

DICP 70th Anniversary Conference-IV

**DICP Symposium (No.48) on Separation in Chemical Industry
--New concepts, Materials and Methods**

Program Booklet

October 12-14, Dalian, China



DALIAN INSTITUTE OF CHEMICAL PHYSICS

CHINESE ACADEMY OF SCIENCES

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✚ Reception

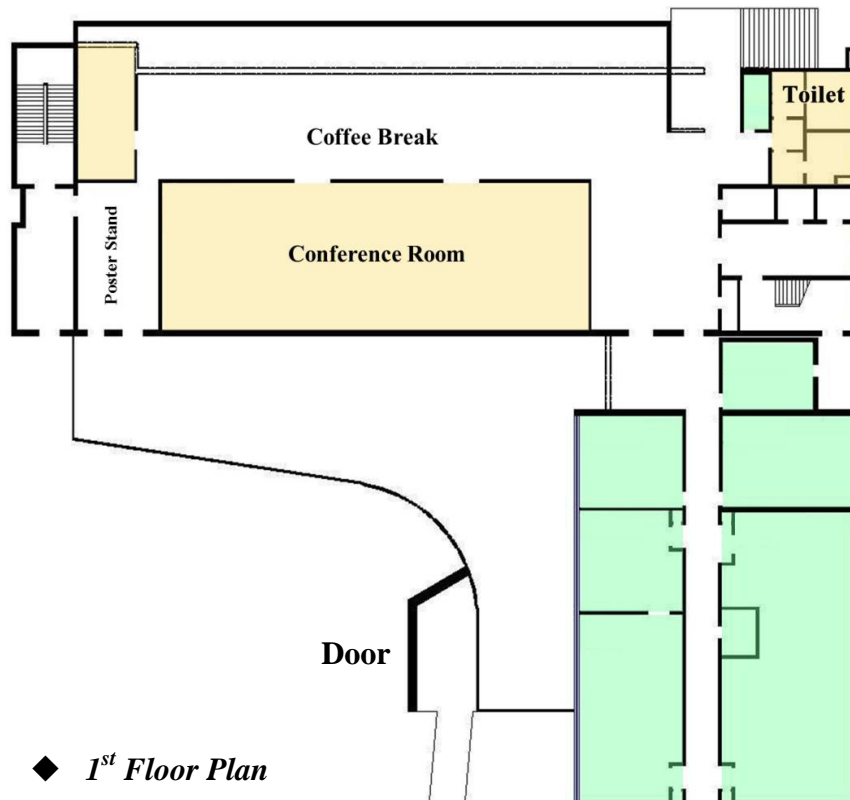
- Reception on the 25th Floor at Bayshore Hotel Dalian

(大连星海假日酒店 25 楼)

✚ Venue

- Biotechnology Building of Dalian Institute of Chemical Physics

(大连化学物理研究所生物技术部)



- Free shuttle buses will operate between Bayshore Hotel (7:50 am) and DICP venue

Scientific Program

(Abbreviation: PL--Plenary Lecture, KL--Keynote Lecture)

| Scientific Program Overview | | | | |
|-----------------------------|--------------------------|-----------------------|----------------------|---------------------|
| OCT.12, Friday | OCT.13, Saturday | | OCT.14, Sunday | |
| | Chair: Weishen Yang | | | |
| Registration 13:00-20:00 | 8:20-8:30 | Opening | Chair: Jinping Li | |
| | 8:30-9:10 | PL01-Jürgen Caro | 8:30-9:00 | KL13- Qilong Ren |
| | 09:10-09:40 | KL01-Lijun Zhang | 09:00-09:30 | KL14- Chongli Zhong |
| | 09:40-10:00 | Coffee Break | 09:30-10:00 | KL15- Xianfeng Li |
| | Chair: Tongwen Xu | | 10:00-10:20 | Coffee Break |
| | 10:00-10:30 | KL02-Bo Wang | Chair: Qilong Ren | |
| | 10:30-11:00 | KL03-Guangshan Zhu | 10:20-10:50 | KL16- Chusheng Chen |
| | 11:00-11:30 | KL04- HJM Bouwmeester | 10:50-11:20 | KL17- Haihui Wang |
| | 11:30-13:00 | Lunch | 11:20-11:50 | KL18- Jiepeng Zhang |
| | Chair: Chongli Zhong | | 11:50-13:30 | Lunch |
| | 13:00-13:30 | KL05-Gaohong He | Chair: Rong Wang | |
| | 13:30-14:00 | KL06- Wanqin Jin | 13:30-14:00 | KL19-Zhongyi Jiang |
| | 14:00-14:30 | KL07-Zