2]. While already widely used in water purification, advanced membrane approaches cannot yet be applied widely, due to the lack of membranes suitable for aggressive non-aqueous feeds. Recent developments in membrane materials and formation approaches provide tools to extend the low energy intensity separation revolution beyond water to include a broader spectrum of large scale feeds[3-18]. This paper focuses on specific new materials from this group of materials with a realistic potential to enable economical gas and selected vapor separations. An important aspect of the focus in this paper is the need to be able to form economical large scale modules based on the preferred materials. To provide context, I will briefly consider a broader framework, including all membrane separations, and then focus on the special challenges associated with gas and vapor cases.

In 2005, I participated in a National Research Council workshop entitled "*Sustainability in the Chemical Industry: Grand Challenges and Research Needs*"[19], and the report from the workshop provides useful insights and guidance, even in 2013[20]. I participated in a session in the workshop entitled "*Reducing the Energy Intensity of the Chemical Process Industry*", which focused on the high energy intensity of the chemical and allied industry. Improvement in energy efficient separation processes was a key topic that I focused on in that session, and I have continued to pursue this actively since that time. Indeed, the present paper provides an update on some of the important developments that have occurred since the time of the workshop. Jeff Siirola, who at the time was a senior researcher at Eastman Chemical Company, noted points that are still valid today, despite the much more optimistic picture regarding the likely availability of hydrocarbon resources—especially natural gas. Dr. Siirola noted that 80 percent of all chemical manufacturing energy is associated with the processing of materials derived from methane, ethane, propane, and aromatics[21]. The rebirth of the US chemical process industry has been largely driven by availability of lower cost natural gas and natural gas liquids related to the so-called shale gas revolution[22]. The reduction in energy costs in the United States has given the U. S. a favorable worldwide position that is expected to be maintained for decades. Despite this advantage, with acknowledged increases in the global long term demand for energy and hydrocarbon resources, lower processing energy intensity remains at least as important in 2013 as it was in 2005. World population growth to 9 ~ 10 billion people (1.6 ×) is expected over the next several decades. Moreover, growing demand in developing countries with already large populations will drive chemical industry output much beyond the 1.6X fold growth in population growth—perhaps by as much as 5-fold[23].

Short term economics favor rapid deployment, with energy efficiency and environmental sustainability given secondary status. Even if local government regulations encourage adoption of environmentally beneficial approaches such as membranes, global competition may favor a lower cost, less sustainable process option. Despite this hurdle, if done wisely, technology-enabled energy efficiency can be a truly “no regrets” opportunity for far-sighted industrial adopters to gain long term competitive advantages as well as being good global citizens.

A useful benchmark to guide thinking with regard to separation issues is the well-studied US case where the industrial sector is responsible for 33% of total energy consumption. Over 40% of the energy consumption in the massive chemical and refining and petrochemical industry is consumed by separation processes[24]. The scaling $0.4 \times 0.33 = 0.132$ suggests that over 13% of total energy consumption is associated with separation operations. The implications of a “business as usual” scaling to accommodate the projected 5X increase in global commodities correspond to the equivalent of 66% *of all energy consumed in all sectors of today's global economy.* Since the bulk of such energy will come from hydrocarbon sources for many years, this energy burden would bring with it a similar increase in CO_2 emissions. Fortunately, membranes offer a viable option to address this challenge to control manufacturing energy costs and CO_2 emissions. Nevertheless membrane technology must be introduced *before installation of energy inefficient thermally intensive processes*, since once such energy inefficient processes are installed, their long (30 ~50 years) lives will require regulatory intervention to force their replacement.

To illustrate this issue, one needs to only consider production of fresh water by desalting brackish and sea water brines. Currently more than 9 billion gallons per day worldwide desalting capacity exists, and roughly half is membrane-based, while half is thermally-driven (e. g., multi-effect and flash evaporators)[1]. Modern reverse osmosis (RO) desalting technology continues to claim an increasing fraction of the ever-growing market; however, despite RO's more than 10X higher energy efficiency, old thermal plants with fully depreciated capital equipment remain in use. A similar situation can be envisioned in chemical processing industries if scale up to handle the 5 × capacity expansion is done by conventional thermally intensive approaches. Indeed, energy-efficient alternatives must be developed soon for non-aqueous feeds to avoid building in long-term inefficient processes as the chemical processing industries make capacity expansions.

To have a large impact, *large scale processes* must be the focus to enable significant reductions in energy use (and *CO_2 emissions*). Moreover, while many net driving forces can be imposed to drive permeation between upstream and downstream membrane faces, transmembrane pressure differences are economical and simple to apply. Since large scale pressure-driven gas and vapor separations are large payoff targets for which science and technology are still under development, they are the main focus of this paper.

Continuous steady state membrane operations of all types involve feed, permeate, and nonpermeate streams. The separation of a permeated A from a second, rejected B component is characterized by the so-called "separation factor", given in Eq. (1), which shows the relative membrane enrichment A vs. B:

$$SF = \frac{\left(\frac{\text{Composition of A downstream}}{\text{Composition of B downstream}}\right)}{\left(\frac{\text{Composition of A upstream}}{\text{Composition of B upstream}}\right)} \tag{1}$$

Since the SF is a "ratio of ratios", any measure of composition (mole fraction, mass fraction, concentration, etc.,) can be used in Eq. (1) as long as one consistently uses the same measure for both upstream and downstream phases in contact with the membrane. Locally within a module, the ratio of compositions leaving the downstream face of a membrane equals the ratio of the transmembrane fluxes of A vs. B. Since fluxes are determined by transmembrane driving forces and resistances acting on each component, the ratio of the feed composition in the denominator normalizes the SF to provide a measure of efficiency that is ideally independent of the feed composition. Minimization of membrane resistance requires minimizing effective membrane thickness without introducing defects, and requires "micro-morphology control", which is a topic that impacts virtually all membrane applications.

2 Hydrodynamic sieving (MF & UF) separations—generation 1 membranes

Practical microfiltration (MF) and ultrafiltration (UF) liquid separation membranes rely upon a porous membrane to filter particles or macromolecules (B) suspended in a low molecular weight feed fluid (A). While pores in MF membranes are larger than in UF membranes, in both cases transmembrane pressure differences motivate the suspending fluid (usually water) to pass through microscopically observable *permanent pores* in the membrane. The fluid flow drags suspended particles and macrosolutes to the surface of the membrane where they are rejected due to their excessive size relative to the membrane pores. This process concentrates "B" components in the upstream nonpermeate stream. On the other hand essentially pure low molecular weight "A" is present in the downstream permeate if the pore size distribution prevents any "B" from passage across the membrane (i.e., SF→∞).

Concentrating liquid feeds represents major energy costs for paints, foods, and many waste recycle streams. Often in such cases, MF and UF can enable large energy savings compared to evaporation approaches[1]. Even if thermal energy input is needed in a final finishing step, using membranes in primary concentration steps can provide large overall processing cost savings.

3 Transition from porous to nanoporous or nonporous selective layers- generation 2 membranes

As shown in Fig. 1, when permeated and rejected components approach micromolecular dimensions(< 20 Å) hydrodynamic sieving forces no longer are adequate to perform the subtle size and shape discrimination required. Progressing from nanofiltration(NF) to reverse osmosis(RO) to gas separation (GS) involves finer and finer size discrimination between permeated and rejected entities. For gas separations, in fact, only fractions of an angstrom are involved, and in all of these cases, *intermolecular forces* are the dominant determinants of the resistance acting on each penetrant.

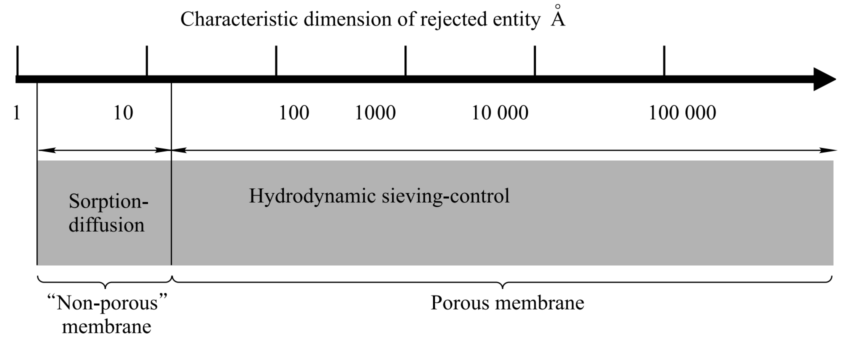


Fig. 1 Size spectrum of permeate and the controlling mechanism of transport[19]

For all micro-molecularly selective NF, RO and GS processes, a thermodynamic "partitioning" also affects the flux expression and must be considered to describe the process in terms of external phase conditions. Specifically, a so-called "partition coefficient", K_i, is typically defined as:

$$K_i = \frac{[\text{Composition of Component } i \text{ in membrane}]}{[\text{Composition of Component } i \text{ in external phase}]} \qquad (2)$$

Since K_i is expressed as a ratio, any consistent measure of composition in the membrane and external phases may be used in Eq. (2). When $K_i > 1$, the membrane acts as a "concentrator" to attract component *i* from the external phase to the membrane surface for transmembrane movement. Entropic as well as enthalpic effects can be at play, and the balance of these can cause either a higher or lower concentration of a given solute inside the membrane relative to the external phase. If the tendency to enter the membrane is negligible, the partition coefficient approaches zero, i. e., $K_i \rightarrow 0$.

Combined size discriminating and thermodynamic partitioning permits adjustment of the relative compositions of different small molecules or ions having transmembrane chemical potential differences between the membrane upstream and downstream faces. The ratio of the effective resistance acting on B vs. that acting on A in the membrane specifies the membrane-specific ability to separate this A-B pair. The membrane thickness cancels from the ratio, so the key ratio of resistances acting on component B vs. A is comprised of a product of partitioning and mobility ratio factors. For most membranes, the mobility ratio can be approximated as D_A/D_B, the ratio of the average diffusion coefficients for component A vs. B within the membrane phase. In this common case, therefore the effective ideal membrane selectivity, α_{AB}, is given by Eq. (3):

$$\alpha_{AB} = \frac{[D_A]}{[D_B]}\frac{[K_A]}{[K_B]} \tag{3}$$

In principle, "mobility selectivity", D_A/D_B, and "partitioning selectivity", K_A/K_B, can be tuned to develop advanced materials for any small molecule separation using any type of molecularly selective membrane material. RO purification of potable water from brine relies upon both "partitioning selectivity" and "mobility selectivity" contributions from Eq. (3). Practical optimization of the membrane material and structures for aqueous reverse osmosis has occurred for several decades and has resulted in very efficient high performance systems[25-27]. On the other hand, non-aqueous nanofiltration cases involving the ability to separate organic streams remain a highly challenging and still emerging area[3-5]. "Pervaporation" is a variant of reverse osmosis that uses a low pressure liquid feed with a *vapor permeate* under vacuum. Since pervaporation involves permeation and evaporation of a portion of the feed it requires significant thermal energy input, and because reverse osmosis eliminates this requirement, it became the favored process for water desalination. This will probably be the case for organic stream separations as well.

Economical manufacturing of modules with high surface area is needed to enable practical large scale membrane systems. This basic fact is clear from Eq. (4), where productivity (e. g., tons per day, etc.) is represented as the product of a flux and area.

$$\text{Productivity} = [\text{Flux}] \cdot [\text{Area}] = \frac{[\Delta\mu(\text{Chem}, \text{Potential})]}{[\text{Resistance}]} \cdot [\text{Area}] \qquad (4)$$

Practical limits exist on reducing membrane thickness in economical manufacturing processes, but required $\Delta\mu$ can be minimized by maximizing the contact area across which transport occurs. The ability to configure membranes to maximize the thermodynamic separation efficiency to a value approaching the free energy of demixing distinguish them from less advanced separation approaches. Of course, creating high contact surface area modules requires balancing capital cost with operating cost advantages, so there is a critical need to create *low cost but effective high surface area devices*. Indeed, while special materials are critical to achieve the separations needed, it is module manufacturing, rather than specialty materials that is usually the limiting cost factor. This fact makes device engineering and fabrication more important in all advanced low energy intensive processes by comparison to conventional thermally driven bulk separations. In reverse osmosis, ultrathin film interfacially polymerized polyamide (<500 Å) selective layers provide sufficiently high fluxes to allow the use of spiral wound modules, which provide areas up to 400 m^2/m^3, to be viable. The situation is arguably different for gas separations where fluxes are lower, leading to lower module productivities than in liquid systems.

4 Gas and vapor separations—generation 3 membranes

Membrane-based applications for removal of organic vapors from gas streams and even the separation of permanent gases (e. g., O_2 vs. N_2, CO_2 vs. CH_4, H_2 vs. CH_4) are commercial realities, and are sometimes referred to as Gen-3 membranes[1-2]. Organic vapor removal from permanent gases typically relies upon *rubbery polymers*. The partitioning term in Eq. (3) always favors the more condensable vapor molecule, but in rubbery polymers like silicone rubber, the diffusion coefficient ratio favors the smaller gas less than it would be in a highly rigid glassy polymer. Membranes for capture and recycle of volatiles from polyolefin storage bins (e. g., polyvinyl chloride, polyethylene, polypropylene) and for removal of natural gas liquids from fuel gas use this principle favoring sorption and permeation of the more condensable organic component using rubbery membranes[27-29].

On the other hand, most gas separations of one permanent gas from another permanent gas rely primarily upon mobility selectivity, based on size differences leading to preferred permeation of the smaller penetrant. Even for these cases, however, the condensable nature of CO_2 also helps promote high separation factors relative to more supercritical gases like N_2 and even CH_4[30,31]. An early successful major application of gas separation membranes in large scale separations involved CO_2 removal from CH_4 in natural gas[28]. The ability to incrementally add installed capacity is a particularly attractive aspect of membrane-based processes that allows expenditures only as needed. *Cellulose acetate* (*CA*) hollow fiber membranes are the most commonly used materials for current CO_2/CH_4 separations involving moderate CO_2 contents. Since the initial deployment of membranes at the SACROC facility, the unit has been expanded from only 70 MMscfd (millions of standard cubic feet per day, 1 scf = 0.028 316 8 m^3) to over 600 MMscfd currently.

The technology to create ultrathin skins via reactive interfacial polymerization, which is the dominant paradigm for aqueous RO, proved impractical for dry gas separations. Nevertheless, the roughly 10X higher surface-to-volume of fiber modules vs. spiral wound modules still enables commercially viable module productivity for gas separation[1,19,27,32]. These Gen-3 fibers are more sophisticated than earlier reverse osmosis fibers and have thinner selective layers that can be "caulked" to repair nanoscopic defects, allowing them to approach thicknesses of the reactively formed Gen-2 reverse osmosis layers. In addition, advanced Gen-3 fibers were spun as composite structures comprising more costly but more selective thin sheath layers[34]. Such membranes, with ~ 250 μm diameters, yielded economically productive high surface-to-volume ratio modules suitable for separation of even relatively low sorbing gas penetrants, e. g. O_2 and N_2. Fig. 2 gives a schematic representation of the hollow fiber approach with highlights regarding the advantages it offered to enable success in Gen-3 applications.

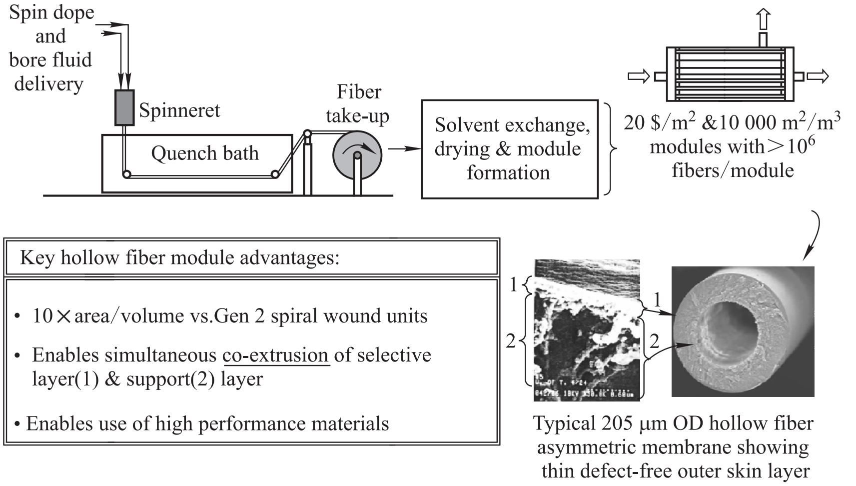


Fig. 2 Gen-3 hollow fiber asymmetric membrane modules exceed capabilities of spiral wound flat sheet module technology that has much lower module surface to volume ratios[27, 33-34]

5 Generation 4—highly challenging gas & vapor separation cases

To significantly impact global energy use, a wide spectrum of separations must be addressed effectively, and it is strategically wise to select an approach capable of optimizing performance vs. cost *across the large scale energy-intensive molecular separations spectrum*. Hollow fibers are key elements in such a strategy. In addition, appropriate candidate "advanced materials" should be selected to enable evolutionary advancement of the technology base without disruptive changes in the existing manufacturing paradigm.

Gen-3 gas separations such as O_2 removal from air or CO_2 removal from natural gas using glassy polymers were a major technical step beyond Gen-2 liquid separations and even vapor-gas separations. Indeed, size and shape discriminations up to 10 times finer in percentage size difference between permeated and rejected components compared to those in RO were achieved in Gen-3 (2). At low CO_2 partial pressures, where membrane matrix swelling is low, continued refinement in intrinsic size and shape discrimination is an adequate strategy. Unfortunately, the tendency for supercritical CO_2 to swell and soften rigid matrices of typical polymers used for moderate CO_2 partial pressure Gen - 3 feeds presents new challenges. Indeed, natural gas feeds containing 40 mol% - 50 mol% CO_2 at high pressures (800 ~ 1000 psia, 1 psia = 1 lb/in^2 = 6.895 kPa) represent the demanding conditions typical of those that "Gen-4" systems must face. Such feeds cannot be addressed realistically by Gen-1 to Gen-3 membrane types mentioned above.

Fig. 3 illustrates typical Gen-4 challenges. Beginning at the high upstream pressure production wellhead, removal of contaminants (generally CO_2 and sometimes H_2S)[35] occurs to make the produced gas suitable for transfer to a downstream facility. At the downstream site, many energy intensive separations occur. In such a downstream facility, separation of C_2 and C_3 olefins from paraffins are major energy-intensive activities and are useful to consider for illustrative purposes. Ideally, CO_2 removal from raw natural gas can even enable reinjection at the well site with multiple benefits to provide enhanced production by maintaining reservoir pressure and reduces viscosities of co-produced associated crude oil, rather than causing environmental impacts due to atmospheric venting. Natural gas consumption comprises roughly 25 trillion scf/a in the U. S. and 116 trillion scf/a (2.5 billion t/a), worldwide[35]. Moreover, natural gas is one of the fastest growing energy and feedstock sources, because it is abundant and relatively cleaner than liquid fossil fuels or coal. Carbon dioxide, as the most abundant contaminant, can

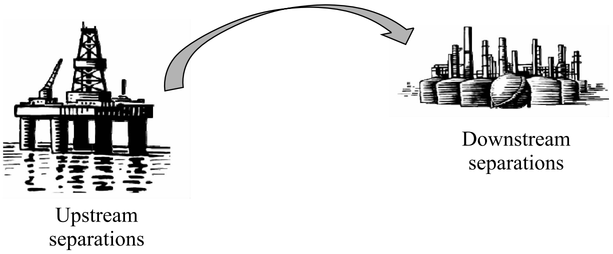


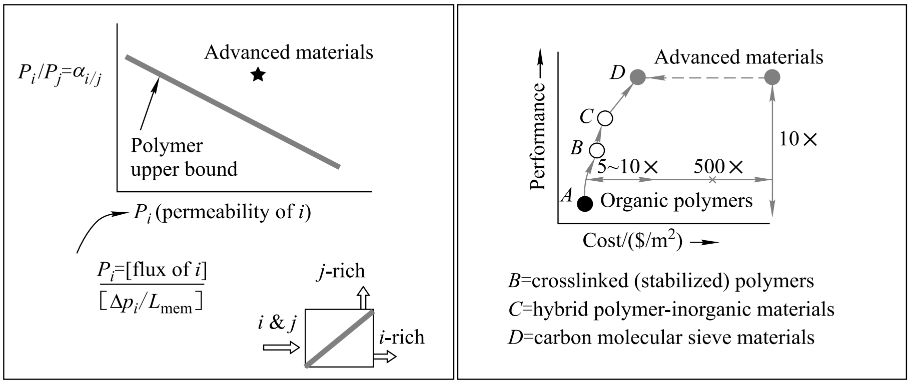
Fig. 3 Upstream (production) and downstream (cracking and refining) involve separations that can benefit from Gen-4 membrane processes to reduce process energy intensity and CO_2 footprints

exceed 50 mol% in some natural gas feeds, with CO_2 contents above 70% being common in enhanced oil recovery applications[1]. These facts make the CO_2/CH_2 pair an especially important separation target. Although membranes intrinsically offer the most efficient separations option, improved materials, beyond those in Gen-3 cases are needed to enable their broad use in this application[6-19,32,36-60].

Downstream processing of hydrocarbons, especially naphtha and natural gas liquids, transforms these feedstocks into an array of components in huge cracking furnaces. Subsequent separation of valuable C_2 and C_3 olefins from the complex mixture leaving the cracking units are the most energy intensive part of such processes. In 2010 global ethylene production capacity was 145 million tons[61]. Cryogenic distillation, performed at −25℃ and 320 psig (1 psig = 6.895 kPa) in a column containing over 100 trays, is currently the highly energy intensive approach that dominates ethylene/ethane separations. Propylene is also a crucially important feedstock for polymers and diverse derivatives for manufacturing valuable chemicals, and the propylene-propane splitter can contain 200 trays. Typically, these units are capacity-limited with up to 7% annual growth and a demand of 77 million tons in 2010[62].

Intrinsically highly selective advanced materials, such as zeolites, ceramics, metals and metal organic framework materials, have not yet been economically scalable to large modules. Indeed, forming such advanced materials that offer higher selectivity performance currently requires a radically different manufacturing paradigm from that which has led to high surface-to-volume Gen-1 to Gen-3 modules. This simple fact represents the major practical hurdle to using these advanced materials to address Gen-4 needs. On the other hand, the evolutionary fiber-based path noted in Fig. 4 appears likely to enable development of increasingly sophisticated materials beyond Gen-3 polymers in order to create membranes with performance and cost combinations that meet many challenging separation requirements noted earlier.

The first step on this path to practical Gen-4 materials begins with crosslinked polymers to overcome swelling-induced performance losses. The possible next step involves hybrid materials, comprising polymer with



(a) (b)

Fig. 4 (a) selectivity – permeability tradeoff performance relationship between advanced materials and polymers that can be processed into asymmetric hollow fibers using the approach shown in Fig. 2; (b) advantages of polymer – derived routes to advanced materials vs. other advanced materials with similar performance options but which require more costly processing to scale – up from lab to large commercial scale modules

embedded inorganic or metal organic framework nanoparticles to use advantages of hard-to-process pure advanced materials while maintaining processing simplicity of polymer fiber spinning. Finally, the most evolved form—comprising carbon molecular sieve (CMS) materials—offers extraordinary capabilities like other advanced materials but with only a single pyrolysis step using precursors derived from Gen-3 type polymer fibers[1]. This increasingly sophisticated family of materials offers the potential to address all but the highest temperature, most oxidizing feeds. This family also addresses most important large scale separation needs of interest to both current and alternative feedstock processes. A workable strategy to implement this vision will be illustrated next by consideration of some specific cases. Clearly, for the most challenging (e. g., high temperature oxidizing feeds) zeolite, metal and advanced ceramic materials will still be needed[16, 18]. These cases truly represent a "fifth generation" vision, which must be pursued; however, it seems wise to first focus on the fourth generation topics noted here. Indeed, lessons learned in developing cost-effective modules from fourth generation materials are likely to be helpful in ultimately identifying economical approaches to such fifth generation materials.

6 Upstream separation examples: aggressive natural gas purification

Covalently crosslinking membranes to prevent plasticization in aggressive feeds have primarily focused on already rigid polyimide backbone materials with typical glass transition softening points approaching 300 –400℃. Clearly, many approaches to stabilization can be envisioned, but whichever one is considered *should be extendable to asymmetric hollow fiber structures* to have a practical impact. One approach in this regard relies upon optimizing a diol crosslinking agent attached to a free acid of the polymer in solution[36, 37]. Such monoesterified polymers can be solution cast (or spun into fibers) followed by heating to only 220℃ to complete the trans-esterification crosslinking reaction shown below. The method is adaptable and HO-R-OH can be many possible linkers; however, propane diol offers a good balance of mechanical and transport properties.

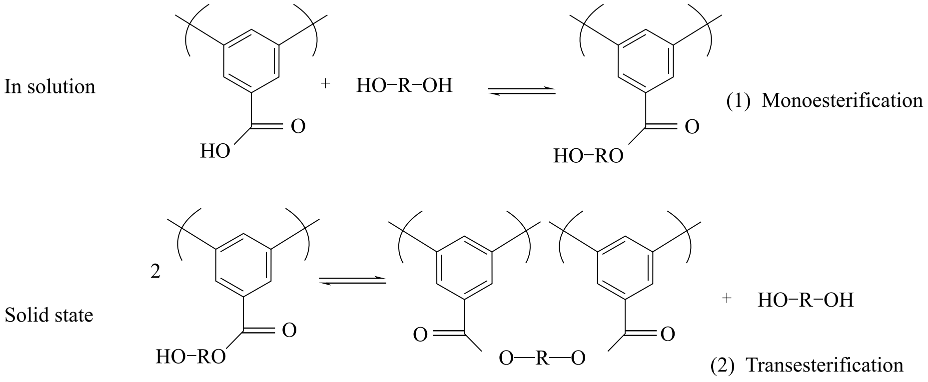


Fig. 5 Esterification-based crosslinking to achieve stabilized high performance polymers for advanced size selective membrane materials[36]

The copolyimide structure shown in Fig. 6 has an intrinsically high permselectivity based on it rigid sized and shape discriminating matrix. The presence of the monoesterified unit also provides the ability to be spun into a high productivity asymmetric structures that can be subsequently crosslinked. This crosslinking stabilizes the material against swelling-induced selectivity losses, even in an asymmetric hollow fiber form. The intrinsic performance of this material falls close to the upper bound line selectivity-permeability tradeoff line defined in 1991[39], and later extended in 2008[40]. For convenience, this structure based on a 3:2 ratio of diamino mesitylene and diamino benzoic acid with 6FDA dianhydride is referred to as PDMC (e.g., propane diol monoesterified crosslinked polymide); however many variations on this structure could be used[60]. The PDMC intrinsic permeability and selectivity are somewhat higher than that of CA even for low feed pressures of a 50∶50 mixture. More importantly, however, PDMC, *maintains a high* CO_2/CH_4 *selectivity of* ~ 45 *at very high feed pressures of* 50∶50 *mixtures*. By comparison to the above CA case, for roughly every 45 CO_2 molecules that permeate, only 1 CH_4 permeates to be re-injected, which is roughly only a 2.2% product loss compared to the 1/8 or 12.5% loss in the case of CA. This excellent performance is indicated by the essentially unchanged selectivity and permeability for the open red point vs. the solid red point at low and high feed pressures, respectively in Fig. 6. Not only is the membrane performance attractive, but also the process shown in Fig. 2 and Fig. 6 to achieve this performance is attractive, requiring minimal changes vs. Gen-3 materials to form a fully asymmetric crosslinked membrane. By tuning the dope composition and spinning conditions, monoesterified copolymer with at least one diol per two carboxylic acids can be spun as an asymmetric fiber via the approaches used for simple non-crosslinkable fibers in Fig. 2. The fibers are then solvent exchanged to prevent capillary-force- induced pore collapse during drying. However, unlike a simple Gen-3 material like cellulose acetate (CA), crosslinking can be achieved using the propane diol side chains. To achieve this crosslinking, by performing the final drying stage at an optimized higher temperature, intersegmental crosslinking and rigidification occurs while the desired asymmetry is maintained. Indeed, the final membrane adds virtually no new processing steps and is effectively an "evolved Gen-3" material, illustrating a truly economical Gen 4 membrane.

An alternative approach to stabilization against penetrant-induced swelling eliminates the need for the ester crosslinking in Fig. 5 & Fig. 6. This approach, termed DRIC, Decarboxylation, Radical-Induced Crosslinking, can be useful for even more aggressive feeds for which the ester crosslinking approach may be compromised by hydrolysis. Both the ester crosslinked, and DRIC materials *maintain their high selectivity in the presence of realistic aggressive*

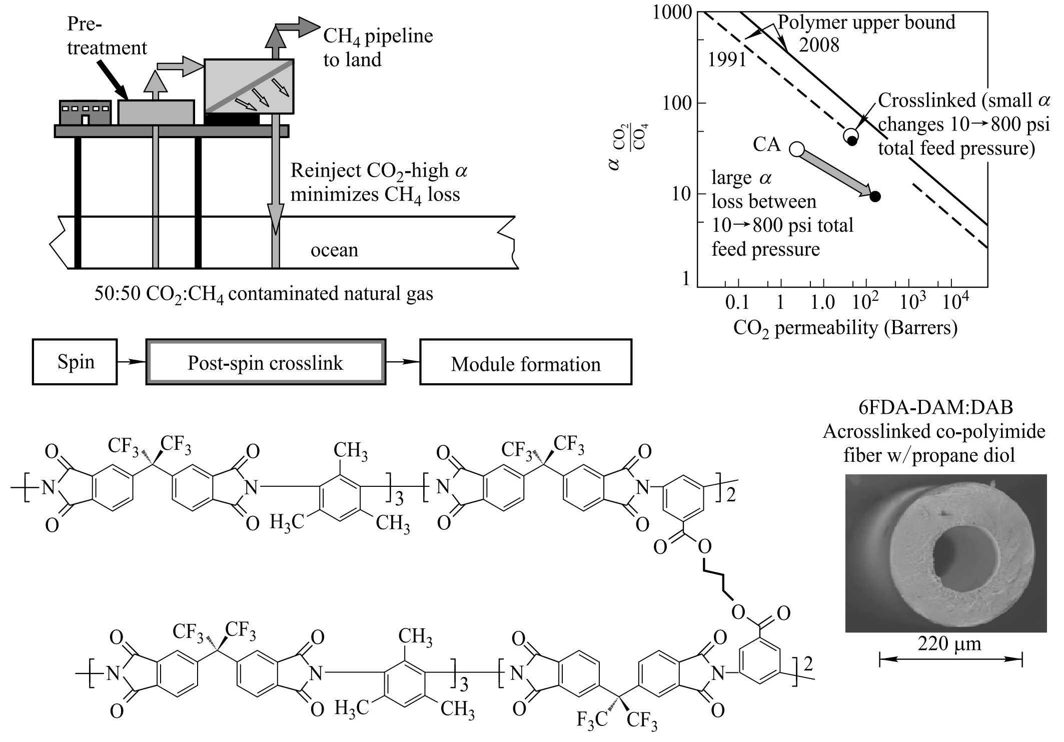


Fig. 6 Gen-4 crosslinked membranes for high CO_2 content natural gas clean-up

feeds. Other (Gen-3) materials without some additional stabilization may lie on or near the upper performance bound under mild feed conditions (say <50 psi CO_2 partial pressure), but lose selectivity badly when exposed to actual aggressive swelling feeds. The DRIC polyimide was derived from the same precursor as that in Fig. 6, but in the free acid form, *without propane diol monoesterification*. This free acid form can be transformed to a crosslinked, CO_2 plasticization resistant material by simple heating below T_g, to induce decarboxylation, radical-induced crosslinking DRIC stabilization[63,64]. The reaction proceeds via a dianhydride intermediate, which is typically formed around 150 – 200℃ in carboxylic acid containing polymers[65-72]. IR data suggests likely crosslinking sites, noted in Fig. 7.

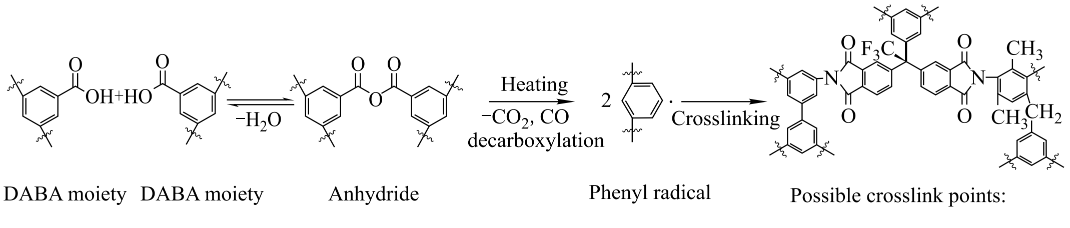


Fig. 7 Crosslinking for decarboxylation/radical-induced crosslinking (DRIC)

A complex pathway with multiple possible intermediates is possible during heating above 220℃, but the final results leads to crosslinking similar to that noted in the related work by Eskay[70-72]. A key step in the crosslinking appears to involve formation of anhydride moieties from DABA-containing units on neighboring chain segments. Subsequent creation of free radicals on the formerly connected phenyl rings (that are on the DABA groups in the polyimides) can then occur at sufficiently high temperature. The most likely crosslinking site is the combination of neighboring free radicals created on the phenyl rings formerly part of the anhydride, which recombine to form a biphenyl linkage. Nevertheless, all three potential sites illustrated in Fig. 7 are viable stabilizing linkages. The free radical decomposition of the anhydride does not occur efficiently until temperature rises above 220℃, and other sites may require higher temperatures. In any case, large-scale backbone decomposition does not begin to occur until much higher temperatures near 450 - 470℃[63-64]. Like the PDMC material, the DRIC material maintains selectivity under aggressive conditions noted in Fig. 6.

Similarly, so-called "thermally rearranged" (TR) and other stabilized polymer-derived samples noted earlier[6-15,32,36-59] can maintain attractive selectivity properties in the presence of swelling feeds. In fact, however, few potentially stable spinnable polymeric materials have actually been tested as asymmetric membranes under extreme conditions above 50 atm (1 atm = 1.01325×10^5 Pa) with high CO_2 contents noted in Fig. 6 for the PDMC (and DRIC) materials. Also, as noted earlier, while pure zeolite membranes show durability under aggressive conditions like those noted in Fig. 6, cost has hindered their large scale use. For all polymer-based materials, some degree of crosslinking is likely to be required to maintain performance near the spinnable polymer upper bound tradeoff lines noted in Fig. 4. This reality makes the high-payoff Gen-4 topic of swelling-stabilized asymmetric hollow fiber membranes an active area of development.

Hybrid materials—a step beyond "simple" crosslinked materials: The progression in performance "evolution" suggested in Fig. 4 indicates that an obvious step beyond crosslinking stabilization involves the use of hybrid materials[38]. Hybrid combinations of polymers with high separation performance materials, which are expensive as pure membrane materials, offer opportunities beyond those of even rigid crosslinked polymers such as PDMC or other spinnable stabilized polymers. To be economical, this may require nano-composite spinning of dopes to form composite sheath-core fibers. Such added complexity may make it tempting to bypass the need for hybrid materials and to proceed directly to carbon molecular sieve materials noted in Fig. 4. Another aspect of this issue will be discussed later in the context of a *specialized* olefin-paraffin downstream separation application, where only CMS appears to be fundamentally and economically workable. For natural gas, ZIF (zeolitic imidazolate frameworks) and other metal organic framework "inserts"[73-86] appear viable to boost CO_2/CH_4 selectivity of stabilized spinnable matrices like those noted in the preceding section. In fact, however, an additional issue complicates such hybrids that rely upon coordinating metal ions to make the "inserts". Specifically, reactivity with H_2S[87], which sometimes accompanies CO_2 as a contaminant in natural gas, limits the available "insert" choices. The use of H_2S-stable zeolites instead of ZIFs can eliminate H_2S stability concerns; however, additional surface functionalization is required to promote compatibility between the totally inorganic dispersed particles and the continuous organic matrix (79,81). In such cases, which are not so rare, the more robust carbon matrix offers advantages. Therefore, due to space limitations in this paper, although the hybrid approach offers a potentially attractive option, it will not be discussed further here in the context of upstream separations. Instead, the advantage in taking the step from a purely Gen-3 material to CMS will be illustrated for the CO_2/CH_4 gas pair without passage through "hybrid" materials.

Extension to carbon molecular sieve (CMS) membranes for aggressive CO_2/CH_4 separations: The special properties of carbon molecular sieves result from their highly rigid matrices, which make them a limiting case for polymer-derived membrane materials[88-110]. The ability to use differences in penetrant configurational entropy[90] in the activated state of subtly different penetrants provides an additional tool for engineering mobility selectivity in Eq. (3). Use of the configurational entropy factor in the activated state is typically not available with even rigid polymers that can be formed into asymmetric fibers, due to segmental motions within the matrix. These motions are effectively absent in CMS, zeolites and ceramics. This additional feature allows one to extend mobility selectivity capabilities in cases where the shape, rather than only the nominal Lennard-Jones tumbling diameter differ between two similar molecules like propylene and propane or ethylene and ethane. Until recently, CMS materials were too difficult to fabricate reproducibly and economically to make into high performance hollow fiber membranes for the large scale applications discussed in Fig. 3. Recent work has revealed practical ways to work with these materials in actual asymmetric fiber forms. Despite these encouraging developments, work is needed to better define structure-property relationships. Translating properties of precursors to ultimate CMS properties created under different pyrolytic processing atmospheres still have many elements of art as well as science. The understanding of the interesting CMS class of materials is in a similarly emerging state to that which rigid glassy polymers were in when Gen 3 membranes began to be pursued several decades ago. At that time, rigid glassy polymers provided large improvements over simple rubbery polymers with only low mobility selectivities. Similarly, CMS materials appear likely to enable the next step in mobility selectivity to be achieved beyond rigid glassy polymers *using the added configurational entropy control afforded by their intrinsic natures.*

CMS membranes can be formed by thermal decomposition of polymer precursors, resulting in almost pure carbon materials, in many cases above 90% carbon[90-92]. Depending upon the precursor, pyrolysis tends to form coke or char. Coke tends to form graphite at a temperature above 2473 K, but char remains in an amorphous structure. Such amorphous char-rich materials are believed to have a highly aromatic structure comprised of disordered sp^2 hybridized carbon sheets with angles of disorientation of several degrees as illustrated in Fig. 8 (a) and (b)[88, 93]. The structure can be envisioned to comprise roughly parallel layers of condensed hexagonal rings with no three-dimensional crystalline order. Pores are formed from packing imperfections between regions in the material, and the pore structure in CMS membranes is described as "slit-like" with an "idealized" structure illustrated in Fig. 8 (c). This pore structure can be further represented as shown in Fig. 8 (d) with an idealized bimodal pore distribution. This distribution consists of "micropores" of 6 −20 Å connected by smaller so-called "ultramicropores"[94-96]. The combination of ultramicropores and micropores provides the molecular sieving function *and* high permeability characteristic of these unusual materials. The disordered structure of the carbon material is different from zeolites, which have a uniform, well defined set of pores. Despite the distribution of the ultramicropores, CMS materials offer the important advantage of facile formation of highly selective defect free membranes useful in gas separation applications. Moreover, despite their high moduli and rigidity, CMS hollow fiber membranes (unlike thicker dense CMS films) are remarkably flexible. The basis for this valuable macroscopic flexibility is not completely understood, but may reflect the ability of the noncrystalline array of graphene-like sheets to slide past each other during deformations.

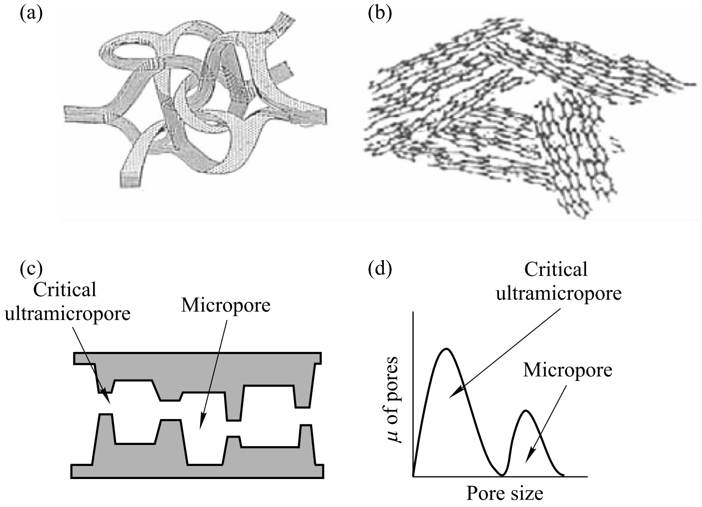


Fig. 8 Idealized structures of glassy carbons and an idealized pore size distribution of carbon molecular sieve materials representing micropores and ultramicropores

Structures of CMS membranes have been investigated by many researchers using traditional techniques, such as X-ray diffraction (XRD), transmission electron microscopy (TEM), and adsorption[89,97,98]. Unfortunately, the amorphous nature of CMS, makes it difficult to determine the detailed structure, especially the ultramicropore nature that governs the molecular sieving process. When XRD is performed, broad peaks are observed due to the amorphous structure of CMS, thereby complicating estimation of actual pore structure[97]. High resolution TEM results are also inconclusive due to the amorphous structure, and possible pores of the material are difficult to truly define. Chen, Loo, Wang, and Do conducted an argon adsorption isotherm to obtain a pore size distribution of CMS membranes, but could not usefully analyze the selective ultramicropore region. Similarly, Steel and Koros and Campo and Mendes concluded that the pore size distribution derived from CO_2 adsorption equilibrium was inadequate to explain CMS pore structures that are responsible for molecular sieving[97,99]. Despite these difficulties, the importance of these unusual CMS structures, namely the applicable ultramicropore distribution, can be probed by using various gas molecules as probes (99).

As in the case of polymers, transport through CMS membranes is modeled by the sorption-diffusion selectivity mechanism represented in Eq. (3). Even in CMS materials, gas molecules sorb into the membrane at the upstream, diffuse under the influence of a chemical potential gradient, and finally desorb from the membrane at the downstream. For CMS materials, the diffusion coefficient, D_i, in CMS membranes is an even stronger function of penetrate size vs. glassy and rubbery polymers. As a result, CMS membrane enable molecular sieving discrimination between similarly size and shape penetrants. The sorption coefficient, equal to the concentration of gas sorbed divided by the penetrant partial pressure at equilibrium, depends upon the condensability of the gas penetrant and its interactions with the membrane material.

The polymer precursor, 6FDA/BPDA-DAM, has a structure somewhat related to that of the crosslinkable polyimide noted in Fig. 6, but is not crosslinkable, since it lacks the DABA repeat unit. Rather than relying upon the single 6FDA dianhydride and two different diamines in the copolymer, 6FDA/BPDA-DAM, uses the single DAM diamine and two different dianhydride units selected to balance backbone packing disruption and rigidity. Specifically, 50% of the highly packing disruptive 6FDA is replaced by the highly packable BPDA dianhydride as shown in Fig. 9.

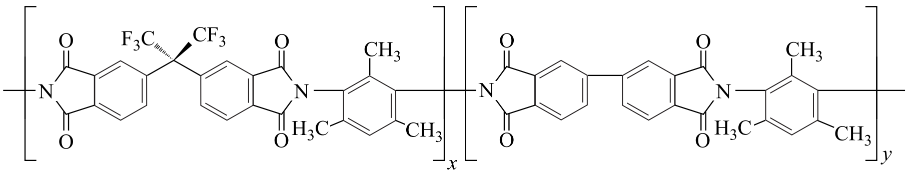


Fig. 9 6FDA/BPDA – DAM polyimide precursor for carbon molecular sieve

A pyrolysis temperature of 550℃ with a 2 h soak time at of 550℃ can be used with 30 ppm O_2 in argon pyrolysis atmosphere using a pyrolysis system like that shown in Fig. 10 with ability to monitor oxygen concentration during pyrolysis studies; however, the simplest case corresponding to ultrahigh purity argon also is attractive where larger ultramicropores are needed (99).

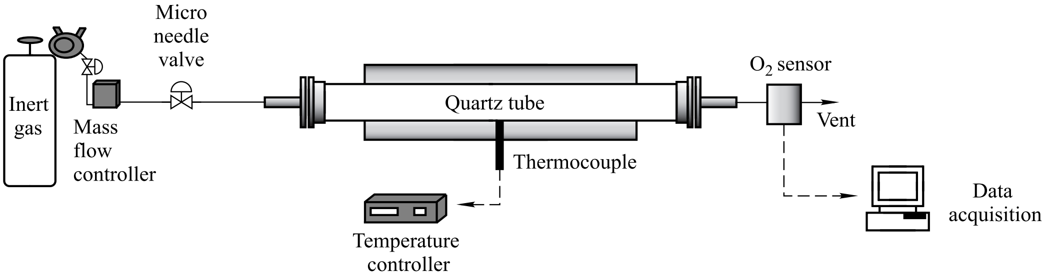


Fig. 10 Pyrolysis system with O_2 monitoring capability during pyrolysis

Fig. 11 compares performance at 35℃, including cellulose acetate (CA), which was discussed in Fig. 6. As shown again in Fig. 11, the CO_2/CH_4 selectivity of the CA falls dramatically from around 40 at 10 psi to about 8 at 800 psia for a 50∶50 CO_2∶CH_4 feed, so at the high pressure, a loss of 1 CH_4 occurs for every 8 CO_2's permeated, i. e., 12.5% CH_4 loss occurs. This lost CH_4 is either wastefully vented or re-injected into the reservoir with the CO_2 permeate stream, where it is subsequently unrecoverable in its diluted form. The stable PDMC and DRIC decarboxylated materials show selectivities of roughly 45 and 28 at 800 psia, and 2.5% and 3.6% CH_4 loss, respectively—very large improvements vs. CA.

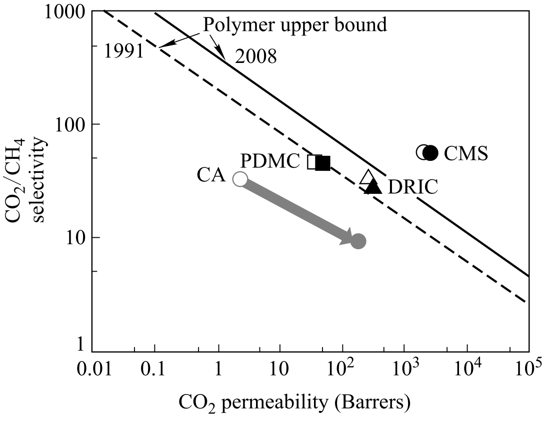


Fig. 11 Comparison at 35℃ of PDMC & DRIC vs. cellulose acetate (CA) & 6FDA/BPDA-DAM CMS (550℃ with 30 ppm O_2 doping)

Even more impressive, however, the CMS membrane shows an intrinsically higher selectivity of roughly 65 with a permeability of 2500 Barrers in the 50:50 CO_2:CH_4 feed. In this case only 1 CH_4 for every 65 CO_2's permeated is lost, i. e. , 1.5%, representing a valuable improvement over both the state of the art CA and even over the PDMC and DRIC polymers. The open and closed circles at 1 atm and 800 psia are virtually the same for the CMS. The significance of 3.6% loss in the case of the DRIC sample vs. 1.5% loss for the CMS sample in the case of a typical large field (500×10^6 scf per day) illustrates possible impacts of improvements. For instance, for a 50:50 feed of 500×10^6 scfd, 2.1% loss prevention savings in CH_4 resource equals $0.02 \times 0.5 \times 500 \times 10^6$ scfd $= 5 \times 10^6$ scfd, corresponding to roughly 5×10^9 BTU/d, which is equivalent to 62.4 MW—a large amount of energy! The 2500 Barrer CO_2 permeability of the CMS vs. the state of the art DRIC polymer with 250 Barrers CO_2 permeability for 800 psia feed of 50:50 CO_2:CH_4 mixture is also significant (note the log scale on permeability in Fig. 11). The more permeable CMS will reduce module size if equivalent thickness selective layers can be created for the CMS vs. DRIC membranes. The higher selectivity PDMC material can enable less CH_4 product loss vs. the DRIC material; however, more modules would be required for the lower permeability of the PDMC. On the other hand, for the same selective layer thickness for CMS, PDMC and DRIC materials, less CH_4 loss and fewer modules would be required using CMS. Recent work has successfully formed asymmetric CMS fibers with similar, but still thicker, selective layers compared to those achievable with PDMC and DRIC. Recent advances to suppress collapse of the asymmetric support layer above the polymer glass transition have, however, been reported[100,101], so the CMS technology is very promising.

7 Downstream separations examples: olefin-paraffin separation membranes

As noted earlier, ethylene and propylene are important synthetic chemicals in the petrochemical industry but are intrinsically difficult to separate due to the similar physical properties of saturated/unsaturated hydrocarbons. A 1993 review noted the energy use for olefin/paraffin separations to be 1.2 ×

10^{14} BTU/a[102] and based on a conservative 4.5% global growth over this period[61], this translates to 1.9×10^{14} BTU/a currently. Conventional technology to separate olefin/paraffin mixtures is energy intensive distillation, and is performed at elevated pressures in traditional multi-tray fractionators. The large energy cost creates an incentive for alternative technology. Considerable research indicates the potential of membranes in the olefin/paraffin separation arena, but this potential has not yet been realized in actual large scale processes. Capacity expansions of existing thermally-driven separation units are ideal ways to introduce membranes into large scale use while minimizing risks and building familiarity with this relatively new technology. This approach leverages existing investments without the need to build entirely new thermally-driven separation units. Within an existing integrated plant, valuable compounds in a vapor feed stream currently sent to another thermally driven separation unit could be *membrane-fractionated* into higher value products with minimal expense and significant energy savings.

Debottlenecking of C_2 and C_3 Splitters: Fig. 12 illustrates this application of advanced of membranes units. Depending upon the separation characteristics of the membrane material, this approach could allow a significant debottlenecking of the C_2 and C_3 splitters. Conventional polymer materials are limited by the performance upper bound between productivity and selectivity

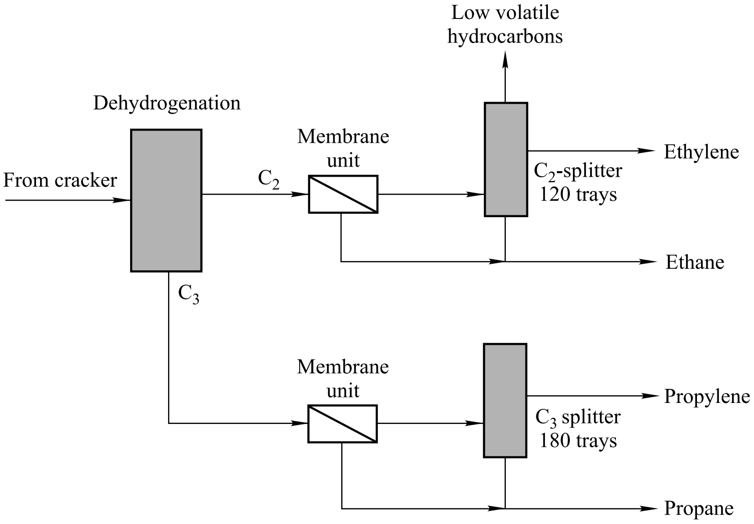


Fig. 12 Conventional separation of C_2 and C_3 mixtures integrated with possible membrane units[108,111]

trade-off[103] such as that illustrated schematically in Fig. 4—especially under the aggressive swelling conditions of such under aggressive hydrocarbon feeds. Moreover, while, facilitated membranes offer high selectivity, they are more complex than traditional membranes and have been under development for decades[104,105]. Purely inorganic and Metal Organic Framework (MOF) membranes with rigid pore structure, occupy the region in Fig. 4 above the upper bound; however, expensive fabrication cost and their brittle natures have hindered their use in such large scale applications. Recent work involving "hybrids" based on speciality MOFs and selected polymer matrices has shown promise for the C_3 olefins vs. paraffin separations in Fig. 12[106]. Moreover, since such hybrids can still be processed using the approach shown in Fig. 2 for economical fiber formation, hybrids may be attractive for such debottlenecking applications like those in Fig. 12. A more complex spinneret is required to produce a sheath-core structure, but avoidance of the additional CMS pyrolysis step for membrane formation makes this approach attractive.

In recent papers fabrication of Matrimid ® derived CMS membranes for both ethylene/ethane and propane/propylene separation were described[107-109]. The translation of superior CMS dense film properties into asymmetric hollow fiber membrane is a challenging step in asymmetric CMS hollow fiber membrane formation. Substructure collapse of the supporting wall was found to occur in Matrimid ® polymer fiber during intense heat-treatments. Such a porous wall collapse results in increased effective separation layer thickness and reduced permeance. Recent developments based on simple precursor treatment prior to pyrolysis overcome this porous wall collapse issue, providing a path to form CMS hollow fibers with high productivity and selectivity membranes[100-101]. In fact, by tuning properties of CMS membranes discussed for the CO_2/CH_4 case, optimized CMS membranes useful for olefin-paraffin membrane applications in Fig. 12 can also be created. The same pyrolysis temperature (550℃) used for the CO_2/CH_4 application is effective the olefin-paraffin pairs; however, for these larger penetrants, a pure argon pyrolysis atmosphere was useful, rather than the 30 ppm O_2 in argon pyrolysis atmosphere used for the CO_2/CH_4 pair[100, 107-111]. The slit-like pore structure created in this case, provides a unique combination of ultramicropores (responsible for molecular sieving) and micropores (responsible for sorption), that are ideal for olefin-paraffin separations[96, 99, 107-111]. Moreover, since CMS membranes are produced via controlled pyrolysis of asymmetric hollow fiber polymer precursors, they provide high performance and economical scalability compared to standard inorganic membranes and metal organic membranes.

8 Olefins-selective membranes for olefin/paraffin separations

Besides the application in Fig. 12, CMS membranes appear to be suited for an even more advanced application illustrated in Fig. 13[108,111] based on a *mixed olefins-paraffins-selective membrane*. This new concept is a step beyond the concept in Fig. 12 involving separate C_2 olefin-paraffin and C_3 olefin-paraffin debottlenecking membranes, and focuses on the deethanizer shown in Fig. 13 as discussed by Xu et al.[108]. Polymeric membrane cannot do this separation, but the data in Table 1 show that the CMS membrane discussed for the binary separations in Fig. 12 is also useful for this deethanizer debottlenecking case.

Table 1 Olefin/paraffin transport properties for hollow fiber membranes[108]

CMS Precursor	(P/l) C_2H_4	(P/l) C_2H_6	(P/l) C_3H_6	(P/l) C_3H_8	$\alpha C_2H_4/C_2H_6$	$\alpha C_3H_6/C_3H_8$	$\alpha C_3H_6/C_2H_6$	$\alpha C_2H_4/C_3H_6$
6FDA/ BPDA-DAM	15.9	4	17.5	0.85	3.9	20.5	4.38	0.91

Permeance unit is GPU; 35℃ testing temperature, pure gas C_2H_4 and C_2H_6 tested at 100 psia, pure gas C_3H_6 and C_3H_8 were tested at 50 psia for CMS derived from Fig. 9 precursor pyrolyzed at 550℃ under UHP Argon.

Besides pure components, Xu et al. also tested a typical realistic mixed gas, typical of a deethanizer feed, and showed that it can be separated using such a CMS membrane. The gas mixture mostly contains two and three carbon atoms hydrocarbons (C_2's and C_3's), and was tested at 25℃ and 60 psig. The feed and permeate compositions listed in Table 2 demonstrate enrichment in olefins (ethylene and propylene) to more than 91%, while 7.2% ethane and only 0.7% propane was retained in the permeate stream.

Table 2 Feed and permeate compositions of a mixed gas permeation test using the deethanizer feed as feed mixture to a CMS membrane with similar properties to that used to produce the pure gas binary separations in Table 1

Gas	Feed/ (mol%)	Permeate/ (mol%)
C_2H_4	54.4	75.3
C_3H_6	14.8	16
C_2H_6	17.1	7.2
C_3H_8	13.5	0.7
Other hydrocarbons	0.2	0.8

The Xu et al. study indicates the viability of the olefins-selective membrane for mixed carbon number olefin/paraffin separations and suggests the possibility of the high payoff debottlenecking opportunity shown in Fig. 13[108, 111]. Clearly, the membrane with performance in Table 1 & Table 2 can also concentrate olefins (ethylene and propylene) in the permeate stream while propane will be concentrated in the retentate stream with some ethane in both permeate and retentate stream. The propane and ethane in the retentate can be returned to a cracker with two useful products (ethylene and propylene) being simultaneously enriched in the process. The ternary

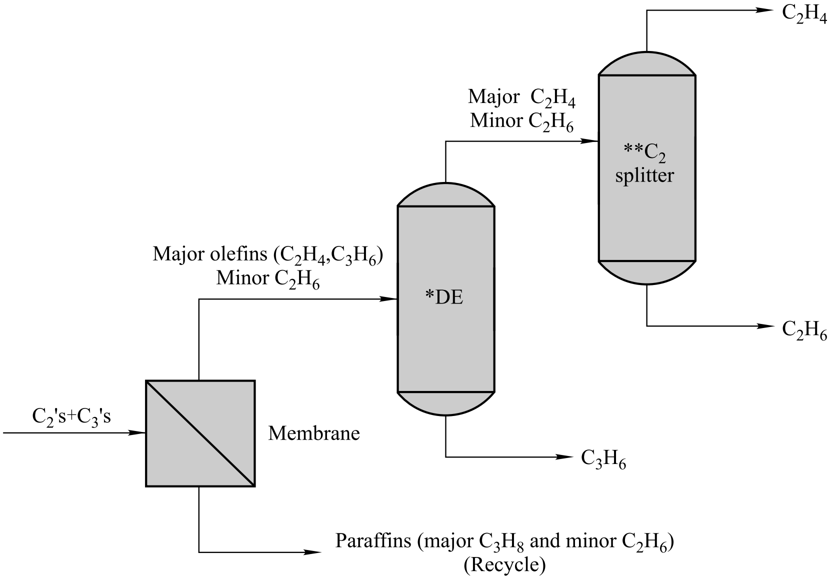


Fig. 13 Hybrid process of one olefins-selective membrane unit and two distillation columns

＊DE = deethanizer, and ＊＊C_2 = a conventional C_2 splitter permeate stream (ethylene, propylene and minor ethane) can be separated easily. After such an olefins-selective membrane, an existing deethanizer could remove both C_2s from propylene *with lower heat duty*, since propane and some ethane are already removed by the membrane unit. A second distillation column, essentially a C_2 splitter could then separate ethylene and ethane, but with increased capacity having advantages beyond the de-bottlenecking strategy in Fig. 12.

Xu et al. also note that even the use of other high performance microporous materials (zeolites, metal organic frameworks (MOFs)), such an olefins-selective membrane has not been reported previously[108]. In fact, for a pure ZIF-8 membrane transport properties of ethylene, ethane, propylene and propane[112] show a permeance order of: $(P/l)_{C_2H_4} > (P/l)_{C_2H_6} > (P/l)_{C_3H_6} > (P/l)_{C_3H_8}$. Clearly, while such a membrane can separate C_2's from C_3's, it is unable to separate olefins from paraffins to enable the above flowsheet. Zeolites (and zeolites-like materials) with 2-dimensional pores able to limit penetrant configurational entropy in the diffusion transition state like the CMS membranes reported by Xu et al., may also be attractive for olefin/paraffin separations; however, the pores in CMS material are more easily optimized.

Ethylene has a significant advantage over ethane in CMS membranes, due to differences in constraints on the degrees of freedom in the activated state[90,109,110]. A combination of such an effect for propylene, coupled with its higher critical temperature (and hence higher sorption) vs. ethane is likely the cause of the favorable propylene-ethane selectivity. In such a case, besides the debottlenecking noted in Fig. 12, reconfiguring the current ethylene plant may save significant capital costs, operational energy as well as reduce process footprint and CO_2 emissions. While further process integration and materials will be needed, the example shows the exciting opportunities available with the advanced CMS type membrane platform.

9 Summary and conclusions

Large-scale membrane-based gas and vapor separation processes present both challenges and opportunities for CO_2 emission reductions and energy efficiency improvements. Combined needs for more advanced materials and economical manufacturing approaches can be best accommodated using a polymer-derived asymmetric hollow fiber technology platform. Introducing increasingly sophisticated membranes with performance and cost to meet specific needs beyond those currently available is a pragmatic evolutionary strategy that minimizes risks and maximizes the likelihood of acceptance by industry. The increasingly sophisticated family of polymer-derived materials encompasses conventional polymers, crosslinked polymers, polymer-inorganic hybrids and carbon molecular sieves. This strategy allows addressing all but the highest temperature, most oxidizing feeds, and will potentially even provide a framework for ultimately creating economical membranes suitable for these types of feeds.

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Preparation and Application of Zeolite Membranes in Pervaporation

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Good afternoon, ladies and gentleman. It is my honor to be here to present our recent work. The topic for my talk is *Preparation and Application of Zeolite Membranes in Pervaporation*. My name is Xuehong Gu from Nanjing University of Technology.

This presentation includes four parts. First, I would like to make a brief introduction on the zeolite membrane. Then, I will talk about our efforts on membrane synthesis for improving separation performance. And then, I will also tell some application of zeolite membranes, especially, some industrial application cases in dehydration of organics by NaA zeolite membranes.

With the development of membrane separation, separation objects have been moving from big size to small size. For the porous membranes, we have microfiltration for virus and small particles separation, ultrafiltration for protein and macromolecule separation, nanofiltration could be used for oligosaccharides and multivalent ion separation. But what about the separation for small molecules? Here, I am going to talk about zeolite membranes.

Zeolite is a kind of crystalline aluminosilicate. The crystals have well-defined micropores with a size of less than 1 nm. If we pack zeolite particles closely on the porous substrate, then the zeolite layer can be used for molecular separation based on zeolitic pores. The separation is based on molecular exclusion or adsorption-diffusion. This membrane shows high thermochemical stability and mechanical strength.

There are several types of zeolite membranes like NaA and MFI. Those could be used for different separation systems depending on their pore structure and surface property. The applications included organic dehydration, organic/organic separation and gas mixture separation. There are some typical separation systems such as dehydration of organics, xylene separation, hydrogen separation and CO_2 separation.

If we look at figure for publications in the past 10 years, we can see the publication number has been increasing year by year. This means that zeolite membranes have received more attention. Many research groups have been done a lot of research work on zeolite membranes, but there are very limited companies to be able to provide commercial products. The applications are only related to dehydration of organics. This suggests that it is difficult to industrialize zeolite membranes for practical applications. The main reason for that concerns the reproducibility of large-scale preparation, membrane stability in industrial systems and fabrication costs.

How to improve separation performance for zeolite membranes? Since zeolite membrane layers are supported by porous substrate, the substrate surface would have important effect on the growth of zeolite layer. Also, because this is multi-crystalline structure, intercrystalline pores or nonzeolitic pores embedded in the layer will affect the separation performance. To address those issues, we propose some strategies for zeolite membrane preparation, like improving substrate surface, reducing seed size and healing nonzeolitic pores.

I will show you the preparation of NaA zeolite membrane. This membrane is highly hydrophilic and has pore size of 4.2 Å. The membrane can be used for dehydration of organic. This type of membrane is prepared by secondary growth method. Generally, used dip-coating as seeding method. Substrate was first coated with seeds and then further put into synthesis solution for hydrothermal crystallization.

We realized that the surface morphology had a very important effect on membrane quality. If the substrate surface has pinholes, then defects would be generated in the zeolite layer. We tried to use sandpaper to treat substrate surface. The surface roughness improved but there are some dents or caves on that. When using dip-coating method as seeding approach, we found those membranes showed low reproducibility. For industrial productions, it is unavoidable to have defects or dents on substrate surface. So how can we do with that?

Here, we proposed a combined seeding approach. First, we used seed paste to rub the substrate surface. This could mend some defects and improve substrate surfaces. After this operation, we followed by dip-coating method to provide a uniform seed layer. We then used the seeded substrate for membrane synthesis.

It was interesting to find that very high reproducibility for membrane synthesis. If you look at the table, we can find that all five membranes had high separation performance. Compared with dip-coating or rubbing, the combined method showed better performance. This approach could be used for large-scale production of zeolite membrane. The result also suggested that the surface microstructure of substrate has an important effect on the zeolite membrane quality.

On the other hand, we tried to reduce the particle size of NaA zeolite seeds by ball-milling treatment. After treat for 3 h, the particles could reduce from 2 μm to 0.3 μm. The treatment can generate lattice defects on the ball-milled particles. It is interesting to find when we use the ball-milled seed to induce NaA zeolite membrane, the synthesis time could be reduced largely from 3.5 h twice to 4 h once.

If we look at the SEM images, we can find the ball-milled seeds coating could provide a very uniform zeolite layer. Also the as-formed zeolite layer was denser than the layer when we synthesized it at 100℃ for 4 h. The small particle size and lattice defects could accelerate crystallization.

Do we have post-treatment to improve membrane performance after membrane synthesis? Here, we proposed a simply method for healing nonzeolitic pores by hydrolysis of silane. We used DMDS silane, which has kinetic diameter larger than zeolitic pores. This silane was introduced into one side of zeolite membrane. The other side was swept by DI water. The silane encounters with water in the defects. Thus, hydrolysis of silane would occur to generate amorphous SiO_2 in the defects.

If we used permporometry to examine the He permeance through nonzeolitic pores, we can find that the permeance for the modified membrane dropped largely. After 1 h modification on MFI zeolite membrane, the He permeance through nonzeolitic pores decreased by about 62%.

This method has been used to heal the defects of MFI zeolite membranes. Looking at this table, the original MFI membrane has a separation factor of 2.3 for separation of xylene mixture, after 1 h modification, the separation factor could increase to 5.5. After 2 h modification, this could be 10.8. However, the permeation flux decrease very limitedly. This method can be used for healing nonzeolitic pores of NaA zeolite membranes. After 3 h modification, the separation factor increased from 51 to 1103.

The zeolite membrane has showed great potential applications in molecule separation. How to further expand the applications? The key point is to reduce the investment costs. So it is necessary to improve membrane flux. Zeolite membrane includes two layers membrane, layer and substrate. When we reduced the substrate thickness, we found that significant improvement in permeation flux was obtained. The large effect from substrate was related with PV operation. The low operation pressure on the substrate side leaded to severe mean free patch for diffusing molecule. So the substrate wall would have stronger effect on molecular transfer.

We used a model to describe the diffusion process of pure water through membrane. For membrane layer, we used Fick law to describe adsorption-diffusion mechanism. On the substrate, we used Knudsen diffusion and viscous flow to describe it.

This is calculated permeation flux through membrane. We can see that the permeation flux was affected by the pressure on permeation side. At low permeation pressure, the substrate thickness showed obvious effect on the permeation flux. When reducing the thickness, the permeation flux increased significantly.

To obtain high flux, we can develop hollow fiber supported zeolite membrane. The reduce thickness wall can improve flux. Moreover, the membrane has small outer diameter, which could improve packing density significantly.

We first prepared Al_2O_3 hollow fibers by spinning method. The fiber has about 1.8 mm in outer diameter, about 0.5 mm in thickness, which is much lower than the ceramic tubes used right now for industry. This fiber has finger-like structure, which is helpful to reduce the transport resistance.

We used the fibers to synthesize NaA membranes. Two seeding methods including dip-coating and vacuum seeding were used for membrane synthesis. Considering large-scale production, vacuum seeding method would be preferred. The achieved membrane showed high permeation flux of 2 – 3 times than tubular membranes.

To improve acid-resistance, we also prepared T-type zeolite membrane on YSZ hollow fibers. This membrane has been successfully used for dehydration of ethanol with pH value of 3. When we compared the permeation flux of methanol, ethanol and isopropanol, we could find the permeation flux following the sequence of Arrhenius plots. We also obtained very high permeation flux for IPA, which reached 7.36 kg/($m^2 \cdot h$).

After having those hollow fiber structured membranes, we have constructed membrane modules with 0.1 and 0.2 m^2. We have tested the membrane modules for separation of 80 wt.% ethanol solution. The membrane showed high separation efficiency for ethanol dehydration.

Considering with practical application, we also developed 4 – channels Al_2O_3 hollow fiber. The fiber has provided much higher strength than single channel one. We synthesized NaA zeolite membranes on the outer surface of hollow fibers. Very high permeation flux of >10 kg/($m^2 \cdot h$) was achieved. The separation factor was higher than 10 000. This is due to the special pore structure for 4 – channel hollow fibers with finger-like structure. This configuration might be able to use for practical industrial application.

Based on above synthesis approaches, we have produced tubular NaA zeolite membranes in large scale. We care about the practical applications. The challenge for NaA membranes in practical application is stability. After investigation, we realized that the membrane was not suitable for operate in acid system. Also, it could not be operated in alkaline system and having cations. Besides, the membrane was not good for high water content. So we proposed a pretreatment for the feed before membrane separation. The feed solution should be controlled neutral and low conductivity in advance.

This is our first plant for recovery of waste isopropanol from 85% to 98%. The waste isopropanol comes from production line of cephalosporin. After production, the waste isopropanol was generated, which contained some salts and alkali. The original method for dehydration used NaOH extraction. We used membrane separation plant to replace that. The capacity for this plant is 5000 t/a. The total membrane area is about 70 m^2. This has shortened the process steps. This equipment has been running for over 3 years.

We made a technical and economic comparison among membrane process, alkali dehydration and adsorption. We can see that the membrane process demanded very few vapor consumption. Furthermore, it only needed 1 people to handle the automatic system. The treatment cost could be saved by 65% –75% by the membrane approach.

Here is another application case for production of IPA, which is obtained by acetone hydrogenation. The reactant from reaction tower mainly includes IPA, acetone and water. The mixture was fed to a distillation tower. The product from bottom is introduced to another tower for further rectification. The top generates ternary azeotrope including acetone, IPA and water. We have used NaA membranes for dehydration and return to the feed for reaction. This system can improve acetone conversion and obtain high productivity. The system has a capacity of 1500 t/a.

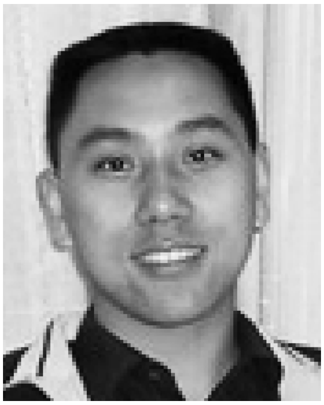
The third application case I am going to introduce is the recovery of ethanol. This solvent has been used for pharmaceutical production. This is required to dehydrate from 90 wt.% to 99.5 wt.%. The original method used extraction distillation by salts. This consumed much energy also cause pollution and corrosion. The plant was established in pharmaceutical company in last year, and has a capacity of about 1500 t/a and a membrane area of 42 m^2.

The fourth application case I would like to introduce is also about recovery of isopropanol. The original separation method used rotating packed bed plus NaOH extraction. In this case, we used NaA zeolite membrane separation to replace that, which has a capacity of 3000 t/a and a membrane area of 56 m^2.

Now, we have established about 20 plants for industrial solvent dehydration, the separation systems concerning methanol, ethanol, isopropanol and butanone.

Since 2007, we have started research work on zeolite membranes for several years. In 2011, we established a company for promoting the technology, which has a NaA zeolite membrane production capacity of 10 000 m^2/a.

Finally, I would like the government for the financial supports. I thank my team for their hard work. Thanks for your attention.



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Nanoparticles(and Nanotubes)in Membranes for Liquid and Gas Separations:A Brief Overview

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Abstract: The earliest known example of very small particles in polymeric membranes used for separation of gaseous mixtures appeared in 1965 when thin flat silicone rubber membranes containing silica particles were developed for commercial applications. Mixed-matrix membranes where inorganic nanoparticles, zeolite nanocrystals etc. are incorporated in a polymer matrix started appearing in early-to-late eighties. A brief overview of such research directed toward overcoming the Robeson (1991) limit is provided. High aspect ratio flakes facilitated development of barrier membranes. Influenced by gas separation investigations of such mixed-matrix membranes, efforts were initiated in later half of 2000-2010 to explore liquid separations through mixed-matrix membranes of polymer-nanoparticles/nanocrystals. Emergence of carbon nanotubes during this very time generated an interest in carbon nanotube (CNT)-based membranes where the liquid flowed through the inner core of CNTs. Substantial interest was generated as well in polymeric membranes whose liquid phase separation performance could be substantially influenced by incorporation of CNTs or modified CNTs as an inclusion phase. There have been a number of investigations in CNT-based or zeolite-containing polymeric membranes in reverse osmosis (RO), forward osmosis (FO) and nanofiltration (NF) including solvent-resistant NF. A variety of inclusions including metal-organic-framework (MOF) based nanoparticles in a polymer matrix have been studied. These developments will be briefly identified and the performances of such membranes will be reviewed.

1 Introduction

Synthetic nonbiological membranes can be made from a variety of materials including polymers, ceramics, metals and metallic alloys. In addition membranes can be made of hybrid materials such as organic-inorganic, ceramic-metallic, polymeric-biological etc. Further gels as well as liquids can serve successfully as membranes. Membranes in commercial use are in general polymeric in nature although ceramic membranes are also used but much less often; metallic systems are being developed especially for hydrogen separation. For an introduction to various membrane technologies, see Ho and Sirkar (2001). For advanced membrane technologies and applications, see Li et al. (2008).

The feed mixture for separation may be in gas phase or liquid phase. Gas phase separations of interest include gas mixtures, gas-vapor mixtures and vapor-vapor mixtures. Liquid phase separation systems are broader in that molecular mixtures, molecule-macromolecule mixtures, macromolecule-macromolecule mixtures, particle suspensions and their various combinations are involved. For a long time the distinguishing characteristic of the polymeric membranes in overwhelming commercial use for both types of feed phases was that only polymers were involved.

This paper will provide a limited overview of developments in mixed-matrix membranes for liquid separations as well as gas separations. In a mixed-matrix membrane, the matrix is usually polymeric in nature; but it can contain solid inorganic inclusions, organic inclusions or even liquids. Historically mixed-matrix membranes were first introduced for gas separation. A brief list of inclusions used to that end is as follows: zeolite nanocrystals, fumed silica (13 nm), silica nanopowder (10 nm or 30 nm), carbon molecular sieve (CMS) particles (submicron to 2 μm), single wall carbon nanotubes (SWCNTs), activated carbon, graphite flakes, graphene, TiO_2, polyethylene glycols (PEGs), polyamidoamine (PAMAM) dendrimers, other amines etc. Mixed-matrix membranes for liquid separations were introduced recently (around 2007); the inclusions of interest there are zeolite nanocrystals, SWCNTs, multiple wall carbon nanotubes (MWCNTs), silica nanoparticles,

TiO_2 nanoparticles etc.

In view of the extensive literature on membrane gas separation using mixed matrix membranes, it is appropriate to begin the treatment by identifying major characteristics of membrane gas separation. This will provide a useful background for this area of evolving membrane technology. We will provide first a very brief introduction to membrane gas separation and then discuss important developmental aspects and problems vis-à-vis mixed-matrix membranes. We will then focus on mixed-matrix membranes for liquid separations. For a recent review of the state of the art in membrane gas separation till 2008, see Bernardo et al. (2009). A chapter by Liu et al. (2008) provides a comprehensive account of the progress in mixed-matrix membranes for gas separation till 2007.

2 Basis for mixed-matrix membranes for gas separation

For separation of gas mixtures through a polymeric membrane, it is well known that the selectivity of a species A over another species B in terms of a separation factor α_{AB} is given by

$$\alpha_{AB} = \frac{Q_{AM}}{Q_{BM}} = \left(\frac{D_{AM}}{D_{BM}}\right)\left(\frac{S_{AM}}{S_{BM}}\right) \tag{1}$$

Here the ratio (D_{AM}/D_{BM}) is called the diffusivity selectivity where D_{AM} identifies for example, the diffusion coefficient of species A in the membrane M. The ratio(S_{AM}/S_{BM}) is called the solubility selectivity with SAM representing the solubility of species A in the membrane. For gas separation through glassy polymers, diffusivity selectivity dominates; for gas separation through rubbery polymers usually solubility selectivity is far more important. Diffusivity selectivity is determined primarily by the diameters of the gas molecules of the two species, d_A and d_B, vis-à-vis the chain gap openings in the polymer.

For most polymers, the diffusivity selectivity is proportional to exp ($-f_m \{d_{An} - d_{Bn}\}$) where the value of the power n for rotationally hindered stiff-chain polymers is 2; the value of n for flexible rubbery polymers is 1. As a result, when the diameters of the two species to be separated are somewhat far apart as for example in the case of H_2 (0.289 nm) versus CH_4 (0.38 nm) or CO

(0.376 nm) the selectivity achieved in commercialized glassy polymeric membranes with $n = 2$ varies between 30 and 250 (Zolandz and Fleming, 2001). This range is economically quite good. Although there can be better membranes in terms of selectivity, improvements in other properties are of primary interest. Contrast this situation with that when the species dimensions are not far apart as for example in the case of air separation (O_2 (0.346 nm) and N_2 (0.364 nm)) or natural gas processing (CO_2 (0.33 nm) and CH_4 (0.38nm)). Here one needs to achieve a higher selectivity for each system. For example, the observed selectivity for O_2-N_2 system for glassy polymers ranges between 3-7 (Zolandz and Fleming, 2001), while that for CO_2-CH_4 system ranges between 5 and 30 (Zolandz and Fleming, 2001). There are other factors which lead to further reductions in the selectivity; for example in natural gas processing, high CO_2 partial pressure plasticizes glassy polymeric membranes leading to a significant reduction in CO_2-CH_4 selectivity from 30-40 to 15-20 or lower.

On the basis of a large amount of literature data on permeability vs. selectivity of a wide variety of polymeric membranes for gas separation, Robeson (1991) had concluded that there is an upper bound in the curve of selectivity vs. permeability for any binary gas mixture. This study essentially postulated that there is an intrinsic upper limit to how high can the selectivity be for a given value of the permeability (of the more permeable species; e.g., O_2 in O_2-N_2 system). The higher the permeability, the lower is the selectivity. A phenomenological basis for such a behavior has been provided by Freeman (1999). Since very low permeability is also not acceptable, this postulated upper limit tended to suggest that alternate strategies are needed if a membrane is to have high permeability as well as high selectivity in gas/vapor separation applications.

In the field of nonpolymeric materials, inorganic molecular sieves, such as zeolite 4A crystals, have an O_2-N_2 selectivity of around 37 at 25℃. Although the permeability of O_2 through this molecular sieve is a low 0.77 barrer compared to, say, 1.3 barrer through a glassy polyimide (PI) film of interest, its very high selectivity ought to increase the selectivity of a glassy PI membrane (which has a selectivity of 7.2 at 25℃) if the zeolite crystals could be incorporated in a PI film without a substantial reduction in permeability. Mahajan and Koros (2000) illustrated this possibility by plotting the calculated value of the permeability of such a mixed matrix membrane against the O_2-N_2 selectivity for various loadings of the zeolite. As the zeolite loading increased beyond 40% the selectivity went beyond the Robeson upper limit for the given value of permeability.

It is useful to point out the basic relationships that govern the permeability of a mixed matrix membrane based on polymeric blends (Robeson, 2010). The mixed-matrix membrane may be composed of a miscible or an immiscible polymer blend. Focus now on immiscible polymer blends (note that most mixed matrix membranes are made of disparate phases almost invariably immiscible, e.g., zeolite in a polymer; therefore surface compatibilization may be needed). Let the permeability coefficients of the immiscible blend and the polymer components 1 and 2 present in volume fractions of φ_1 and φ_2 respectively are P_b, P_1, and P_2 respectively. These permeability coefficients are related by either

$$P_b = \varphi_1 P_1 + \varphi_2 P_2 \qquad (2)$$

for a parallel model, or

$$P_b = P_1 P_2 / (\varphi_1 P_2 + \varphi_2 P_1) \qquad (3)$$

for a series model. The parallel model provides an upper bound whereas the series model provides a lower bound.

A model frequently used with mixed matrix membranes for gas separation involves Maxwell's equation (Maxwell, 1873) for the effective permeability Peff of the mixed-matrix membrane containing dispersion of spheres of one material (subscript d) in a continuous or matrix phase (subscript m)

$$P_{\mathrm{eff}} = P_{\mathrm{m}}\{[P_{\mathrm{d}} + 2P_{\mathrm{m}} - 2\varphi_{\mathrm{d}}(P_{\mathrm{m}} - P_{\mathrm{d}})]/[P_{\mathrm{d}} + 2P_{\mathrm{m}} + \varphi_{\mathrm{d}}(P_{\mathrm{m}} - P_{\mathrm{d}})]\} \qquad (4)$$

When the dispersed phase is nonporous, i.e., P_d is zero, the relation gets simplified to

$$P_{\mathrm{eff}} = P_{\mathrm{m}}\{(1-\varphi_{\mathrm{d}})/[1 + (\varphi_{\mathrm{d}}/2)]\} \qquad (5)$$

This relation shows that nonporous dispersed phase will lead to lower permeability through the mixed-matrix membrane. Earlier it was pointed out that Mahajan and Koros (2000) had calculated the permeability of a mixed matrix membrane of zeolite 4A in PI and the permeability coefficient exceeded the Robeson (1991) upper limit when the zeolite loading went beyond 40%; they had employed Eq. (4) with appropriate permeabilities for the two phases, the matrix and the zeolite.

3 Mixed-matrix membranes for gas separation: examples

Let us recognize at the outset that the dispersed phase in the polymeric matrix can be a solid or a liquid which can be an oligomer. In terms of solid fillers, the earliest commercial example was that of 33 % (mass fraction) silica particles in flat and thin silicone rubber membranes manufactured by General Electric (Robb, 1965). It is not known whether these silica particles were nanoparticles or not. Oxygen permeabilities in dimethyl siloxane films decreased from 700 Barrer to 400 Barrer when silica mass fraction was increased from 0 to 60%. Robb(1965) indicating that the permeability did not decrease as much as the parallel model (Eq. (2)) would suggest; however Maxwell's Eq. (4) does predict this value. There was a significant amount of research going on investigating various permeation/transport properties in studies on diffusion in polymers containing a variety of fillers (see Barrer, 1968); these fillers were generally inert. For polymer membranes containing adsorptive fillers, Paul and Kemp (1973) carried out time-lag studies whereas Kemp and Paul (1974) carried out gas sorption studies.

The next earliest study of gas separation using a mixed-matrix membrane appeared in a UOP patent (Kulprathipanja et al., 1988; there are several other US Patents issued to UOP in this general area around 1988) using silicalite zeolite in cellulose acetate (CA) membranes for CO_2/H_2 separation. Normally a dense CA membrane is selective for H_2 over CO_2; the zeolite made it a CO_2 selective membrane. Since then a considerable amount of research has been carried out with a variety of mixed-matrix membranes for gas separation. A whole range of glassy polymers has been used just as a variety of adsorbents and molecular sieves were explored; a short list of glassy polymers includes brominated polyphenylene oxide, cellulose acetate, perfluoropolymer Teflon AF-2400, polyetherimide, various polyimides, polyethersulfone, poly (4-methyl-2-pentyne) (PMP), polymers of intrinsic microporosity (PIM), polysulfone etc. See Liu et al. (2008) for an extensive list of earlier references. These studies pointed out certain common features.

1) There must be good interfacial adhesion/compatibility between the matrix phase and the filler/nanoparticle being used; otherwise voids at the matrix-filler interface will allow nonselective gas mixture transport through these corridors. Interfacial compatibilization is therefore practiced often.

2) In semicrystalline polymers it is known that in the region at the interface between the amorphous polymer and the crystalline region, polymer chains are somewhat more immobilized than in the bulk of the amorphous region leading to lower permeability. The filler in the polymer matrix phase plays a similar role as the crystalline regions in a semicrystalline polymer.

3) Nanosized nonporous silica particles which tend to form aggregates introduce disruption in polymer packing density and create additional free volume/void space which leads to increased permeability but reduced selectivity for systems based on small gas molecules such as $O_2 - N_2$ etc. However for more condensable gases, one observes higher selectivity at the same time.

4) Accidental plugging of the all-important pores in the zeolite or other adsorbents has to be avoided.

5) The filler should be a nanoparticle. Since the skin thickness of commercial gas separation membranes are in the range of 50 – 100 nm and since it is necessary to have a percolation threshold via a sufficient density of nanoparticles, the nanoparticle dimensions should preferably be in the range of no more than 5–20 nm.

We will now identify briefly the performances of selected mixed-matrix membranes for gas separation to highlight specific behavioral aspects mentioned above. To avoid the possibility of voids at the polymer-crystal interface due to the extreme rigidity of a PI matrix originally selected for its high $O_2 - N_2$ selectivity, Mahajan and Koros (2000) used a flexible polymer such as polyvinyl acetate (PVAc) with zeolites such as an aluminosilicate type zeolite 4A. It is known that PVAc has affinities for alumina and therefore for the aluminosilicate zeolite. They observed a significant enhancement in $O_2 - N_2$ selectivity from the value of 5.9 of pure PVAc with unchanged or slightly lower permeabilities at 15% zeolite loading; at 40% zeolite loading, the selectivity went up to a high of 9.7–10.4 but the permeabilities were reduced by almost 40% due to inhibition of chain mobility near the crystal surface. Pechar et al. (2006) adopted an alternate strategy. Zeolite L crystals whose surfaces were functionalized with amino groups which could link covalently with carboxylic acid groups on a polyimide backbone were dispersed in a PI matrix to ensure the absence of interfacial voids; there was a slight enhancement in permeabilities but no substantial enhancement in selectivity (Pechar et al., 2006). Further with the amino-functional silane coupling used, sorption capacities of the zeolites were substantially reduced.

Carbon molecular sieves when incorporated in rigid glassy polymers such as polyimide (Matrimid) and polyetherimide (Ultem) yielded enhanced selectivities as well as increased species permeabilities (Vu et al., 2003) in both O_2-N_2 and CO_2-CH_4 systems. Activated carbon incorporated in glassy acrylonitrile-butadiene-styrene (ABS) led to both increased selectivity and permeability (Anson et al., 2004). Another carbon-based filler, crystalline graphite flake, (particle size range, 1 – 15 μm) yielded (Peng et al., 2007) considerable enhancements in a slightly different problem namely, pervaporation separation of benzene-cyclohexane mixture via a polyvinyl alcohol membrane containing a graphite loading that varied from 0 to 10%. For 1 μm particles at 6% loading, the permeation flux was enhanced 4-fold and the benzene-cyclohexane selectivity was increased 6 times. The enhancement in benzene permeability is explained primarily by the changed free volume characteristics of the PVA-graphite membrane.

Merkel et al. (2002) studied the effect of fumed silica (TS-530, particle size ~ 11 – 13 nm) content on n-butane permeability and n-butane/methane selectivity of glassy poly (4-methyl-2-pentyne) (PMP) at 25℃ using mixtures composed of 98 % (mole fraction) methane and 2 % (mole fraction) n-butane at a feed pressure of 11.2 atm and a permeate pressure of 1 atm. They found that n-butane permeability increased about 5 times and the selectivity went up about 2 times as one goes from pure PMP to 40 % (mass fraction) fumed silica. By disrupting the packing of rigid bulky PMP chains, fumed silica nanoparticles apparently increases accessible free volume in the polymer matrix without introducing cavities large enough to promote weakly selective or nonselective free-phase flow mechanisms (e. g., Knudsen or Poiseuille transport). This increase in free volume augments diffusivity, weakens the size-sieving nature of PMP, factors that increase both permeability and reverse selectivity by increasing the solubility of the condensable C_{3+} hydrocarbons over noncondensable ones such as, methane in that the larger molecule permeates faster.

The changed performance is highly dependent on the nature of the polymer and its interaction with the silica nanoparticles and their tendency to form aggregates/agglomerates. Silica nanoparticles of 10 nm size were incorporated in the glassy polymer brominated poly (2, 6-diphenyl-1, 4-phenylene oxide ($BPPO_{dp}$)) (Cong et al., 2007); the resulting membranes were flexible and achieved a CO_2 permeability of 436 barrer at 23% silica loading without affecting the permselectivity of the systems CO_2/N_2 and CO_2/CH_4. The CO_2 permeability was much higher than that of the straight polymer namely, 78 barrer. The enhanced permeability is ascribed to the development of nanogaps around the silica nanoparticles whose surface was not compatibilized. Such nanogaps will disappear if the silica nanoparticle surface is compatibilized. Ahn et al. (2010) studied mixed-matrix membrane behavior using the fumed silica nanoparticles (used by Merkel et al., 2002) dispersed in a polymer of intrinsic microporosity (PIM-1). They observed considerable enhancement of individual gas permeability as the silica volume fraction was increased. This may be due to polymer chain disruption or nanovoids forming at the particle-matrix interface. However, the selectivity decreased with increased silica nanoparticle loading. It appeared that the observed decrease in selectivity in O_2-N_2 system with increased O_2 permeability was following the directional profile of Robeson (1991) upper bound limit.

It therefore appears that performance of a mixed-matrix system in gas separation will be very system-dependent. In a mixed matrix system containing impervious nanoparticles, there probably will be permeability enhancement of an individual gas unless there is a perfectly compatibilized interface between the matrix and the nanoparticle and there is no chain disruption. It is more than likely that there will be permeability enhancement for individual gas/vapor species due to chain disruption or development of nanogaps. On the other hand, with impervious nanoparticles, the selectivity may remain the same or be reduced unless there is significant disruption of the chain packing and there is considerable difference between the species in condensability. However where permeable nanoparticles are involved it is often possible to enhance both the system selectivity and individual species permeability. Pore plugging of permeable nanoparticles/zeolites/activated carbon will reduce the performance. Specific interactions between the permeating gas/vapor species and the nanoparticle are especially useful for enhancing both permeability and selectivity.

There is another kind of solid nanoparticle/filler which introduces a different dimension because of their shape/aspect ratio. When thin impermeable flakes are used with a large aspect ratio between their length and the thickness, the permeation path length is considerably increased leading to reduced permeability. Such membranes are quite useful as a permeation barrier. If the flake becomes permeable to only one of the species then the enhancement in selectivity as well as permeability becomes considerable. As the flake aspect ratio increases beyond 15, a mixed-matrix membrane with a selectively permeable flake achieves an extraordinary enhancement in selectivity close to that of the flake selectivity (Cussler, 1990). This is in contrast to spherical inclusions. Graphical illustrations of flakes (vis-à-vis the aspect ratio and the exfoliation issue), nanoparticles, zeolites etc. in membranes for gas separation are available in Sirkar (2008).

Mixed-matrix membranes have also been prepared with inclusions of small molecular weight compounds, oligomers, polymers etc. yielding membranes with highly enhanced performances. Liu et al. (2008) illustrate considerable earlier research on liquid-polymer mixed-matrix membranes especially involving polyethylene glycol (PEG). Here we point out an example of an amine-based polymer incorporated in a polyvinyl alcohol-poly (siloxane) matrix to separate CO_2 from H_2. Moderately hindered poly-N-isopropylallylamine (MW, 120 000–200 000) was incorporated as a fixed-site CO_2-carrier along with mobile carriers in the polymer matrix which primarily served as the medium to provide the dispersed amines (Zhao and Ho, 2013). Such a membrane provided a CO_2/H_2 selectivity greater than 90 and CO_2/N_2 selectivity higher than 150 at

120℃ from a feed at two atmospheres in the presence of considerable water vapor. Consult Zhao and Ho (2013) for additional references on similar/related mixed-matrix membranes.

Oligomeric amines are of special relevance in mixed-matrix membranes for enhanced and selective CO_2 transport. Pure polyamidoamine (PAMAM) dendrimer of generation zero was found by Kovvali et al. (2000, 2001) to have exceptionally high selectivity for CO_2 over a variety of gas species such as N_2, O_2 etc. as long as there is considerable moisture in the feed gas environment. The RITE Group in Japan has exploited this feature to develop highly efficient membranes for CO_2 capture from flue gas. Taniguchi et al. (2008) incorporated PAMAM dendrimers of various generations (e.g., 0, 1, 3, 5) in an UV- crosslinked PEG membrane matrix for CO_2-N_2 separation; generally Gen 0 performed the best. However, the overall selectivities were quite high and ranged between 200 and 500 for all membranes investigated.

There is another dimension to the practical realization of mixed-matrix membranes for gas separation. One common form of commercial membranes is hollow fibers; generally they have either a composite or an asymmetric structure with the selective layer being very thin. Liu et al. (2008) have provided a useful description of various considerations in the fabrication of such hollow fibers. Specifically, fabrication of a dual-layer mixed matrix membrane with the thin layer on the outside containing the dispersed phase has been treated. Some of the challenges for achieving such a layer using molecular sieves are: Reducing aggregation level of the molecular sieves; reproducibility issue; interaction of the polymer and the molecular sieve; interaction between hard crystalline sieves and the die surface etc. Softer non-aggregating nanoscale dispersed phase entities are likely to reduce some of these problems.

4 Mixed-matrix membranes for liquid separation: introduction

Ever since the first description of carbon nanotubes (CNTs) by Ijima in Nature (1991), exploration of its usefulness in a variety of applications has expanded exponentially. The particular topic of interest here is molecular transport leading to highly selective separations from liquid solutions for reverse osmosis (RO), forward osmosis (FO), nanofiltration (NF) and ultrafiltration (UF). The earliest example was provided by Holt et al. (2006) who provided data wherein double wall carbon nanotubes (DWCNTs) with diameters of less than 2 nm serve as pores (in an impermeable matrix) through which water was transported at rates three orders of magnitude faster than those suggested by continuum models. Molecular dynamics simulations suggest also such fast transport as indicated in Holt et al. Observed gas flow rates through such CNTs also indicated an order of magnitude higher transport rate than that predicted by Knudsen diffusion.

Holt et al. (2006) did not achieve desalination since the DWCNTs had much larger inner core diameters to be able to reject salt. However, this particular development along with experiments on enhanced gas separation by using zeolites in a polymer matrix opened the possibilities for achieving improved desalination performance via a mixed matrix desalination membrane. The workhorse of most desalination membranes is an interfacially polymerized (IP) ultrathin polyamide membrane on a porous polysulfone membrane support. Such membranes are often identified as a thin-film composite (TFC). Jeong et al. (2007) created a so-called nanocomposite desalination membrane by having NaA zeolite nanoparticles dispersed in the 50–250 nm thick interfacially polymerized film on a porous polysulfone support.

Zeolite nanoparticles were dispersed (0.004%–0.4%, *m/V*) in the organic phase solution containing trimesoyl chloride (TMC) in hexane; this solution reacted with a 2% aqueous solution of m-phenylenediamine (MPD) soaking the porous polysulfone support membrane to form the ultrathin polyamide membrane for RO on the porous support (Jeong et al., 2007). At the highest nanoparticle loading, pure water permeability was nearly double that of regular polyamide films with equivalent NaCl rejections. Since the interfacial polymerization takes place in the organic phase for the monomers used, the zeolite nanocrystals introduced in the hexane phase were incorporated in the thin polymerized film. Note that zeolite membranes based on only NaA zeolites had been developed already for highly selective water removal by pervaporation from a solution of ethanol-water (Kondo et al., 1997, 2010). The zeolite crystals are expected to pass only water selectively thorough its subnanopores and enhance water permeability of the IP-based membrane without compromising salt rejection capabilities unless nanogaps are created at the interface between the crystal and the polyamide matrix. Note further that larger size nanocrystals could traverse the whole thickness of the interfacially polymerized skin if it is quite thin. Such a membrane was identified as a thin film nanocomposite(TFN).

At this stage, two alternate routes appeared in the search for better liquid phase separation membranes: Incorporate zeolites or other water selective molecular sieves or microporous solids in the IP film and create a mixed-matrix membrane; or develop carbon nanotube-based membranes. It is useful to critically evaluate the status of CNT-based membranes following what Roy et al. (2011) wrote. Holt et al. (2006) developed a vertically aligned array of DWNTs on a silicon chip by a many-step process including a combination of chemical vapor deposition, ion milling and reactive ion etching ending up with a membrane containing CNTs open at both ends. The membrane however had a low CNT-based porosity of only around 0.5%. This procedure for membrane fabrication is demanding. The CNT-based membranes in Majumder et al. (2005) require a demanding fabrication procedure as well even though the rate of water permeation through the inner core of the CNTs was 4 to 5 orders of magnitude higher than those predicted by conventional fluid flow theory. Yu et al. (2009) prepared a vertically aligned CNT membrane having a high CNT-based porosity of 21% via solvent evaporation and collapsing of CVD synthesis-based array of CNTs. Gas permeated at a high rate through the interstitial pores as well as the inner core of the CNTs; they demonstrated nanofiltration of 3.2 nm gold nanoparticles as well. This structure would limit the smaller dimensions of solutes that can be rejected due to the dimensions of the interstitial openings. A brief review of CNT-based membranes is available in Löpez-Lorente et al. (2010).

We will quote now what Roy et al. (2011) opined on this topic. “Fabrication of membranes based on transport through the inner core of CNTs is very demanding. Large scale inexpensive fabrication of CNT-based membranes needs to be carried out on a readily scalable platform which should be easily implemented in a polymer matrix leading to a compact and economical membrane device. Polymer matrix itself which can be nonporous, mesoporous or microporous, may have considerable solvent flux and solute selectivity. In fact, polymeric membranes can achieve selectivity between two species/macromolecules/particles over an extremely wide range of molecular weights and species/particle sizes. Species discrimination over such a broad range of molecular weights/sizes etc. is likely to be difficult at this time for CNT inner core-based separation processes since the inner core dimensions of CNTs are available only in particular sizes and are not infinitely variable with the current synthesis capabilities. ”

On the basis of such constraints, Roy et al. (2011) pursued a different strategy which relied on utilizing the interaction or lack of interaction between the external surface of the carbon nanotube and the polymer matrix in the context of fabrication of solvent resistant nanofiltration (SRNF) membranes to start with. From gas separation research on mixed-matrix membranes it is known that a nanoparticle dispersed in the polymer matrix may create an interfacial region with enhanced gas permeability due either to lack of interfacial bonding leading to nanogaps or local disturbance to the matrix chain packing around it. Since the solutes to be separated in SRNF have molecular weights between 200 – 1000 dalton, one could assume that nanogaps of smaller dimensions will reject such solutes; yet the solvent transport rate would be considerable enhanced through such nanogaps.

Interfacial polymerization (IP) was utilized to fabricate solvent-resistant nanofiltration membranes of polyamide containing a polymer-CNT composite on porous hydrophilized polypropylene substrate (Roy et al., 2011). In this nanocomposite membrane, the IP-generated polyamide provides the selectivity and the nanogaps between the external surfaces of the MWCNTs externally functionalized with hydrophilic/hydrophobic groups and the matrix polymer enhance solvent flux by almost an order of magnitude. Membranes achieve high rejections of solutes brilliant blue R (826, MW) and Safranin O (351, MW) from their methanol and aqueous solutions. In the fabrication procedure, MWCNTs are dispersed in one of the monomer-containing phases. The outside surfaces of MWCNTs were rapidly functionalized earlier with hydrophilic (– COOH) groups or hydrophobic groups via microwave treatment (Wang et al., 2006); those with hydrophilic groups are generally dispersed in monomer-containing aqueous solution and those with hydrophobic groups are generally dispersed in monomer containing organic solvent prior to fabricating IP-based membranes. Otherwise surfactants are used.

The MWCNT levels used in making these membranes were in the range of 0.01 % –0.06 % (mass fraction). One CNT can potentially provide through its interface with the polymer matrix a continuous transport corridor from one end of the CNT to the other thus eliminating the need for a substantial CNT volume fraction to achieve a percolation threshold. This is particularly valid in IP-based membranes whose skin thicknesses are of the order of 100 nm whereas CNT lengths were at least in the range of 1 to a few micrometers. It is not known clearly whether in the present case microwave treatment opened up the CNT or not. Suppose it did. Then one has to contend with the possibility of the test solutes entering a MWCNT mouth at the feed solution interface (if the mouth is open to the feed solution and not buried inside the polymerized skin) and go easily to the other end of the IP film. This would be a very large source of leakage of test solutes unless the other end of the MWCNT did not open up. Further the open interior dimension of the MWCNTs (30 nm) was quite large. It was observed instead that the solute rejections of the membranes formed were not affected whether there was MWCNTs or not. If the interior surface of the MWCNTs were functionalized by microwaves, the solvent flux would be reduced substantially; further the solute flux will increase leading to lower solute rejection.

If one were to think of desalination using the inner core of the single wall CNT, other considerations come in. The ionic radius of Na^+ and Cl^- are 1.16 Å and 1.81 Å respectively (Burgess, 1988). The kinetic sieving diameter of water in zeolites is ~ 2.7 Å (Breck, 1974). It is known for polymeric sea-water reverse osmosis membranes that water molecule cluster sizes exceeding 4 in number are the minimum needed to transport salt ions through a polymeric membrane (Strathmann and Michaels, 1977). It is clear then that the internal tube diameter in single wall carbon nanotubes (SWCNTs) (~4–5 Å) will not provide such an opening for the water cluster around a salt ion thus allowing only water molecules to go through SWNTs. However one has to have only SWCNTs with open mouths to take care of this mechanism. Without a highly controlled chemical vapor deposition (CVD)-based fabrication procedure and additional steps, such a scenario is difficult to achieve; if achieved it is likely to be quite costly and challenging to scale up.

5 Mixed-matrix membranes for liquid separations in RO, FO and NF: examples

We will first consider examples of thin film composites (TFCs) prepared by interfacial polymerization with nanoparticles (that are not nanotubes) incorporated in the polymerized film: the TFNs. The nanoparticles incorporated were as follows: zeolite crystals, silica, silver, TiO_2, silica sols (to avoid agglomeration of silica nanoparticles), metal-organic framework (MOF), aquaporin etc. Of these silver nanoparticles were introduced to provide antibacterial property. Four studies using zeolite crystals are relevant. Three are from UCLA, Los Angeles, CA (USA): Jeong et al. (2007) (already considered), Lind et al. (2009), Lind et al. (2010). The latest one is from Singapore: Ma et al. (2012).

Lind et al. (2009) employed Linde type A zeolite crystals in the NaA form having the following dimensions: 97 nm, 212 nm, 286 nm; 0.2% (*m/V*) crystals were dispersed in the organic phase prior to polymerization. Rejections of NaCl, $MgSO_4$ and PEG 200 (3.5 Å radius) by the TFN membranes were studied and found to be quite close to or slightly less than that of the TFC membrane without the nanoparticles. The TFN membranes were found to be somewhat more permeable and more negatively charged and thicker than a regular TFC membrane. TFN membranes having smaller size zeolite crystals produced higher fluxes; the authors could not conclude whether it was due to an increased amount of nanochannels. Preferential interaction between the polymerized film and the nanocrystal including lower extent of crosslinking is likely. Lind et al. (2010) demonstrated NaCl rejection levels comparable to commercial sea water desalination RO membranes (~ 99.4%) with TFN membranes containing 0.2% zeolites in the organic phase and a few post-treatments; the flux levels were also comparable. In general, the salt rejection levels were slightly lower for other TFN membranes with water fluxes somewhat higher. Ma et al. (2012) employed conventional TFC formulation for an interfacially polymerized polyamide membrane with 40 – 150 nm NaA zeolite particles dispersed in the organic phase at loadings between 0.02 to 0.4 (*m/V*, %). The loading of 0.1% yielded the best FO performance with a water permeability 80% higher than the baseline TFC membrane but a somewhat lower salt rejection. The surfaces of the membranes were rougher than the baseline membranes.

A few remarks to characterize some observations in these publications follow:

1) zeolite nanocrystals were dispersed in the organic phase prior to IP;

2) TFN membranes had high charge density (much more negatively charged than the base PA membrane) and exhibited superhydrophilicity;

3) pore-filled (templating agent not removed after hydrothermal synthesis) zeolite flux was less than pore-open zeolite flux;

4) smaller zeolites produced greater permeability enhancements;

5) TFN membrane permeability of water is generally higher than the corresponding TFC membrane;

6) higher zeolite loading reduces water permeability due probably to a thicker PA layer; the loading level found useful is around 0.1–0.2 (*m/V*, %);

7) the salt rejection virtually never exceeded the corresponding TFC membrane and is usually marginally or significantly lower.

Studies conducted earlier as well as subsequent to the above-mentioned studies utilized other nanoparticles. The polyamide thin film composite membranes obtained by incorporating TiO_2 nanoparticles (Kwak et al., 2001; Lee et al., 2008), silver nanoparticles (Lee et al., 2007) displayed nanofiltration behavior namely, high solvent flux, high rejections of salts such as $MgSO_4$ containing divalent ions and low rejections of NaCl. This behavior suggested that nanogaps created between the nanoparticle inclusion and the polyamide membrane are responsible for the observed behavior even though the membranes developed had some antifouling/antibacterial properties. Results of incorporation of silica nanoparticles were studied by quite a few investigators with variable results.

1) Jadav et al. (2009) employed 3 nm and 16 nm silica nanoparticles in

the TFN membrane of polyamide; they could achieve brackish water desalination but no further indicating that some nanogaps were acting as defects.

2) Hu et al. (2013) employed in interfacial polymerization 2,2′-bis(1-hydroxyl-1-trifluoromethyl-2,2,2-trifluoroethyl)-4,4′-methylenedianiline (BHTTM) in the aqueous phase and trimesoyl chloride in the organic phase on a polyethersulfone support membrane with a silica sol introduced into the aqueous phase; 0.1% silica concentration was found to be optimal. The membranes performed as NF membranes with a maximum of 94% rejection of Na_2SO_4.

3) In an earlier study, Hu et al. (2012) employed piperazine as the aqueous phase monomer for making a TFC polyamide membrane with aqueous silica sol in the aqueous phase and obtained a NF membrane with 97.4% rejection of Na_2SO_4.

We will now summarize results of membranes employing carbon nanotubes (CNTs) in a variety of ways beyond what was done by Roy et al. (2011). The processes of interest studied are NF and FO; the CNTs used were generally functionalized MWCNTs. Goh et al. (2013) fabricated polyamide-imide (PAI) hollow fibers, functionalized MWCNTs with carboxylic acid groups, immobilized these functionalized MWCNTs on the hollow fiber outside surface by vacuum filtration and then this surface was chemically crosslinked with polyethyleneimine (PEI) to develop a positively charged NF membrane. The membranes had a pure water permeability of 4.48 L/(m^2·h·bar) and a $MgCl_2$ rejection of 87.8% at 1 bar indicating a 44% water permeability enhancement for similar solute rejection. These membranes exhibited almost similar enhancement in water flux without compromising solute flux in a FO process with 0.5 mol/L $MgCl_2$ as the draw solution and deionized water as feed. Shen et al. (2013) employed piperazine and trimesoyl chloride based interfacial polymerization on a porous polysulfone substrate wherein the organic phase contained MWCNTs whose surfaces having –COOH and –OH groups introduced earlier by acid treatment were grafted with polymethylmethacrylate. This TFN membrane with hydrophobized CNT surface showed 99% Na_2SO_4 rejection with a 2000 ppm feed solution at

1 MPa and a 62% enhanced water flux over the corresponding TFC membrane in NF. Additional results from studies having variations of the same theme are available in the following publications.

In Wu et al. (2013), MWCNTs with functionalized carboxylic groups used at 0.5 mg/mL in the aqueous solution with triethanolamine as well as some surfactants and TMC on a porous polysulfone support membrane yielded double the water permeability of the film without the MWCNTs; however the rejection of Na_2SO_4 did not go beyond 85%. Daraei et al. (2013) grafted polyacrylic acid on the MWCNTs and prepared nanocomposite polyethersulfone-based nanofiltration membrane with high water flux and improved rejection and anti-fouling properties. Zhao et al. (2014) improved the performance of polyamide-based RO membrane without sacrificing salt rejection by incorporating MWCNTs modified to improve their dispersivity; increased MWCNT loading increased the water flux with solute rejection slowly decreasing.

Other inclusions have been used besides those mentioned above. An example is provided by Sorribas et al. (2013) where MOFs were introduced in an IP-based polyamide layer which led to 2 – 6 times solvent permeation enhancements for greater than 90% rejections of styrene oligomers of molecular weights larger than 295 in solvents such as methanol and THF.

A number of corporations are beginning to exploit such membrane technologies employing zeolites or CNTs. Porifera Inc. (Hayward, CA, USA) is employing aligned CNT-based membranes for ultrafiltration and claiming to have achieved 5 – 6 times higher water flux with similar MW cutoff than conventional UF membranes. Porifera Inc. claims to have made 300 millimeter wafers of such membranes. Porifera Inc. is also exploring other applications of aligned CNT membranes. NanoH2O Inc. is another California company (El Segundo, CA, USA) preparing spiral-wound membrane modules for desalination using thin film composite membranes in which nanomaterials have been introduced into the selective layer. Such TFN membranes are claimed to have 50% –100% increase in water permeability with respect to the base TFC membranes. Large membrane units have been manufactured for commercial applications.

A few conclusions are provided now along with a few suggestions.

1) IP-based randomly placed CNT-TFC membranes are relatively easy to fabricate.

2) To improve solute rejection the density of surface functionalization probably needs to go up; the nature of the functionalizing polymer, its water clustering property etc. are of great importance if RO desalination is the objective.

3) Vertically aligned CNT-based membranes obtained via CVD are difficult/costly to fabricate.

4) Vertically aligned CNT-based membranes allow the ID of CNT to control solvent flux and solute separation.

5) Facile fabrication of vertically-aligned CNT-based membrane will yield high solvent flux and appropriate solute rejection.

6) Appropriately purified CNTs are of great use to achieve this goal.

However, the cost of fabricating such membranes with a sufficient density of CNTs having appropriate internal diameters for particular separations is likely to be high; cost comparison with relatively inexpensive polymer-based membranes is inevitable. Concurrently radical enhancement of solvent flux will bring in its wake high concentration polarization on the feed side. Novel fluid management techniques will be needed to control such a level of polarization.

The liquid separation processes discussed so far involved RO, FO, NF and UF. Mixed-matrix membranes have also been used for pervaporation as mentioned already (Peng et al., 2007). The earliest study on pervaporation was done by Hennepe et al. (1987) using alcohol-selective silicalite dispersed in a silicone rubber matrix for separation from an alcohol-water solution. Hydrophilic zeolite 4A particles were incorporated in poly(dimethylsiloxane) (PDMS) and poly(trifluoropropylmethylsiloxane) (PTFPMS) membranes; the latter membranes yielded water-ethanol permselectivities as high as 11.5 and water permeabilities 6 times higher than unfilled PTFPMS membranes (Lin et al., 2013). This last study from Lee Vane group is part of a series of studies using both hydrophilic as well as hydrophobic zeolites in rubbery membranes for pervaporation-based separation of alcohol-water solutions.

In mixed-matrix membranes for gas separation, we had indicated earlier that membranes having selectively permeable flakes could achieve an extraordinary enhancement in the selectivity and permeation of the species selectively permeating through the flake. In hydrogen-based proton conducting fuel cells, the permeation rate of a proton in a humidified environment was enhanced considerably by having a nanocomposite membrane of the following type. In an ionomer membrane of say, sulfonated polyetherketone, lamellar zirconium phosphates were dispersed; these flakes have high proton conductivity leading to enhanced proton conductivity in the membrane along with enhancement in other properties such as reduced swelling, increased mechanical resistance etc. (Alberti et al., 2003).

As in gas separation where distinct molecular entities/polymers such as polymeric amines were added to the polymeric matrix to enhance the permeation of selected gas species, similarly in the performance of proton conducting fuel cells supramolecules have been impregnated in Nafion to enhance its proton conductivity among others at higher temperatures. Photocurable hyperbranched (HB) polyester terminated with functional carboxylic acid groups, namely HBPEAc-COOH, was incorporated in the ionic domains of Nafion to enhance the proton conductivity (Kyu and Nazir, 2013).

6 Summary

The concept of using mixed-matrix membranes for a variety of problems in gas separation as well as liquid separations is quite attractive. Considerable enhancements in membrane performance have been demonstrated in a variety of gas separations. In liquid separations enhancement in solute rejection was generally elusive; however significant enhancement of solvent flux e.g., water flux has been demonstrated. Individual system characteristics are crucial in determining enhancement or deterioration in performance in mixed-matrix membranes containing nanocrystals, nanoparticles, CNTs etc. Concurrently, significant attention has to be paid to the following areas: matrix-inclusion interface, selective membrane fabrication problems, cost, scale up.

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Study and Application of CO_2 Separation Membranes

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1 Introduction

CO_2 separations, mainly from flue gas to reduce warm house effects and raw natural gas to upgrade its quality, are directly related with both environment and energy that have been thought as two key issues human being will face in the new century. Thus study of CO_2 capture and storage has attracted worldwide interests. Currently solvent absorption is still the most successful and widely applied method for CO_2 removal, while usually this process needs high capital investment; regeneration of solvent also requires high temperature leading to large energy consumption. Compared with solvent absorption, separation of CO_2 from a mixture by membrane technology has obvious advantages e. g. : simple process, easy to scale up, no phase change (low energy cost) and environment friendly. We have been focusing on CO_2 separation membrane research for long time and currently three research directions are being explored in this area: polyimide synthesis and membrane fabrication, MOFs containing mixed matrix membrane fabrication and membrane absorption with PTFE membrane contactor.

2 Polyimide synthesis and hollow fiber fabrication[1]

2.1 Polyimide synthesis and intrinsic gas separation property

Polyimides are rigid, owning high-melting point plus glass transition temperature, and thermally stable polymers obtained by polycondensation reactions of dianhydrides with diamines. The interesting aspect of this kind materials is that their separation properties can be tailored by using different combinations of dianhydrides and diamines. A series of polyimide with different gas separation property have been synthesized in our lab. Among them a novel copolyimide (CPI) of ODPA-TMPDA/DAT has obtained more attention because of its excellent separation performance for CO_2/CH_4 separation: it owns an intrinsic CO_2 permeability of 10.82 barrer ($1\ \text{barrer} = 1\times10^{-10}\ \text{cm}^3(\text{STP})\cdot\text{cm}/(\text{cm}^2\cdot\text{s}\cdot\text{cmHg})$) with ideal selectivities of 45.5 over N_2 and 48.6 over CH_4 when tested at room temperature and 0.30 MPa. At present time 20 kg synthesis scale has been successfully realized as shown in Fig. 1.

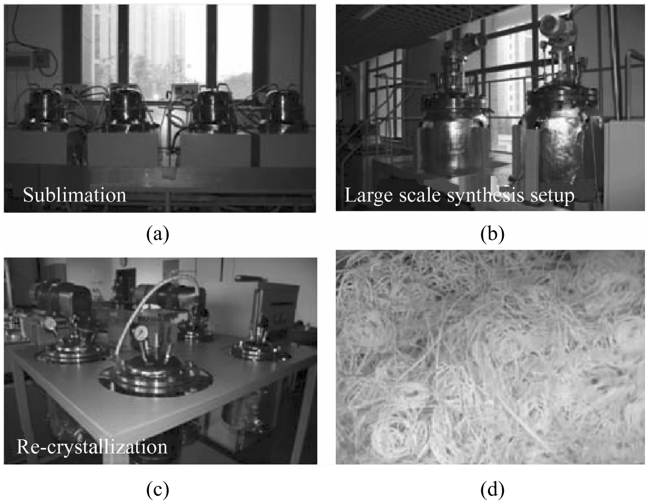


Fig. 1 Large scale PI synthesis setup (20 kg/batch)

2.2 ODPA-TMPDA/DAT copolyimide hollow fiber membrane fabrication

In brief, certain amount of dried CPI and dehydrated *N*-methyl-2-pyrrolidone (NMP) were mixed with little ethanol as a non-solvent additive. CPI was dissolved completely under N_2 protection at 60℃. Gas bubbles in the polymer solution were eliminated under vacuum before spinning. A nascent fiber was extruded through a spinneret and entered a tap water coagulant bath before an air gap of certain distance. The spinning rate was controlled by gear pump and the flow rate of bore fluid was controlled with a syringe pump. SEM observation revealed that the prepared hollow fiber membrane possessed a typical asymmetric morphology of gas separation membrane as shown in Fig. 2.

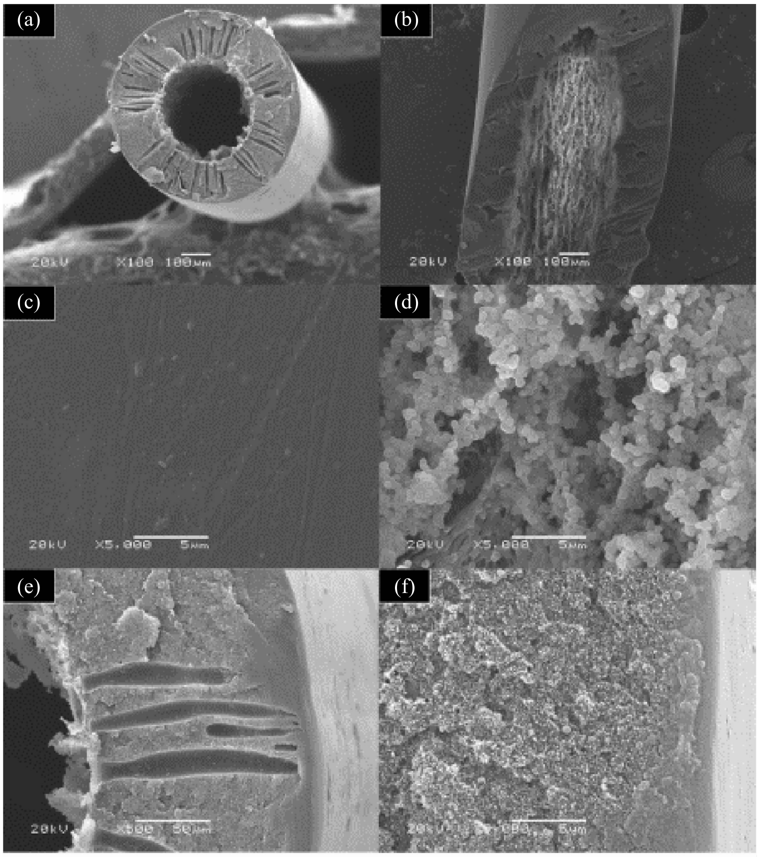


Fig. 2 SEM pictures of prepared PI HFM: (a) cross section; (b) inner surface section; (c) outer surface; (d) inner surface; (e) part of cross section; (f) outer part of cross section

2.3 Gas separation performance evaluation

2.3.1 Pure gas test

Permeation rates of pure gases including N_2, CH_4 and CO_2 were measured with prepared PI HFM at room temperature and 0.3 MPa. The test results are listed in Table 1. Prepared PI HFM had a CO_2 permeation rate as high as 39.4 GPU ($1\ \text{GPU} = 1 \times 10^{-6}\ \text{cm}^3(\text{STP})/(\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$) with an ideal selectivity of 44.7 over N_2 and 47.3 over CH_4. It is not common that such a high performance fiber could be achieved directly without any further coating step. The results proved that PI synthesized in our lab not only has an excellent gas separation performance but also can be easily fabricated in a form of defect-free HFM.

Table 1 Pure gas permeation performance of PI HFM

Fiber properties	P/l (GPU) N_2	P/l (GPU) CH_4	P/l (GPU) CO_2	Selectivity CO_2/N_2	Selectivity CO_2/CH_4
Value	0.88	0.83	39.4	44.7	47.3

2.3.2 Plasticization pressure test

Plasticization means when membrane is facing extremely high CO_2 partial pressure, large amount of CO_2 will dissolve in membrane material thus lead to a sharp increase of gas permeance. As shown in Fig. 3, CO_2 permeance under different pressure was measured and the results showed that within low pressure range from 0.30 MPa to 2.25 MPa, CO_2 permeance in CPI HFM was relatively stable (around 40 -50 GPU). Continued pressure increase led to a sharp CO_2 permeance increase to about 103 GPU at 3.45 MPa. When tested at 5.1 MPa, we saw an extremely high CO_2 permeance of 370 GPU that meant the currently measured CPI HFM was almost completely plasticized. Based on test results it could be determined that CPI HFM prepared in this work owns a plasticization point of 2.25 MPa. This means it can be safely used with CO_2 partial pressure not higher than 2.25 MPa.

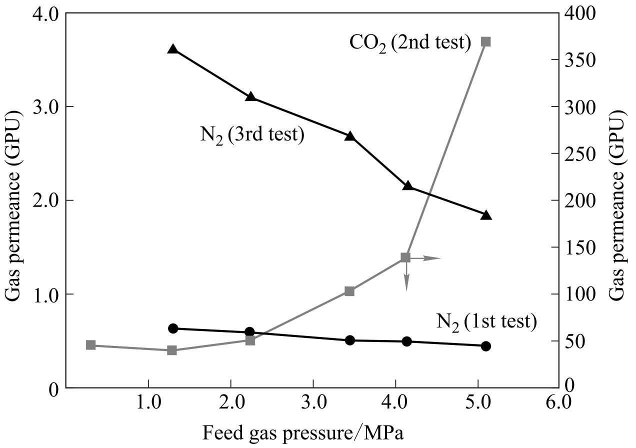
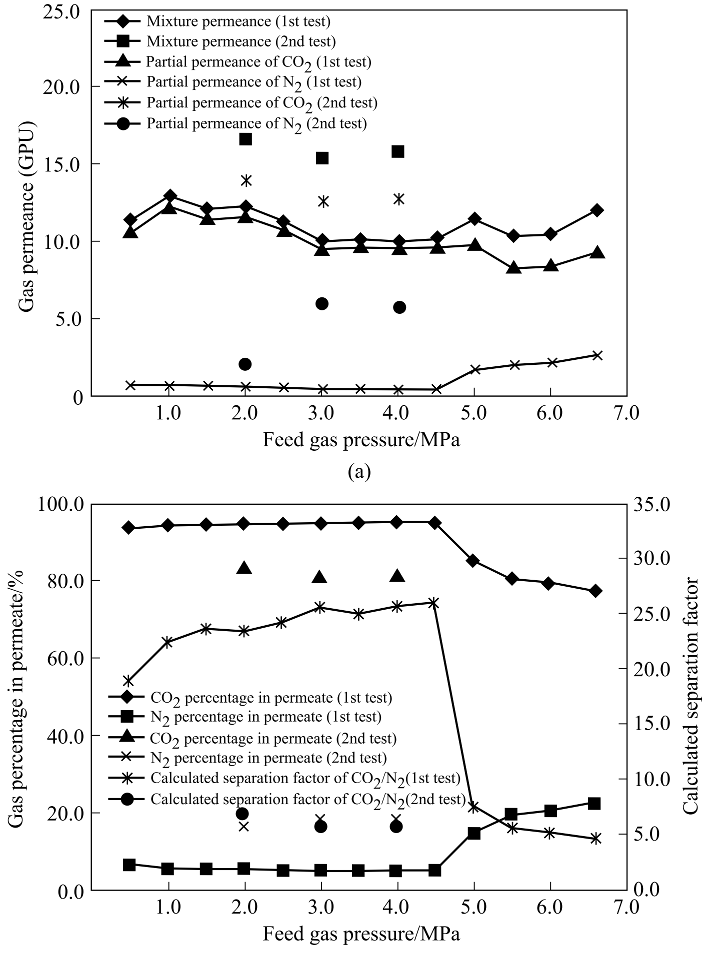


Fig. 3 Plasticization phenomena in prepared CPI HFM

2.3.3 Gas mixture pressure influence

In this section gas mixture of CO_2/N_2 (50%/50%) permeation in prepared

CPI HFM was investigated under different pressure. The detailed results are presented in Fig. 4.



(a)

(b)

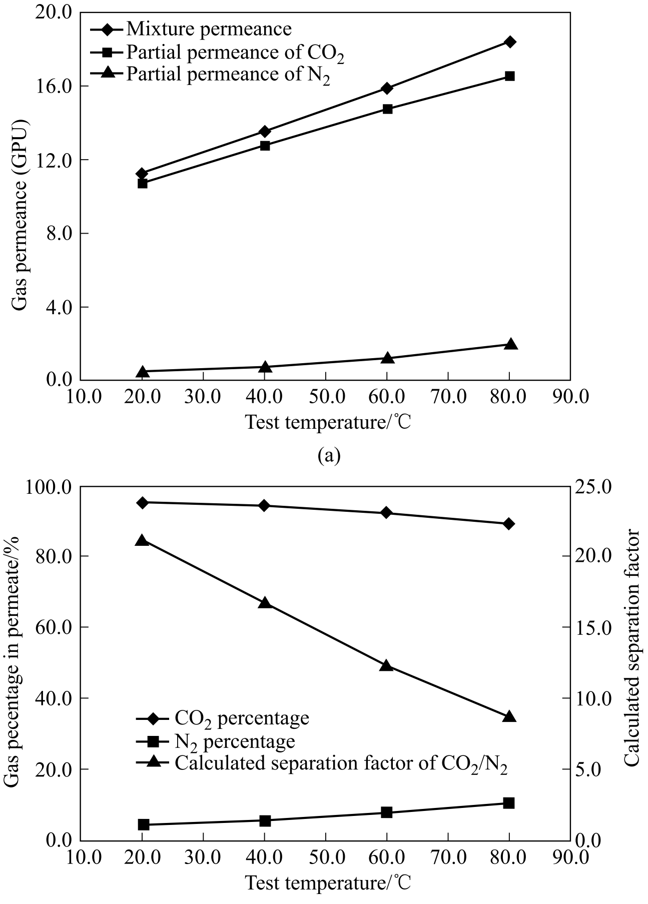
Fig. 4 Pressure influence with CO_2/N_2 (50%/50%) mixture as feed gas (room temperature): (a) gas permeance; (b) gas percentage and calculated separation factor of CO_2/N_2

Information of gas permeance is presented in Fig. 4(a). For gas mixture permeance, a small fluctuation from 10 GPU to 13 GPU could be seen within the tested feed pressure from 0.5 MPa to 6.6 MPa. GC analysis enables us finding out the exact composition of permeate. Partial permeance of N_2 was interesting: in the pressure range of 0.5 MPa to 4.5 MPa, it owned a relatively stable permeance around 0.50 GPU to 0.75 GPU; further feed gas pressure increase led to a sharp increase of N_2 permeance to around 2 GPU. We believe the sharp N_2 permeance increase revealed that fibers were facing plasticization problem because CO_2 partial pressure under this pressure has exceeded its plasticization point. Fig. 4 (b) supplies the information of gas composition in permeate and the calculated separation factor of CO_2/N_2. It is clearly seen that under feed pressure up to 4.5 MPa, feed pressure increase slightly facilitated CPI HFM's separation performance. CO_2 percentage in permeate showed an increase from 93.3% to 95.1%. Unfortunately continued gas mixture pressure increase brought a sharp decrease of CO_2 percentage in permeate, namely, from 85.1% of 5.0 MPa to 77.4% of 6.6 MPa caused by plasticization as explained above. In term of calculated separation factor of CO_2/N_2, before plasticization the CPI HFM showed a separation factor in the range of 19 – 26; and plasticization terribly degraded the separation factor of CO_2/N_2 to as low as 5.9 – 6.9 that was maintained during the second time test.

2.3.4 Operation temperature influence

Gas permeation in polymeric membranes can be perfectly described by solution-diffusion mechanism and gas permeation in polymeric membrane will be influenced greatly by the operation temperature. In this section effect of operation temperature on gas separation performance of prepared CPI HFM was investigated and the results are presented in Fig. 5. Gas mixture of CO_2/N_2 (50%/50%) was used as the sample. Tests were carried out with a feed pressure 3.0 MPa and temperature range applied was from 20 to 80℃.

From Fig. 5 (a) it is clearly seen that temperature enhanced gas permeation in prepared CPI HFM obviously. We saw an almost linear gas mixture permeance increase with test temperatures. In terms of partial permeance for CO_2 and N_2, both showed obvious increase with operation temperature but definitely CO_2 made a dominant contribution. Similar as the trade off effect between gas permeability and selectivity for polymeric membranes, though temperature increase facilitated gas permeance, unfortunately at the same time it obviously changed the gas composition of permeate in an undesired way as shown in Fig. 5 (b). At 20℃, CO_2 concentration in permeate was as high as 95.5%; and continued temperature increase to 40℃ and 60℃ brought relatively lower CO_2 percentages in permeate as 94.4% and 92.5% respectively; at the highest operation temperature of 80℃, CO_2 percentage in permeate dropped to 89.7% that was much lower than 95.5% of 20℃. In term of calculated separation factor, we saw obvious selectivity degradation with temperature increase. What should be pointed out here is that the prepared CPI HFM could withstand severe operation temperature as high as 80℃. This could be concluded as an additional advantage of our in-house synthesized ODPA-TMPDA/DAT CPI.



(a)

(b)

Fig. 5 Test temperature influence with CO_2/N_2 (50%/50%) mixture as feed gas (3.0 MPa): (a) gas permeance; (b) gas percentage and calculated separation factor of CO_2/N_2

2.3.5 Released gas flowrate influence

In this section gas mixture of CO_2/CH_4 (10%/90%) was used as sample and all measurements were carried out at room temperature with a fixed feed pressure of 3.0 MPa. Test results are shown in Figure 6. In term of gas mixture permeance as shown in Fig. 6(a), higher released flowrate obviously facilitated gas permeation in CPI HFM. When released gas flowrate increased from 0.24 to 1.91 cm^3 (STP)/s (1.37 to 8.33 times of the corresponding permeate flowrate), gas mixture permeance increased from 1.3 to 1.7 GPU. Further observation found that CO_2 permeance increase played an absolute dominating role for total gas permeance increase. On the other side, as shown in Fig. 6 (b), within the same released gas flowrate increase range, CH_4 percentage in released gas decreased from 99.5% to 94.6%; and CO_2 percentage in permeate increased from 44.8% to 60.6% obviously. In term of CO_2 recovery, we saw a sharp decrease from 98.4% to 57.3% by increasing the released gas flowrate. What should be specially mentioned is that 4 times of permeate flowrate could be released from shell side as natural gas product with CO_2 percentage still less than 2% meeting strict pipeline specifications.

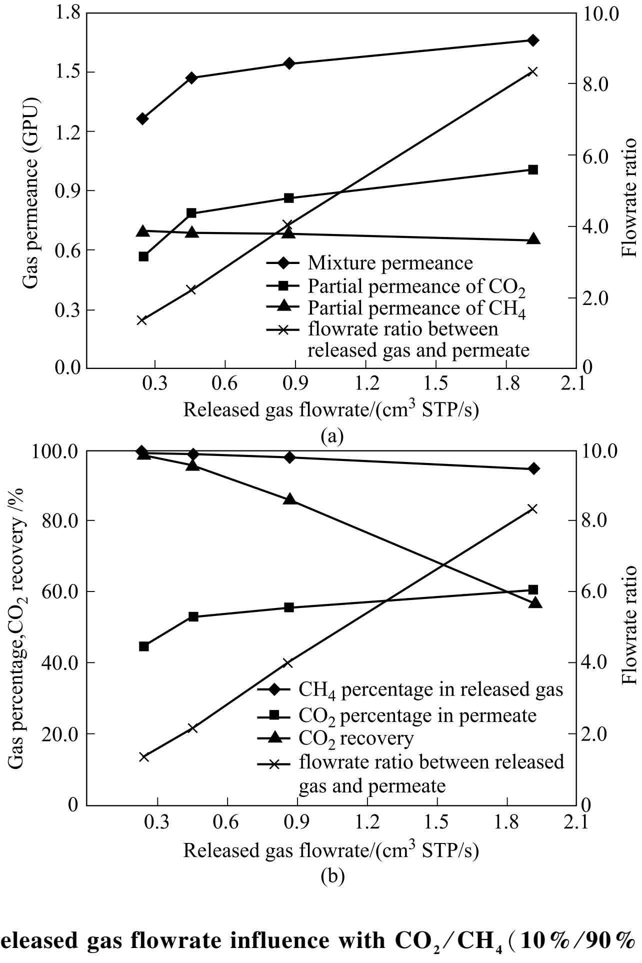


Fig. 6 Released gas flowrate influence with CO_2/CH_4 (10%/90%) mixture as feed gas (room temperature, 3.0 MPa): (a) gas permeance; (b) gas percentage and CO_2 recovery

Gas mixture test results proved that the prepared ODPA-TMPDA/DAT CPI HFM showed promising application potential for CO_2 separation from natural gas and will be able to compete with currently applied commercial hollow fiber membranes if it can generate stable separation performance after long duration operation that will be carried out in our continued research.

2.3.6 Additional information

In 2006 we successfully designed and developed a setup of CO_2 separation from natural gas by membrane technology as shown in Fig. 7. It has a treating capacity of 40 000 Nm^3/d and located in Hualian oil cell of Fushan Oil Field. This setup has been steadily running for several years since then with satisfied separation performance.

(a) (b) (c)

Fig. 7 Setup of CO_2 separation from natural gas by membrane technology developed by DICP

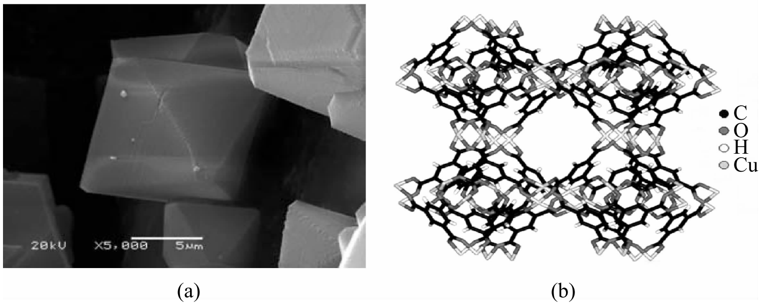
3 MOFs containing mixed matrix membrane fabrication[2]

3.1 Brief introduction

Organic polymer is the dominant material of commercial gas membranes used in industry. However, the further applications of organic membranes are restricted by Robeson upper bound. Therefore, the inorganic membranes such as zeolite, carbon, and silica membranes, have received more attentions in recent years. But there are still some problems for the industrial application of the inorganic membranes, including fragility, surface defects, complex preparation process, high cost, and low filling density. Consequently, the mixed matrix membranes (MMMs), as a new type of membranes, which are prepared by adding inorganic particles into the polymeric matrix, combine the advantages of organic membranes and inorganic membranes, and have the potential to show easy operability as well as good gas separation property, has grown up to be a very important research area. MOFs, which are inorganic-organic hybrid materials composed of metals and organic ligands, have large surface areas, tunable pore sizes, and strong adsorption for special gases, thus are ideal additives for MMMs.

3.2 MOFs synthesis and property

MOFs of $Cu_3(BTC)_2$ was synthesized by a modified synthesis process. Its SEM picture and molecule structure are shown in Fig. 8.



(a) (b)

Fig. 8 SEM picture (a) and molecule structure (b) of $Cu_3(BTC)_2$

Continued characterization by nitrogen sorption-desorption isotherm revealed that it has a BET surface area of 1439 cm^2/g and pore volume of 0.612 cm^3/g, and possesses a decomposition temperature higher than 300℃.

3.3 Mixed matrix membrane fabrication and gas separation performance

$Cu_3(BTC)_2$ and Ultem® 1000 polymer were dehydrated at 110℃ for 24 h before membrane fabrication. The $Cu_3(BTC)_2$ powder was dispersed into DMAc with mechanical agitation to obtain fine solution. Ultem® 1000 polymer was dissolved in DMAc to form homogeneous solution. The $Cu_3(BTC)_2$/Ultem® 1000 mixed solution was cast onto a clean glass substrate and heated to volatilize the solvent. The formed membranes were peeled from the glass and further dried in vacuum oven at the temperature range of 80 – 190℃. The pure polymer membrane was fabricated according to the similar process. The SEM picture of fabricated mixed matrix membrane (with 20 wt% MOFs loading) is shown in Fig. 9 and its gas separation performance measured at 35℃ and 3.5 atm are presented in Fig. 10. From cross-section SEM images of the C/U MMMs it can be seen that $Cu_3(BTC)_2$ did not aggregate and disperse uniformly throughout the polymer matrix. The $Cu_3(BTC)_2$ particles were wetted quite well by the polymer and no interfacial defect is found around the $Cu_3(BTC)_2$ particles. In term of gas separation performance, C/U MMMs showed much higher gas permeability than pure polymeric membrane and at the same time gas selectivity was almost remaining unchanged.

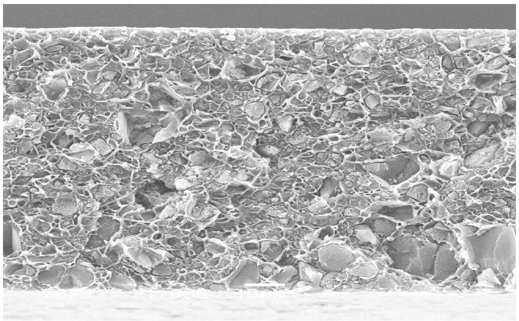
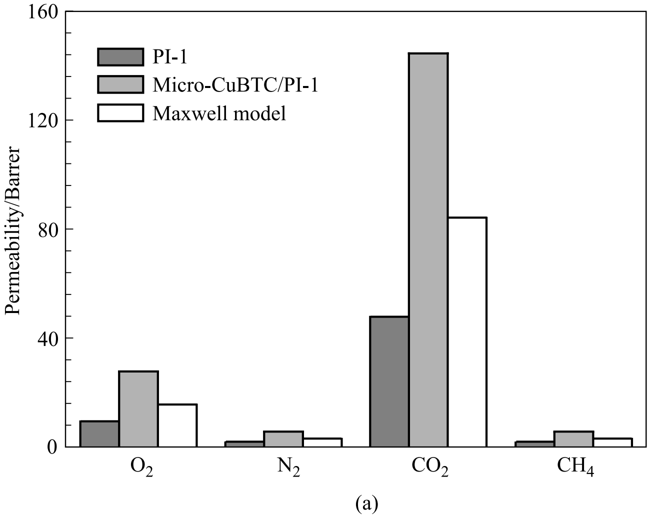
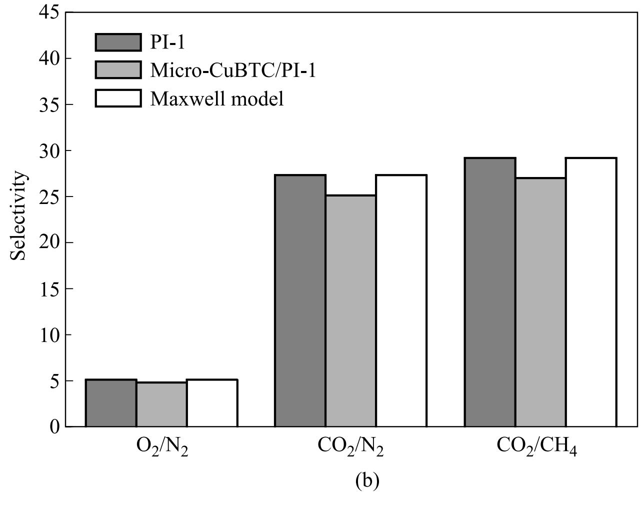


Fig. 9　SEM picture of fabricated mixed matrix membrane



(a)



(b)

Fig. 10　Gas separation performance of fabricated mixed matrix membrane

3.4 MOFs loading influence

In this section influence of MOFs loading on gas separation performance was carried out. Fig. 11(a) shows the separation properties of pure Ultem® 1000 membrane and C/U MMMs for CO_2/N_2 and CO_2/CH_4. The CO_2 permeability of the C/U MMMs increased as the $Cu_3(BTC)_2$ loading increased, and the selectivity of the C/U MMMs for CO_2/N_2 and CO_2/CH_4 increased or remained compared with the pure Ultem® 1000 membrane, when the $Cu_3(BTC)_2$ loading of the C/U MMMs was no more than 30% (mass fraction). It can be concluded that the $Cu_3(BTC)_2$ particles were wetted well by the polymer and there was no non-selective interfacial defect in the C/U MMMs. When the loading increased to 35% (mass fraction), the CO_2 permeability exhibited an obvious increase: the permeability of CO_2 increased by 262% compared with the pure Ultem® 1000

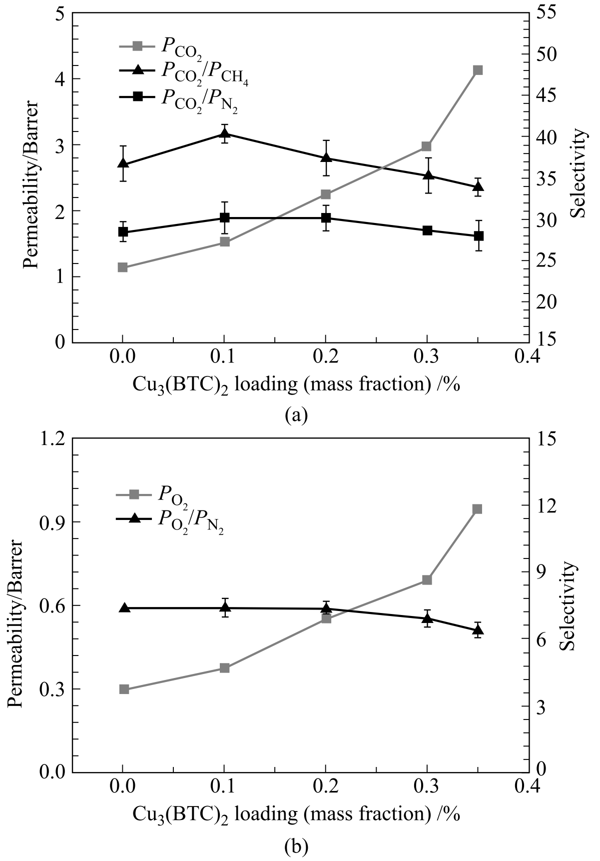


Fig. 11 CO_2, O_2 permeabilities and ideal selectivities ((a) CO_2/N_2 and CO_2/CH_4, and (b) O_2/N_2) of pure Ultem® 1000 membrane and C/U MMMs with different loadings at 35℃ and 0.35 MPa

membrane, while the selectivity for CO_2/N_2 was unchanged and for CO_2/CH_4 decreased slightly (about 10%). The separation property for O_2/N_2 (Fig. 11 (b)) was also improved as the $Cu_3(BTC)_2$ was added, the O_2 permeability increased with slight decrease of the O_2/N_2 selectivity.

In brief conclusion it has been proven that with polyimide as base membrane material the addition of MOFs can greatly enhance its gas permeation performance without any obvious selectivity loss. Currently attempts to fabricate a hollow fiber hybrid membrane with optimized morphology and enhanced gas separation performance are being carried out.

4 Membrane absorption with PTFE membrane contactor[3]

4.1 Brief introduction

Recently research on combination of membrane with other traditional separation methods is attracting more attentions and among them membrane absorption has stepped out as a promising technology. Membrane absorption has advantages of high selectivity and large CO_2 absorption capacity. Compared with traditional absorption tower, it possesses extra advantages in case of off-shore application because of its much compacted setup and better operation flexibility. A typical sketch for membrane absorption is given in Fig. 12. Flowing feed gas and absorbent was separated by porous hollow fiber membranes in a contactor. What should be pointed out is that micro-pores of hollow fiber must be occupied by feed gas otherwise if it was wetted gas absorption capability of membrane absorption system will be deteriorated terribly.

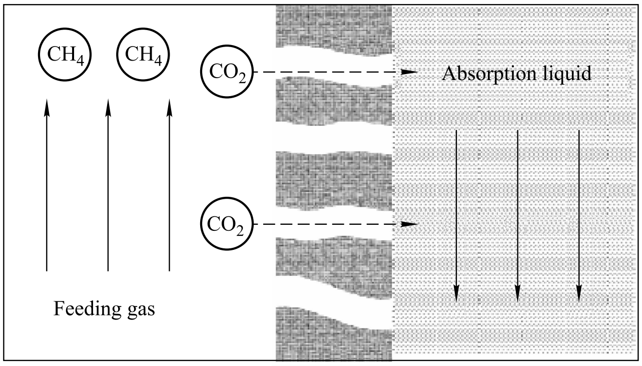
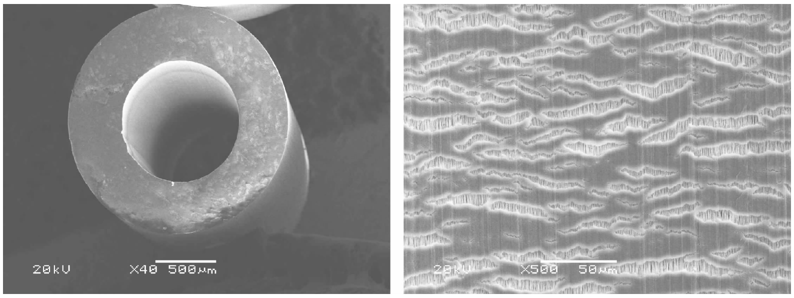


Fig. 12 Membrane absorption system sketch

4.2 PTFE hollow fiber membrane fabrication and morphology

In order to avoid micro-pore wetting, a proper choice of membrane material and careful manipulation of porous morphology are very important. In other words, the methods for breakthrough pressure improvement mainly include increasing material hydrophobicity, reducing pore size and selecting absorbent with larger surface tension. PTFE is a superior polymer with excellent chemical stability and mechanical strength. With a novel self-developed and patented fabrication process, PTFE hollow fiber membrane with finely controlled porous structure has been successfully prepared as shown in Fig. 13. The membrane has an average pore diameter around 0.1 – 0.4 μm and porosity as high as 60%.



(a) (b)

Fig. 13 SEM picture of PTFE hollow fiber membrane

4.3 Membrane contactor test and evaluation

A simple membrane absorption test system sketch is presented in Fig. 14. In general, feed gas mixture with certain pressure was introduced to tube or shell side of membrane contactor, and absorbent was counter-flowing on the other side with a little bit higher pressure for bubbling avoidance. Gas and absorbent contacted with each other at the outer surface of micro-pores and CO_2 in gas mixture was selectively absorbed. An exactly controlled gas release flowrate was maintained at feed side that was the purified product gas with much lower CO_2 percentage. Gas mixture composition was analyzed by GC. CO_2/CH_4 (10%/90%) mixture was used as feed gas.

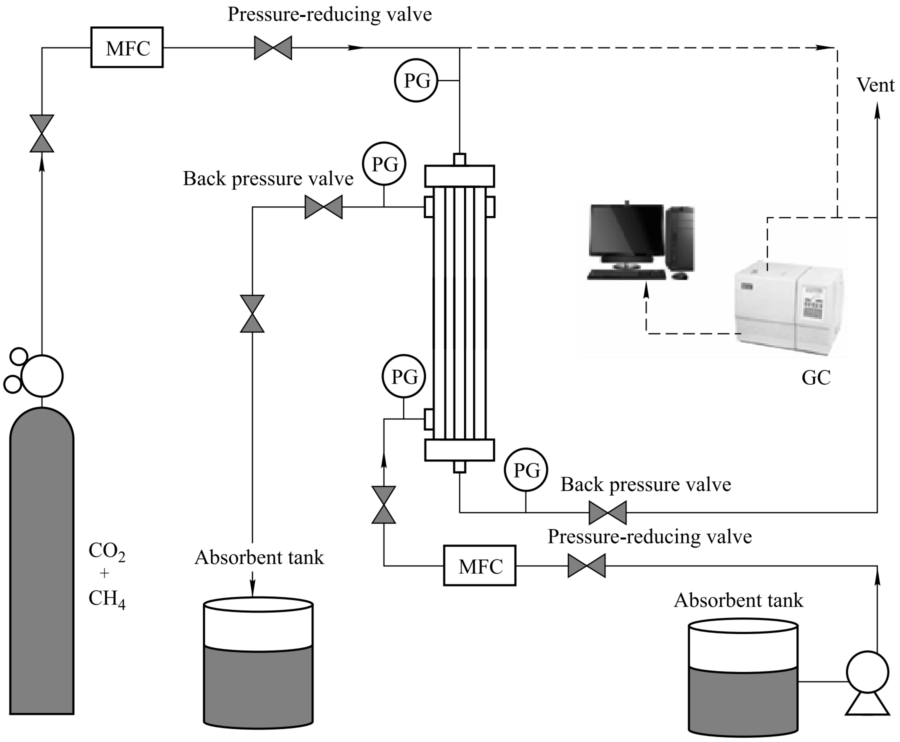
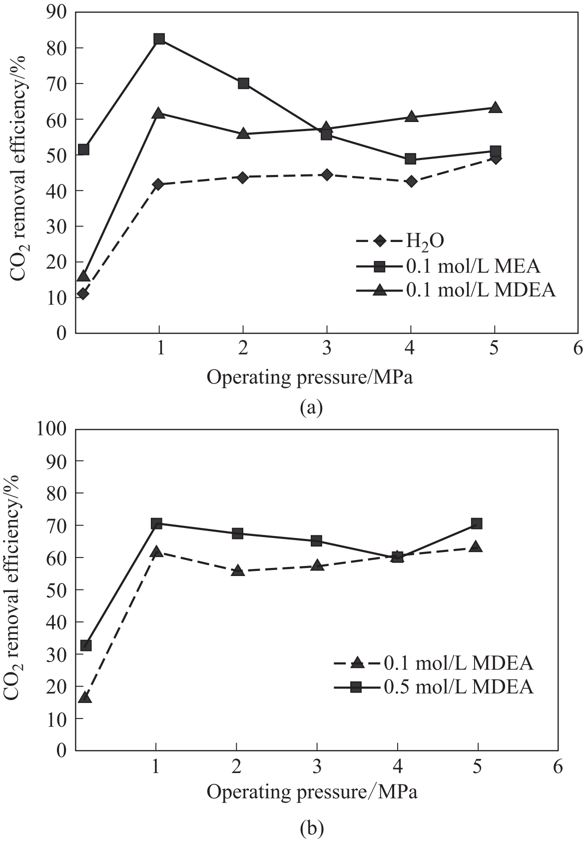


Fig. 14 Membrane absorption test system

4.3.1 Influence of feed pressure and MDEA concentration in absorbent

In this section influence of feed pressure and MDEA concentration in absorbent was systematically investigated and the results are presented in Fig. 15. All tests were carried out at room temperature with a feed gas flowrate of 0.8 L/min and absorbent flowrate of 0.1 kg/min.

From Fig. 15 it can be clearly seen that operation pressure brought obviously different effect to CO_2 removal efficiency. The starting low pressure was an exception since at this point all CO_2 removal efficiency was quite low when water and MDEA solution were applied as absorbent. Continued pressure increase did not show too much influence for these two absorbents. MEA solution presented a highest CO_2 removal efficiency of 82% when running at 1 MPa. In term of MDEA concentration influence, the results showed that 0.5 mol/L MDEA solution possessed relatively better CO_2 removal efficiency than 0.1 mol/L MDEA solution. This can be easily explained since higher MDEA in solution means more available reactant for CO_2 absorption.



(a)

(b)

Fig. 15 Influence of feed pressure and MDEA concentration in absorbent

4.3.2 Influence of operation mode

In this section two different operation modes (feed gas was kept either on shell side or tube side) were applied to find out if there was any change of absorption effect. Absorbent of 0.5 mol/L MDEA solution was selected and other operation conditions were exactly same as above. The results are presented in Fig. 16 and generally speaking gas in tube side brought a better

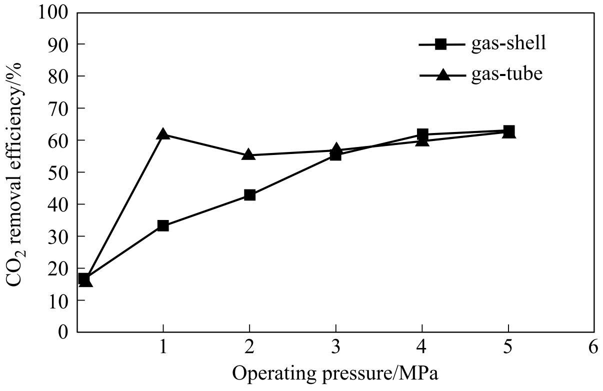


Fig. 16 Influence of feed operation mode

CO_2 removal efficiency. We believe a proper explanation of the phenomena must consider the configuration of membrane contactor including fiber packing density, shell side flowing distribution design, etc. We strongly believe a higher CO_2 removal efficiency means a better CO_2 contacting opportunity with absorbent in the contactor, in other words, less dead volume on feed gas side.

4.3.3 Influence of feed gas and absorbent flowrate

In this section a detailed investigation of feed gas and absorbent flowrate influence was carried out at room temperature and 1 MPa. Feed gas flowrate of 0.8 L/min was maintained during absorbent flowrate effect test and absorbent flowrate of 0.1 kg/min was maintained during feed gas flowrate effect test. The results are shown in Fig. 17.

First we noticed that among all three absorbents applied, pure water showed the poorest absorption capability and 0.1 mol/L MEA solution brought a best absorption effect. Gas flow rate increase obviously enhanced the overall CO_2 flux since higher feed gas flowrate means gas composition in tube side will have a higher CO_2 concentration thus brought more absorption and higher flux. Unfortunately the trade-off effect between released gas flowrate and separation performance determined that higher feed gas flowrate inevitably led to a decrease of CO_2 removal efficiency. Compared with it, an increase of absorbent flowrate increase brought positive effect to both overall CO_2 flux and CO_2 removal efficiency. This should be quite reasonable since higher absorbent flowrate on shell side means liquid at this side could be replaced more quickly thus absorbent could be much “fresher” and possess better CO_2 absorption capability. This is why we see enhanced effects on both terms. What should be pointed out here is that a drawback of larger liquid flowrate will be more energy consumption in order to drive this highly viscous liquid flowing on shell side.

4.4 Additional information of pilot system

As we can see from all above test PTFE membrane contactor for CO_2 removal from raw natural gas has been systematically investigated and the results are quite encouraging. Currently cooperated with a foreign company, a

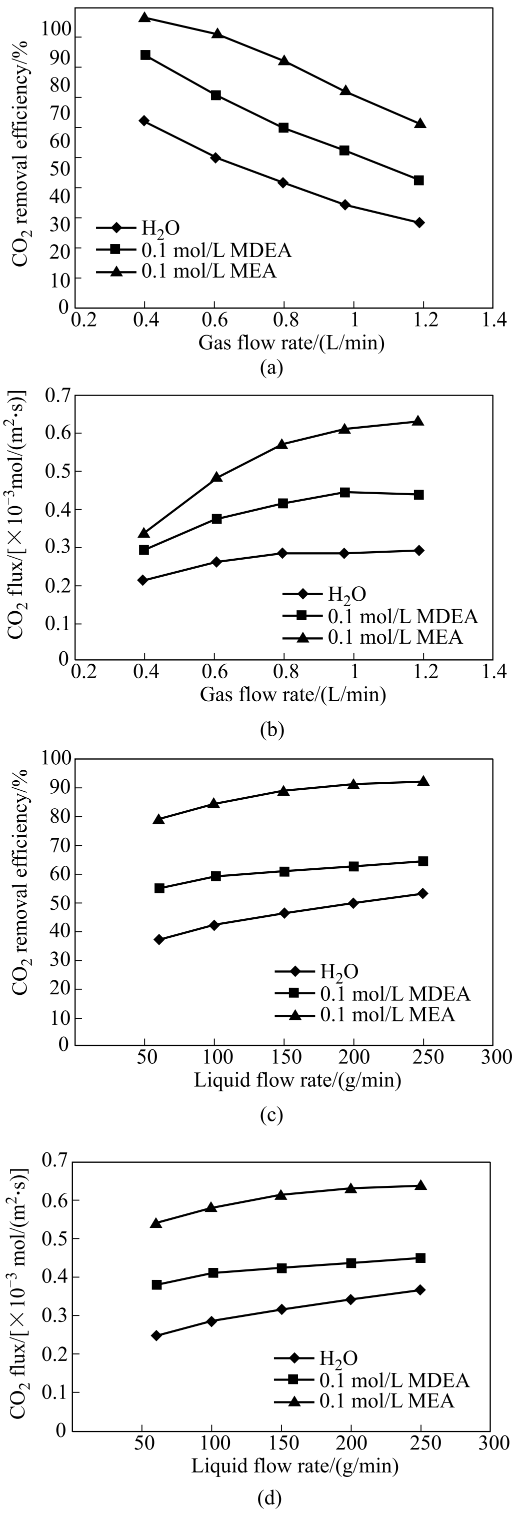


Fig. 17 Influence of feed gas flowrate and liquid absorbent flowrate

pilot membrane contactor system is being assembled which will be tested abroad soon in this year. The detailed setup is presented in Fig. 18.

Fig. 18 A pilot setup of PTFE membrane contactor system

In this paper we briefly introduced our research in the field of CO_2 separation and storage by membrane related technology, and three areas were mainly mentioned, namely polyimide synthesis and membrane fabrication, mixed matrix membrane preparation and membrane absorption process. Though mixed matrix membrane is still at a stage of scientific exploration, the other two, from the point of our view based on research progress, we strongly believe their practical application could be successfully realized.

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Prof. Cao is member of several membrane-related organizations in China such as Membrane Industry Society Expert Committee, National Separation Membrane Standardization Technical Committee, and National Scientific Key Project Expert Committee. He is also serving as editor for journals of *Water treatment technology* and *Membrane science and technology*.

Researches in his group are mainly focusing on CO_2 separation fields including synthesis of polymeric membrane materials (especially polyimide) for CO_2 separation; membrane absorption process for the removal of CO_2 from low-quality natural gas with porous PTFE hollow fiber membrane; MOFs/polyimide hybrid membrane preparation for CO_2 removal. His group is also active in the research of liquid treatment membranes such as MF, NF, etc.

As prime investigator, Prof. Cao has successfully completed many national and international collaborative projects in membrane research area. His research achievements, especially in CO_2 separation area, have attracted wide attention and brought him several important prizes in membrane research field of China.

Anti-protein-fouling Strategy in Microfiltration and Ultrafiltration Membranes：A Mini-review Focusing on “Grafting from” Polymerization of Zwitterions

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Abstract：The protein-fouling on the membrane that is regarded as the first step of membrane fouling limits the wide application of membrane technologies, such as microfiltration (MF) and ultrafiltration (UF). Zwitterionic materials form the hydration layer by electrostatic interaction and hydrogen bond, contributing to the stable anti-protein-fouling property. “grafting from” polymerization that the zwitterionic monomers can be polymerized using an initiation reaction on the membrane surface has been regarded as a simple, useful, and versatile approach to the anti-fouling modification of membrane. This strategy provides controllable introduction of graft chains with a high density and a long-term chemical stability assured by covalent attachment of graft chains. This article presents a mini-review of recent progress on the grafting polymerization of zwitterionic monomers from the surface of polymer membrane, including the introduction of zwitterions and the methods of grafting polymerizations. Various approaches such as free radical grafting polymerization, photo-induced grafting polymerization, plasma-induced grafting polymerization and combined methods were compared on uniformity and grafting amount of zwitterionic polymer, relative flux of modified membrane, simplicity and environment pollution of operation, and cost of technique.

Keywords: anti-protein-fouling strategy; MF/UF membrane; grafting polymerization; zwitterion

1 Introduction

It has been acknowledged that membrane separation has low energy consumption, ease of continuous operation and environmental-friendly characteristics, and is a technology of significant note, not only for wastewater treatment but also for agro-food and biomedical markets[1-8]. Microfiltration (MF) and ultrafiltration (UF) are the pressure-driven membrane processes to retain macromolecules or high molecular-weight compounds, excluding bacteria and viruses[9], which have been extensively used in membrane technology[10,11]. However, the main drawback of this technology is membrane fouling, which often limits its wide applications throughout the world[10,12].

Studies on fouling of membranes have shown that protein adsorption on membrane surfaces has been recognized as the initial step of membrane fouling in numerous practical applications, followed by platelet adhesion or bacterial biofilm formation[5,11,13,14]. It results in deterioration of membrane performance[15]. Thus, protein adsorption is one of the most important phenomena in determination of the biocompatibility of membrane[16]. In general, proteins adsorb onto a surface of membrane within a few minutes when the membrane contacts protein-containing liquids such as blood, plasma, and bio-medical wastewater, etc[16]. One of the crucial factors impacting protein adsorption is the surface property of membranes because it determines the interaction between a protein molecule and the membrane materials which plays an important role in the extent of membrane fouling[11,15]. Therefore, the primary target for inhibiting or preventing protein adsorption is to develop super-low fouling or anti-fouling surfaces[11,14,17,18].

Most of the commercial membranes for MF/UF processes are made from hydrophobic polymers due to the high thermal, chemical and mechanical stability[15,19-22]. However, because of the high hydrophobicity, these materials are prone to adsorption of protein[23,24]. The construction of a hydrophilic surface has been believed to reduce protein adsorption effectively[16], due to the fact that the hydrophilic surface attracts so much water that adsorption of proteins is reduced and even prevented[15]. Therefore, surface modification of membranes with hydrophilic or a water-soluble polymer chain has to be investigated[16]. In the past decades, a promising zwitterionic non-fouling material has been found[25,26]. The materials containing zwitterionic phosphorylcholine (PC) head-groups have become the representatives to create non-bio-fouling surfaces from 1990s, but PC based monomers, such as 2-methacryloyloxy-ethyl phosphorylcholine (MPC), are moisture sensitive and not easy to be synthesized[27]. Recently, sulfobetaine having a kind of zwitterionic material with a similar structure of PC has been proved a biocompatible material with an excellent protein adsorption-resistant property. Sulfobetaine surfaces are capable of binding a significant amount of water molecules because of the formation of a hydration layer via electrostatic interaction and hydrogen bond[28]. Therefore, sulfobetaine can lead to a strong repulsive force to protein at specific separation distances and make the protein contact with the surface in a reverse manner without a significant conformation change[27,29,30].

During the past 5 years, researchers have confirmed the ability of sulfobetaine coatings on the surfaces of various polymer MF/UF membranes to resist protein adsorption and then significantly retard bacterial biofilm formation[4-6,27,29,31-34]. Among the surface modification techniques developed to date, "grafting from" polymerization (monomers are polymerized using an initiation reaction on the surface) has emerged as a simple, useful, and versatile approach due to the controllable introduction of graft chains with a high density and exact localization to the surface without affecting the bulk properties, and the long-term chemical stability which is assured by covalent attachment of graft chains[15,23,35].

In this paper, as the novel modified-materials, zwitterionic materials such as phosphobetaine, sulfobetaine and carboxybetaine, will be focused to enhance the anti-protein-fouling performance of MF/UF membrane. Illustrative examples of grafting polymerization of zwitterion from the formed MF/UF membrane will be discussed. Although more than one membrane parameter is influenced on the performance of MF/UF membrane, which not all may be advantageous, we will mainly focus on decrease in protein adsorption of MF/UF membranes. The methods are compared and rated on their applicability for surface modification of MF/UF membranes.

2 Zwitterions and their property

2.1 Zwitterions

Zwitterions, which bear both anionic and cationic groups in the same monomer unit, have proved promising materials for separation membranes[36]. The typical anionic group for zwitterion is quaternary ammomium group, while the cationic groups include the sulfonic, carboxylic and phosphoric groups. In the past 20 years, zwitterions such as phosphobetaine and sulfobetaine are widely applied in modification of polymer membranes, which not only facilitate the water transport through the membranes, but also improve their antifouling properties[37,38]. The monomers of phosphobetaine and sulfobetaine, such as 2-methacry-loyloxyethyl phosphorylcholine(MPC) and sulfobetaine methacrylate (SBMA), respectively, have the similar structure, as shown in Fig. 1.

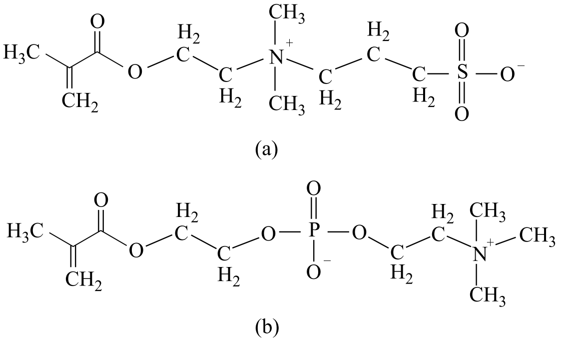

Fig. 1 Chemical structural formula of zwitterions used in the anti-fouling modification of polymer membrane surface: (a) 2-methacryloyloxyethyl phosphorylcholine (MPC); (b) sulfobetainemethacrylate (SBMA)

It is regarded that the biomembrane surface is the best surface for smooth interaction with proteins and cells[19]. In 1972, Singer and Nicolson[39] proposed a model of the structure of a biomembrane, which is well-known as the fluid-mosaic model. According to this model, phospholipids are asymmetry and arranged in a bilayer structure. The negatively charged phospholipids such as phosphatidylserine are predominantly on the inner, cytoplasmic side of the membrane, whereas the neutral, zwitterionic MPC lipids such as phosphatidylcholines are located in the outer leaflet. The MPC surface provides an inert surface for biological reactions of proteins to occur smoothly on the membrane[19]. It provides that phosphobetaine with MPC headgroups is naturally protein resistant in the outside layer of cell membranes[40]. However, the MPC is moisture sensitive and not easy to synthesize and handle, which limits its application in practical fields[41,42].

Poly (sulfobetaine) is reported to exhibit a zwitterionic structure and whole-neutral electricity similar to that of poly (phosphobetaine)-based materials[11,30], which results in the similar protein resistant. It has a very small disturbing effect on the structure of the hydrogen-bonding network of water molecules in dilute solutions because of the intra- and inter-tether proximity between the oppositely charged groups[42,43]. Sulfobetaine monomer is easier to synthesize and handle but SBMA polymers were thought to be less fouling-resistant than PC polymers[44]. In the past 10 years, preparation and characterization of sulfobetaine polymers have been extensively studied[11,27,29,30,33,38,45-48]. Additionally, zwitterionic polymers based on carboxybetaine monomer units not only demonstrate the good resistance to nonspecific protein adsorption and short-term bacterial adhesion but also has abundant functional groups convenient for the immobilization of ligands[49,50]. It has been found that zwitterions in the sulfobetaine polymers remain in their diionic form over a broader pH range than the carboxybetaine polymers[43,49,50-53].

2.2 Resistance to protein adsorption

Ostuni[54] find that the surfaces resisting the adsorption of proteins exhibit four molecular-level characteristics: ① hydrophilic; ② with hydrogen-bond acceptors; ③ without hydrogen-bond donors; ④ overall electrical neutrality, which proves the hypothesis that the interaction of the surface with water is of great importance to the resistance to adsorption of proteins[54,55]. Zwitterionic polymer forms a hydration layer via electrostatic interactions and does not significantly disturb the H-bonded network structure of the water molecules[42,55]. It is expected that zwitterions are capable of binding a significant amount of water molecules and form a hydration layer near the surface which forms a physical and energetic barrier to prevent the adsorption of protein[17]. The amount of free water molecular and the change in structure of protein molecular near the surface of zwitterionic polymer represent its water binding capacity, which plays an essential role in the resistance against adsorption of proteins[56]. Besides, the resistance of poly (zwitterionic) materials to protein adsorption is tightly correlated with the uniformity of charge distribution and the charge neutrality of two opposite charge moieties[17,25]. By using both molecular mechanics and molecular dynamics simulation techniques, it can be found that balanced charge, minimized dipole and close packing density are the key factors for the non-fouling behavior of zwitterions[42,55].

Adsorption of proteins consists of two parts: the formation of an interface between the surface and the protein with release of water and the reorganization of protein on adsorption[54]. The structure of zwitterionic chains will impact the interaction among protein, water and zwitterionic groups. The increase in the alkyl groups of zwitterionic chains may forces the anionic and cationic moieties further apart, which is favorable to the hydration and the counteraction of electrostriction effect[43,57]. Additionally, the high grafting amount and long chain length of MPC polymer contribute to a dramatic reduction in protein adsorption[58]. However, lots of researchers found that the hydration and hydrophilicity of zwitterionic polymer show a “sudden” change rather than a slow increase with increasing thickness or grafting amount[59]. It was found that the thinner polySBMA brushes (<50 nm) show a hydrophilic surface, while thicker brushes (>100 nm) have a more or less linear increase in hydrophobicity with increasing brush thickness[57]. On the other hand, the shorter polySBMA brushes may not form coatings dense enough to resist protein adsorption whereas the longer polymer brushes show as high protein adsorption, which results in a minimal value of protein adsorption at 62 nm in film thickness of polySBMA[58]. All of these may be attributed to the reversible self-association in zwitterionic polymers, including non-association, inter-chain association (between zwitterionic groups on the same chains), and intra-chain association (between neighboring polymer chains)[57,59], as shown in Fig. 2. For the thinner poly(zwitterion) brushes, the steric factors related to the polymer backbone and the hydrated charged groups hinder the formation of ion pairs[57]. There is non-association in zwitterionic polymer, which makes the polymer hydrophilic and swollen. Increase in the thickness of zwitterionic chains results in the enhancement of resistance to protein adsorption. For the thicker poly(zwitterion) brushes, the probability of ion-pairing events or self-association becomes higher, which leads to an increase in polymer volume fraction and a decrease in dielectric constant. Thus, the self-association becomes more favorable and leads to a supercollapsed state[60]. Under such condition, the hydrophilic groups like sulfonate groups and quaternary ammonium groups may hide inside the collapsed chains and the polymer shows hydrophobic property. Therefore, zwitterionic polymer has a wettability transition occurring at precise thicknesses, below which all brushes showed the same hydrophilic character and above which the brushes were more or less equally hydrophobic[59].

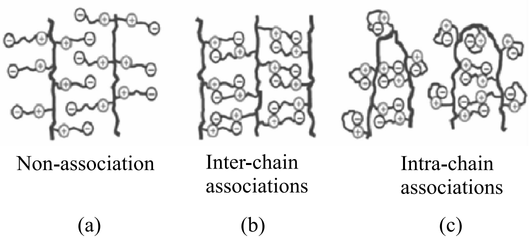

Fig. 2 Different conformational states of polymers in brushes ranging from fully hydrated, non-associated chains to collapsed chains with inter-chain and intra-chain associations

3 Grafting polymerization of zwitterions from MF/UF membrane

Surface modification has been considered a useful method to improve the anti-fouling performance of membrane without destroying the bulk properties[61]. Among various methods, grafting polymerization is regarded as one of the most promising methods to modify the membrane surface through the covalent bonding interaction between the grafted chains and the membrane[20]. To introduce the zwitterionic polymer on the membrane surface via grafting polymerization, both "grafting to" and "grafting from" approaches can be employed. The former involves tethering of zwitterionic polymer chains onto surfaces by one end, which allows a precise control of grafted chain structure but is difficult to obtain dense polymer chains[23,62]. Compared to the former, the latter is more widely used for surface modification of different kinds of membranes, which shows a higher grating efficiency due to the less steric hindrance of diffusing small monomers compared to polymer chains[23]. For the surface modification with zwitterions, "grafting from" has much more choices to control the grafting degree, chain lengths and structure of zwitterionic polymer through varying different initiating means, zwitterionic monomer, concentration, temperature, polymerization time and other reaction conditions[20].

The process of "grafting from" polymerization consists of two steps: ① attachment of initiators onto surfaces; ②polymer growth from initiator sites[62]. According to the versatile initiating means, the grafting polymerization of zwitterionic monomer from the surface of membrane can be categorized as free radical grafting polymerization, photo-induced grafting polymerization, plasma-induced grafting polymerization, and combined methods. All versatile methods to modify the anti-protein-fouling performance of MF/UF membrane in the last 3 years are listed in Table 1.

3.1 Free radical grafting polymerization

3.1.1 "Living"/controlled grafting polymerization

Recently, "living"/controlled grafting polymerization has been used to graft zwitterionic polymer on a membrane surface[64]. This method shows the ease of polymerization without the strict reaction condition required for ionic polymerizations such as complete absence of water. It combines the advantage of living ionic polymerization for a better control and the versatility of free radical polymerization[20,70]. The development of "living"/controlled grafting polymerization in aqueous systems has enabled its application in the surface grafting on the membrane directly using water-borne system as the reaction medium[20].

Table 1 Grafting polymerization of zwitterions from membrane to enhance their anti-fouling performance in the last 3 years

Methods	Nascent membrane	Zwitterionic monomer	Grafting amount /(μg/cm²)	Contact angle/ (°)	Pure water flux /[L/(m² · h)]	Protein/bio-system	Flux recovery ratio/ protein adsorption
Free radical grafting polymerization	PES flat membrane[63]	MCP	–	82.90 ± 2.37 (Nascent) 46.43 ± 1.93 (Modified) after 3 s	156.3 (Nascent) 107.8 (Modified) at 0.1 MPa	1.0 mg/mL of BSA	60.6% (Nascent) 87.0% (Modified) (Flux recovery ratio)
	PSf flat membrane[64]	SBMA	≈1800	≈75 (Nascent) ≈30 (Modified)	0.020 12 (Nascent) 0.046 72 (Modified) at 1 mmHg	1.0 mg/mL of BSA	42.37% (Nascent) 98.01% (Modified) (Flux recovery ratio)
	PVDF flat membrane[33]	SBMA	608	90 (Nascent) 59 (Modified)	≈130 (Nascent) ≈115 (Modified) at 0.25 MPa	1.0 mg/mL of BSA	47.6% (Nascent) 85.1% (Modified) (Flux recovery ratio)
	PVDF hollow fiber membrane[5]	MPDSAH[a]; SBMA	247 338	75.9 (Nascent) 15 (Modified) 40 (Modified) after 100 s	1592 (Nascent) 1482 (Modified) 1365 (Modified) at 0.1 MPa	1.0 mg/mL of BSA	52.0% (Nascent) 93.4% (Modified) 92.8% (Modified) (Flux recovery ratio)
	PVDF hollow fiber membrane[6]	MPDSAH	513	87.5 ± 2.1 (Nascent) 22.1 ± 2.0 (Modified) after 5.5 s	1592 (Nascent) 1319 (Modified) at 0.1 MPa	1.0 mg/mL of BSA	52.0% (Nascent) 97.8% (Modified) (Flux recovery ratio)

Continued

Methods	Nascent membrane	Zwitterionic monomer	Grafting amount /(μg/cm^2)	Contact angle/(°)	Pure water flux /[L/(m^2·h)]	Protein/bio-system	Flux recovery ratio/ protein adsorption
Free radical grafting polymerization	Cellulose flat membrane[62]	CBMA	–	20(Modified)	–	BSA	≈ 5.8 μg/cm^2 (Nascent) ≈ 0.5 μg/cm^2 (Modified) (Protein adsorption)
	Cellulose flat membrane[14]	SBMA; MCP	–	47.64 ± 1.40 (Nascent) 21.7 ± 1.86 (Modified) 20.3 ± 1.33 (Modified)	–	Platelet-poor plasma	1.8 μg/cm^2(Nascent) <1 μg/cm^2(Modified) <1 μg/cm^2(Modified) (Protein adsorption)
	Cellulose flat membrane[32]	SBMA	≈80% (polymerization degree)	–	≈620(Nascent) ≈100(Modified) at 0.02 MPa	1.0 mg/mL of BSA	>90%(Modified) (Flux recovery ratio)
	PU flat membrane[61]	SBMA	≈4% (Grafting degree)	60 ± 2 (Nascent) 33 ± 2(Modified)	–	Human venous blood	13.5(Nascent) 35.6(Modified) (Thrombin time, TT)
	PET^b flat membrane[65]	SBMA	3 – 4.0	–	35 467(Modified) at 0.1 MPa	0.1 g/L of IgG	0.18 μg/cm^2 (Modified) (Protein adsorption)

Continued

Methods	Nascent membrane	Zwitterionic monomer	Grafting amount /(μg/cm^2)	Contact angle/ (°)	Pure water flux /[L/(m^2 · h)]	Protein/bio-system	Flux recovery ratio/ protein adsorption
Photo-initiated grafting polymerization	PES hollow fiber membrane[46]	SBMA; MPC	≈1700 μg/cm^2 ≈1670 μg/cm^2	≈90(Nascent) ≈40(Modified) ≈30(Modified)	≈550(Nascent) ≈350(Modified) ≈400(Modified) at 0.1 MPa	10^6 cells/mL of *Pseudomonas putida*	≈0.4(Nascent) ≈0.8(Modified) ≈0.9(Modified) (Flux recovery ratio)
	Woven PP fiber[66]	TM:SA^c (1:1)	≈12.5% (Grafting degree)	106(Nascent) 27(Modified)	≈ 6100 g/(m^2 · h) (Nascent) ≈ 5300 g/(m^2 · h) (Modified) at 0.1 MPa	1.0 g/L of BSA; 1.0 g/L of Lyz	91.4% (Modified) 90.2% (Modified) (Flux recovery ratio)
	PP flat membrane[27]	SBMA	≈440	145 ±4(Nascent) ≈20(Modified) after 5 s	1091(Nascent) 5250(Modified) at 0.5 MPa	1.0 g/L of BSA; 1.0 g/L of Lyz	40% (Nascent) 97% (Modified) 81% (Modified) (Flux recovery ratio)
Plasma-induced grafting polymerization	PVDF flat membrane[29]	SBMA	≈900	105(Nascent) ≈30(Modified)	–	1.0 g/L of human fibrinogen	100% (Nascent) 10% (Modified) (Protein adsorption)

Continued

Methods	Nascent membrane	Zwitterionic monomer	Grafting amount /(μg/cm^2)	Contact angle/ (°)	Pure water flux /[L/(m^2 · h)]	Protein/bio-system	Flux recovery ratio/ protein adsorption
Plasma-induced grafting polymerization	ePTFE[d] flat membrane[68]	SBMA	850	≈120(Nascent) ≈25(Modified)	–	platelet-poor plasma	100% (Nascent) 20% (Modified) (Relative protein adsorption)
	PP fibrous membrane[69]	SBMA	≈ 2400 (atmos-pheric plasma treatment)	0(Nascent) 135(Modified) for diiodomethane	–	1.0 g/L of human fibrinoge	100% (Nascent) <10% (Modified) (Relative protein adsorption)
Combined methods	PP non-woven membrane(Plasma +UV)[48]	MPDSAH	327.7 μg/cm^2	123(Nascent) ≈20(Modified) after 3 s	11 370(Nascent) 9799(Modified) at 0.1 MPa	1.0g/L of BSA	30% (Nascent) 90% (Modified) (Flux recovery ratio)
	Woven PP fiber (UV + ATRP)[11]	SBMA	≈17% (Grafting degree)	106(Nascent) ≈20(Modified)	≈6.0 kg/(m^2 · h) (Nascent) ≈5.6 kg/(m^2 · h) (Modified) at 0.1 MPa	1.0g/L of BSA	46.5% (Nascent) 91.6% (Modified) (Flux recovery ratio)

a 3-(methacryloylamino) propyl-dimethyl- (3-sulfopropyl) ammonium hydroxide (MPDSAH).

b poly(ethylene terephthalate) (PET).

c [2-(methacryloyloxy)ethyl] trimethylammonium chloride (TM); 3-sulfopropyl methacrylate potassium salt (SA).

d Expanded poly(tetrafluoroethylene) (ePTFE).

The atom transfer radical polymerization (ATRP) process developed by Prof. Krzysztof Matyjaszewski in 1994, which is well-known as one kind of "living"/controlled grafting polymerization for its versatility to monomers, mild polymerization conditions, tolerance in impurities, and the ability to synthesize well defined polymers in a controlled manner[5,6,11,62]. In recent years, surface-initiated atom transfer radical polymerization (SI-ATRP) is most widely used to graft zwitterionic chains or brushes on the membrane surface[20]. This method is able to design and tailor the graft density, chain length and chemical composition of zwitterionic polymer on membrane surface, as a result, the morphology and properties of the membrane surface can be tuned[14,64]. Moreover, compared with the conventional radical polymerization, SI-ATRP can produce more uniform and smooth poly (zwitterion) surface on membrane, which is of great significance for the anti-protein-fouling performance during the MF or UF process[20]. It is crucial to choose the suitable solvent for the poly(zwitterion) grafting on membrane surface[20]: ① it should promote the successful controlled polymerization of grafted zwitterionic chains; ② it should maintain the integrity of membrane bulk without damage or dissociation; ③ it should be environmental-friendly.

In our previous works[5], SI-ATRP was used to prepare hydrophilic PVDF hollow fiber membrane with improved anti-protein-fouling performance, in which the grafting amount of poly(sulfobetaine) was well controlled. Liu et al.[14] prepared three kinds of poly(zwitterion)-grafted cellulose membranes via SI-ATRP. All the zwitterionic monomers were polymerized from the initiator immobilized cellulose membrane surfaces in a mixture solvent of water and methanol using CuBr and bipyridine as catalysts. Their study confirmed that the poly(sulfobetaine) modified membrane surface was as effective as the poly(phosphobetaine) modified membrane surface for resisting adsorption of protein and adhesion of platelet. Yang and Ulbricht's work[65] demonstrated that polySBMA could be grafted from track-etched poly (ethylene terephthalate) (PET) membrane surface via SI-ATRP. The grafting process was well controlled by adjusting the ATRP conditions and a linear increase of degree of grafting could be achieved. The resultant membrane was potential membrane adsorber for protein purification.

For the inert membranes lacking active groups (such as fluoropolymer and polypropylene membranes), the surface modification using SI-ATRP often involves organic solvents and multi-step strategies[71]. Activator Regenerated by Electron Transfer ATRP (ARGET-ATRP), a new ATRP initiating system, is developed to facilitate solution and emulsion ATRP in aqueous media[72]. This process can tolerate excess reducing agent so that Cu(II) can be reduced to Cu(I) rapidly in the polymerization system and then catalytic polymerization ATRP monomer[73]. Thus, the reaction can be conducted in the presence of limited amounts of air[62]. For example, water/methanol and CuBr/Bpy complex could be used as the solvent and catalyst, respectively to graft the poly(sulfobetaine) from the surface of PVDF-Br membrane[5]. In aqueous media, the structure of the catalytic species is a mono-cationic complex $[Cu(I)(Bpy)_2]^+$ with a halide counterion. The ionic catalyst species in aqueous media are active enough, as a result, the addition of water in the solvent will increase the polymerization rate[11]. Yuan's group[62] performed the grafting polymerization of carboxybetaine brush from cellulose membrane via ARGET-ATRP. The results showed that the grafted cellulose membrane had improved resistance to nonspecific protein adsorption and platelet adhesion, as well as reduced hemolysis rate.

3.1.2 Physisorbed free radical grafting polymerization

Azo and peroxide initiators, such as azo-bis-isobutyrylnitrile (AIBN), are adopted as a source of radicals for grafting polymerization of vinyl and acrylic monomers on the surface of polymer membrane since they are able to attach to polymeric membrane and to be decomposed into radicals at moderate temperature[33,74]. Hu et al.[75] proposed a physisorbed free radical grafting technique to create radicals on polymer surface and then react with hydrophilic polymers. Using this technique, the sulfobetaine monomers can be covalently attached onto both the surface and the inside of membrane, and the grafting polymerization can be carried out without limitation of more complicated procedures such as high-energy reactors or intense light sources. PolySBMA was firstly grafted from the surface of PVDF membrane via physisorbed free radical grafting technique and the water contact angle decreased from 59° to 17° within 120 s was achieved at the surface of membrane with 608 μg/cm^2 of grafting amount[33].

3.1.3 Redox graft polymerization

Surface modification by redox graft polymerization using cerium ion (Ce(IV)) as initiator is another well-known method for the polymerization of zwitterionic monomer[63]. This process can be performed at moderate temperature and will make the side reaction minimized, thus, the Ce(IV)-induced grafting polymerization has a minimal extent of ungrafted homopolymer and a high grafting efficiency of initiator[6,77,78]. During the graft copolymerization, the Ce(IV) is reduced to cerous ion (Ce(III)), and free radical sites are created on the membrane surface. The radical sites initiate graft copolymerization of the vinyl group in zwitterionic monomers which are present in the reaction solution.

Our preceding work[4,6] prepared a highly hydrophilic and anti-protein-fouling PVDF hollow fiber membrane with a good stability via ATRP of HEMA and subsequent Ce(IV)-induced grafting polymerization of MPDSAH. The value of contact angle dropped to 22.1° and the amount of protein adsorption almost equaled zero as the grafting amount reached 513 μg/cm^2. The modified PVDF membrane had significantly reduced the extent of protein fouling and most of the fouling was reversible. Shen and Lin[78] grafted poly(sulfobetaine) on the cellulose membrane surface using ceric ammonium nitrate (CAN) as initiator. Liu's[63] study reported on the grafting polymerization of zwitterionic monomer, MPC, on the membrane surface by redox graft polymerization using the same initiator (i. e. CAN), which only required one step reaction and avoided the complex and unfavorable pretreatment process and hydroxylated treatment. All other properties of the modified membrane are listed in Table 1.

3.2 Photo-induced grafting polymerization

Photo (UV)-induced "grafting-from" polymerization method is another common technique for anti-fouling modification of membrane surface due to the low investment cost, mild reaction conditions, simple and versatile operation[27,46,79]. This process occurs at the membrane skin and effectively improves the surface performances of the membrane without affecting the bulk properties because of the relatively low energy of UV source[47]. The grafting amount and permeate performance of the modified membrane can be controlled conveniently in UV-induced grafting process[67,80].

For the membrane made from the photo-sensitive base polymer (photo-reactive side group or part of polymer backbone), this approach involves the direct generation of free radicals from the membrane surface under UV irradiation[23,79]. PES is one of the intrinsic photo-reactive polymers, with which the hollow fiber membrane prepared can be modified by photo-grafting of MPC and SBMA to improve the anti-bio-fouling properties[46].

For the membranes with less electro-active property, such as PP membrane and PVDF membrane, initiating radical sites should be generated at the membrane surface by the introduction of photo-sensitive groups as a result of the reaction of a photo initiator with the membrane under UV irradiation[23]. Benzophenon (BP) and its derivatives are usually needed for the initiation of the UV-assisted grafting polymerization of zwitterionic monomers at the surface of such membranes[20,23]. In this case, BP is decomposed to starter radicals that then transfer to the membrane and abstract hydrogen atom from surrounding chemical species, contributing to the generation of initiating radicals[20,23]. BP can be coated onto the membrane surface by adsorption method which could minimize the homo-polymerization of monomer and enhance the grafting efficiency[20,81]. Compared with PVDF membrane, UV-induced grafting polymerization is more suitable for PP membrane due to the presence of active tertiary hydrogen in PP[27]. The PP microporous membrane can be highly hydrophilized by the UV-induced grafting of polySBMA, the grafting amount and the resistance to protein adsorption can be optimized through altering SBMA concentration, BP concentration and UV time[27]. All other properties of the modified membrane are listed in Table 1.

3.3 Plasma-induced grafting polymerization

To increase the hydrophilicity in order to obtain the low-fouling membrane surface, treatment using plasma has been extensively studied over the last two decades to anchor the zwitterionic graft chains on the surface of membrane efficiently[20,23,68]. Surface zwitterionization by plasma-induced grafting polymerization is easy to operate and especially suitable for biomedical membrane modification in the dry and clean process[69]. It has been reported that low-temperature plasma-induced grafting has been performed to improve the permeate flux and antifouling performance of MF and UF membranes[82].

Plasma-induced grafting of poly (zwitterion) chains on the membrane surface includes two main processes: ① destruction of a polymer support by plasma activating (generation of radicals); ② deposition of a new zwitterionic layer on the membrane surface by zwitterionic polymerization[23]. They can be balanced by altering the kinds of plasma gas and the applied process parameters. Thus, the grafting amount and the length of zwitterionic chains can be controlled by both plasma parameters, such as pressure, power, sample disposition, treatment time, and polymerization conditions, such as monomer concentration, kind of solvent, grafting time, as a result, the thickness of the poly(zwitterionic) layer can be controlled up to the angstrom levels[20,23]. Moreover, the dynamic plasma flow not only presents a longer glow distance than the static plasma but also produces larger quantity of peroxides on the membrane, and even excites the second membrane layer[82]. Recently, Lee's[69] and Chang's[29] groups employed atmospheric plasma-induced surface copolymerization method to prepare polySBMA-grafted PP and PVDF membranes. The results suggested that the hemocompatible nature of grafted polySBMA by controlling grafting amount via atmospheric plasma treatment gives a great potential in the surface zwitterionization of hydrophobic membranes for use in human whole blood. All other properties of the modified membrane are listed in Table 1.

Although plasma-induced surface zwitterionization provides higher grafting yield and shorter modification time than surface grafting via ATRP, it has a relatively high cost of the operation because of the requirement of a vacuum system[20,29,69]. Additionally, plasma treatment usually results in the chemical degradation of grafted poly (zwitterion) due to the high energy of ion bombardment[29].

3.4 Combined methods

Recently, combined techniques were presented for grafting polymerization of zwitterionic monomer on membrane surface. ATRP was usually combined with initiator immobilization as the pretreatment through using chemical treatment[5] and UV[11,47,83]. For example, the poly(SBMA) can be tethered onto the surface of PP flat membrane through a combined method of UV-induced surface graft polymerization followed by ATRP to ensure the high density and controllable structure of the poly(SBMA) chains. The results demonstrated the good anti-protein-fouling performance of modified PP membrane[11]. In addition, O_2 plasma pretreatment combining with UV-induced graft polymerization can be used to achieve the grafting polymerization of MPDSAH on the PP non-woven fabric membrane. The modified membrane exhibited high flux recovery ratio and excellent antifouling stability during the microfiltration process of BSA solution[48]. All other properties of the modified membrane are listed in Table 1.

3.5 Comparison of different grafting polymerizations

Table 2 presents a comparison between the four grafting polymerizations. Here we only attempt to give a general impression according to the presented results in literature, because one method may be influenced by many parameters simultaneously. Free radical grafting polymerization may lead to undesirable surface changes and contamination due to the multi-step strategies, which results in a relatively low uniformity of poly(zwitterionic) layer on the membrane surface. The grafting polymerization induced by photo or plasma probably provides simple operation and good membrane smoothness, but its high costs of equipment leads to the drawbacks for large-scale application. Combination of the different grafting techniques is complex in regard to cost and environment problems. However, it often contributes to high grafting amount and multi-functions of poly(zwitterionic)-grafted membrane. In addition, most of the grafting polymerization methods experienced the reduction of pure water flux due to the pore plugging. Since all of the grafting polymerization methods can be employed to graft zwitterionic polymer on the membrane surface to improve the hydrophilicity and fouling resistance to proteins, we can make up the flux reduction by other ways, such as the increase in operational pressure and temperature, or not consider it further when the requirement allows.

Table 2 Advantages and disadvantages of modification methods

Methods	Uniformity	Grafting amount	Relative flux	Simplicity	Environment pollution	Cost
Free radical grafting polymerization	Low	Low	Low	Common	Common	Low
Photo-induced grafting polymerization	Common	Low	Low	High	Low	High
Plasma-induced grafting polymerization	High	High	Low	High	Low	High
Combined methods	Common	High	High	Low	Common	High

4 Conclusions and prospects

Protein fouling is of great importance for the membrane fouling of MF/UF process, which is the first step of membrane fouling initiating the following platelet adhesion, bacterial biofilm formation and other bio-fouling phenomenon. Therefore, the growth of anti-protein-fouling materials and associated membrane modification (grafting polymerization) is critically significant, especially for biomedical application. Zwitterionic materials that possess the maximum polarity form the hydration layer through electrostatic interaction (e.g. solvation of ion) and hydrogen bond, resulting in the super-high hydrophilicity and super-stable anti-protein-fouling property. With the understanding of anti-protein-fouling mechanism and the grafting polymerization principle of zwitterion on the membrane surface, future research direction could focus on the development of novel zwitterionic monomers that possess more functional groups and combined grafting polymerization methods that render the zwitterionic polymer more efficient and durable on the membrane surface to meet challenge of the excellent membrane uniformity and long-term stable performance. Based on these, the cost on techniques and operations should be reduced appropriately by designing the optimal means to synthesize zwitterionic monomers and complete grafting polymerizations on the membrane surface. In short, the poly(zwitterion)-grafted membrane would be of great interest in the anti-protein-fouling strategies in MF/UF membrane, which helps to expand the membrane application in the fields of agro-food, biomedicine and other bio-filtration process.

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Investigations and Applications of New Type Ion Exchange Membranes

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Abstract: The development of synthetic ion exchange membrane (electro-membrane) reported by Juda and McRae in 1950 stimulated both commercial and academic interest in such membranes and the related processes. Nowadays, synthetic ion exchange membranes have been improved by various methods and have many practical uses. The processes based on electro-membranes such as diffusion dialysis, conventional electrodialysis (CED), electrodialysis with bipolar membranes (EDBM), etc., can realize some new synthesis processes to achieve the maximal utilization of resources and pollution prevention. They can also be flexibly coupled with many other technologies and obtain a better function by means of technological symbiosis and can realize closing loops when inputting waste materials as the feedstock and carrying out production, resource regeneration and effluent treatment at the same time. In this report, preparation of novel ion exchange membranes and their new applications will be described. Specifically, a new platform, polyacylation of ionized monomers, for ion exchange membranes preparation will be introduced in detail. Following this approach, a library of SCT-SAPs is under construction by designing a variety of ionized monomers and comonomers as building blocks in order to tune the structures of the side-chains and main-chains of SCT-SAPs, respectively.

Keywords: ion-exchange membranes; electrodialysis; diffusion dialysis; ionized monomers; polyacylation; side-chains; main-chains

1 Introduction

Ion-exchange membranes (IEMs) are a new branch of polymers, which have been used as a bulk platform for processing and production of materials, chemicals and energy. The development of synthetic ion exchange membrane (electro-membrane) reported by Juda and McRae in 1950 stimulated both commercial and academic interest in such membranes and the related processes[1]. Nowadays, the synthetic ion exchange membranes have been improved by various methods and have many practical uses[2-3]. The IEMs are usually prepared from monomers or polymers that are available to introduce ionic groups into the final formed membrane. Preparation of ion-exchange membranes starting with monomers by polymerization or polycondensation requires that at least one of these monomers must contain a cationic or an anionic moiety. The most significant and the largest scale applied IEMs are the perfluorinated membranes used in the chlor-alkali production and energy storage or conversion system (fuel cell). Even though perfluorinated membranes have excellent mechanical and thermal stability, the high price of the perfluorinated material and many weaknesses such as a high degree of swelling and a poor permselectivity in perfluorinated membranes have directed the attention of preparing membranes from no fluorine material, such as hydrocarbon PE, polypropylene (PP), poly(vinylidene fluoride) (PVDF), polyether ketone (PEK), polyether sulfone (PES), polyether ketone (PEK), poly (phenylene sulfide) (PPS), PPO (polypropylene oxide), PBI (polybenzimidazole), etc[4-5]. Thanks to the outstanding chemical/thermal stability and interesting acid/base amphoteric characteristic of the benzimidazole ring, sulfonated benzimidazole-containing polymers (SBIPs) as promising candidate materials for IEMs have been attracting extensive attention. Meantime, stimulated by the development of new ion-exchange membranes with better selectivity, lower electrical resistance, and improved thermal, chemical, and mechanical properties, many ion-exchange-membranes-based processes such as electrodialysis (ED), electrodialysis with bipolar membranes (EDBM), electrodeionization(EDI), diffusion dialysis (DD), Donnan dialysis, reverse electrodialysis (RED), etc. have been widely used in many processes, such as water desalination, cleaning production or separation, resources recycling, power generation, and sensitive electrode preparation[6]. The study will give a brief introduction of the IEMs prepared by polyacylation of ionized monomers and some new applications of ion-exchange membranes based processes.

2 Preparation of ion exchange membrane by polyacylation of ionized monomers

By referring the structure-morphology of the Nafion membranes, we developed a new route for preparing IEMs from side chain-type sulfonated aromatic polymers (SCT-SAPs)[7-8]. These new polymers include a robust aromatic main-chain to give a high mechanical and chemical stability and pendant sulfonic acid groups linked to the main-chain to give a good electrochemical property. A schematic preparing route of these novel membranes was illustrated in Fig. 1. At first, 4,4′-oxydibenzoicacid (ODBA), 4-phenoxybenzoicacid (POBA), 3, 3′, 4, 4′-tetraaminobiphenyl (TABP), disodium 2, 2′-di (sulfopropyloxy) biphenyl (SBP) and Eaton's reagent were mixed and polymerized to get SPEKEBI polymer. Then, the SPEKEBI polymer was dissolved in *N*-methylpyrrolidone (NMP) to get a dilute solution; the obtained solution was casted on a flat glass plate and dried to get the membrane. The prepared membranes exhibited proton conductivity higher than Nafion while maintaining a low swell ratio. This suggests that these membranes are competitive alternatives to Nafion membranes for fuel cell process. Interestingly, the membranes were prepared by a direct polyacylation of ionized monomers. The main advantages of this preparing route can be summarized in two points. At first, the functional groups (sulfonated groups) were introduced to the monomers before polymerization reaction. The advantage of pre-sulfonation (sulfonation before polymerisation) compared with post-sulfonation (sulfonation after polymerisation) is that this gives an accurate control of the number and position of the sulfonate group by directly using side-chain-sulfonated aromatic monomers. Since the few reported side-chain- sulfonated aromatic monomers were usually prepared under harsh conditions with a complicated reaction process. In contrast,

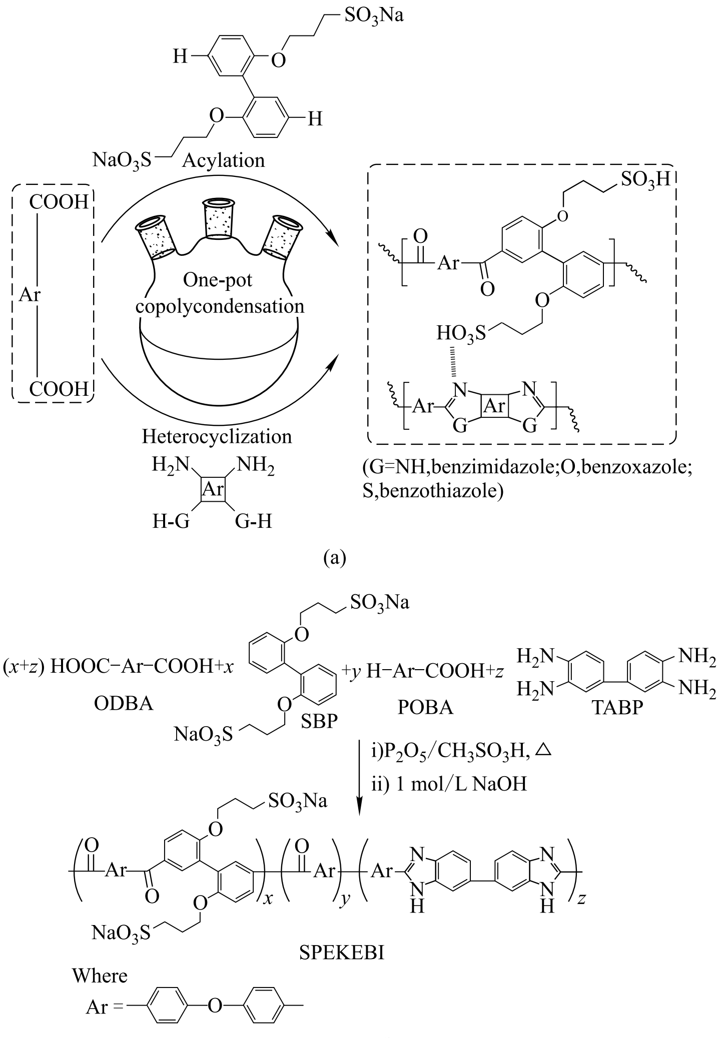

Fig. 1 (a) schematic illustration of the concept of "one-pot acylation/heterocyclization copolycondensation"; (b) synthetic route to SPEKEBI[8]

we present one-pot synthesis of disodium 2, 2′-di (sulfopropyloxy)-biphenyl (SBP) as a novel side-chain-sulfonated aromatic monomer and its polyacylation as a facile and versatile approach to SCT-SAPs for the first time. The introduction of SBP group ensures that there has enough number of acidic sulfonate groups on one polymer chain. Furthermore, the polymerization reactions were conducted by a polyacylation process. By take the advantage of acylation reaction between carboxylic acid and electron-rich arene groups in acidic condition (P_2O_5/polyphosphoricacid, P_2O_5/CH_3SO_3H, etc), a serious of side-chain-sulfonated aromatic membranes can be prepared. The preparation route is a simple, high-effective process, since the reaction was takes place in a “one-pot” way to combine the synthetic advantage of ionized monomers for polyacylation and the structural advantage of aromatic heterocycles. Considering the rich library of possible ionized monomers, polyacylation of ionized monomers opens a new dimension for the preparation of ion-exchange membranes.

3 New applications of ion exchange membranes

In addition to the membrane preparation research, we contributes significantly to the industrial application of the ED based technologies for cleaner production/separation as summarized in Fig. 2. These industrial explorations include the separation of bioproducts from byproducts (organic acids separation from fermentation broths, γ-aminobutyric acid (GABA) separation from NH_4Cl, etc), high salinity wastewater treatment (tetramethylammonium hydroxide (TMAH) recovery from developer wastewater, nitrile butadiene rubber wastewater treatment, pichlorohydrin wastewater treatment, electroplating wastewater treatment, etc).

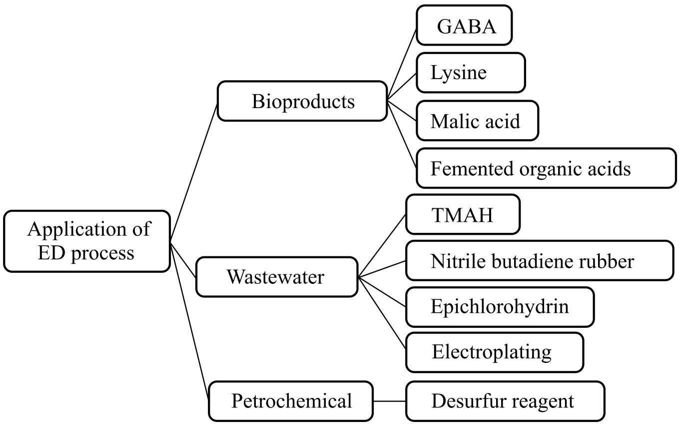

Fig. 2 The application of ion exchange membranes based process

For example, a complicated, labor-consuming, and environmental hazardous process was needed in the conventional production of the gluconic acid (Fig. 2). When bipolar membrane (BPM) is introduced to this preparation route, the water-splitting H^+ ions can be used to acidify the gluconate salt; which the water-splitting OH^- ions can be used as the raw material for reaction. In this way, five steps (in the color boxes of the Fig. 3) can be reduced. This improved route is not only energy-saving but also environment friendly. A pilot BPM ED set-up was established for gluconic acid production in Zhangshu, Jiangxi Province, China. The conversion rate of gluconate was higher than 95.6% with current efficiency of 71.5%.

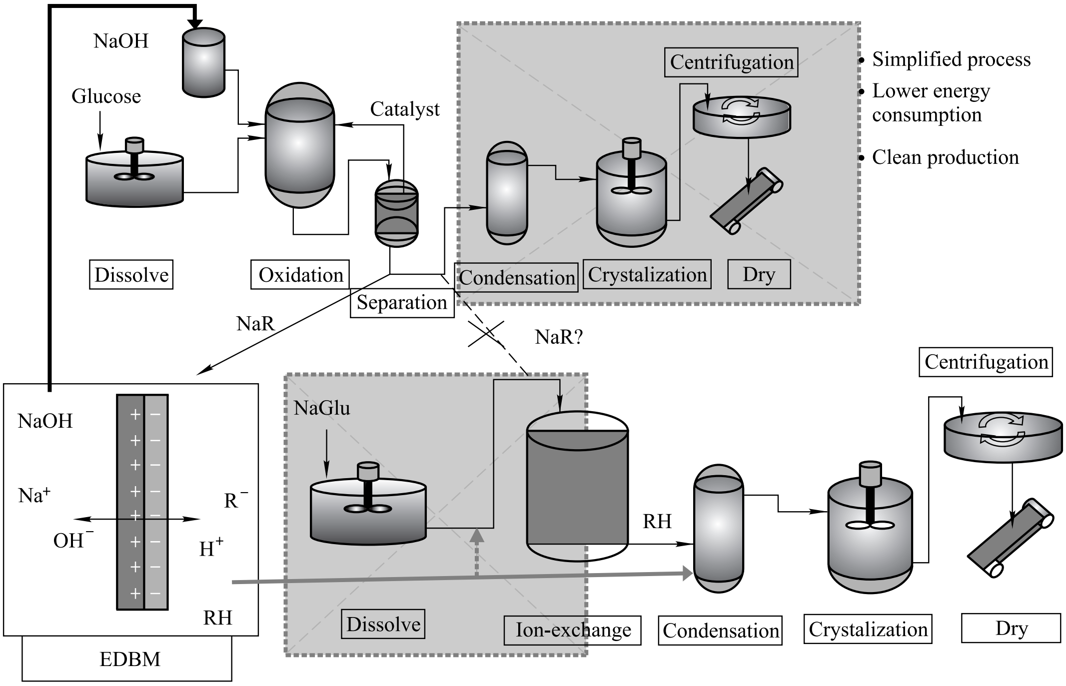

Fig. 3 The conventional route for the production of gluconic acid (gray square means these steps can be reduced by using the EDBM technology, EDBM, electrodialysis with bipolar membranes)[6]

TMAH is the most commonly used developer in during the manufacturing of semiconductors and photoelectric industries. A large amount of wastewater containing TMAH and is generated. Considering the highly alkalinity and toxic property of the TMAH, the treatment of TMAH contained developer wastewater is a tough and difficult problem. The conventional available technologies such as biological degradation, chemical oxidative, and adsorption usually have low efficiency and high process cost for developer wastewater treatment. In practical, the process cost for treating developer wastewater in China is as high as ~200 \$/t. By considering the main characteristics of developer wastewater, TMAH can be separated from the chelating organic agents and surfactant by the introduction of an electrodialysis process. Therefore, the electrodialysis technique was employed for the recovering and concentrating of TMAH from developer wastewater[9]. The effect of current density on the recovery process was investigated by considering the stability of membranes and process cost. Results indicated that the optimal current density was chosen at 30 mA/cm^2. TMAH can be concentrated in the range of 7.45% – 8.33%. The used membranes in the experiments were stable and suitable for this wastewater treatment. The total process cost was estimated to be 36.4 $/t without considering the profit of the recovered TMAH. Naturally, electrodialysis is a cost-effective and environment friendly technology for treating developer wastewater.

4 Conclusions

Ion exchange membranes and related processes have attracted multidisciplinary attentions and also found a variety of applications such as water desalination, cleaning production or separation, resources recycling, power generation, and sensitive electrode preparation. In this study, the "one-pot" polyacylation of ionized monomers has been proposed for the synthesis of side-chain-type sulfonated membranes. The preparation streategy achieve the quantitative design of membranes combine the synthetic advantage of ionized monomers for polyacylation and the structural advantage of aromatic heterocycles. Some examples for the new applications of ion exchange membranes for bioproducts separation and wastewater treatment were also briefly introduced.

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后　记

科学技术是第一生产力。纵观历史,人类文明的每一次进步都是由重大的科学发现与技术革命所引领和支撑的。进入21世纪,科学技术日益成为经济社会发展的主要驱动力。我们国家的发展必须以科学发展为主题,以加快转变经济发展方式为主线。而实现科学发展、加快转变经济发展方式,最根本的是要依靠科技的力量,最关键的是要大幅提高自主创新能力,要推动我国经济社会发展尽快走上创新驱动的轨道。党的十八大报告指出,科技创新是提高社会生产力和综合国力的重要支撑,必须摆在国家发展全局的核心位置,要实施“创新驱动发展战略”。

面对未来发展的重任,中国工程院将进一步发挥院士作用,邀请世界顶级专家参与,共同以国际视野和战略思维开展学术交流与研讨,为国家战略决策提供科学思想和系统方案,以科学咨询支持科学决策,以科学决策引领科学发展。

只有高瞻远瞩,才能统筹协调、突出重点地建设好国家创新体系。工程院历来高度重视中长期工程科技发展战略研究,通过对未来20年及至更长远的工程科技发展前景进行展望与规划,做好顶层设计,推动我国经济社会发展尽快走上创新驱动的轨道。

自2011年起,中国工程院开始举办一系列国际工程科技发展战略高端论坛,旨在为相关领域的中外顶级专家搭建高水平高层次的国际交流平台,通过开展宏观性、战略性、前瞻性的研究,进一步认识和把握工程科技发展的客观规律,从而更好地引领未来工程科技的发展。

中国工程院学术与出版委员会将国际工程科技发展战略高端论坛的报告汇编出版。仅以此编之作聚百家之智,汇学术前沿之观点,为人类工程科技发展贡献一份力量。

中国工程院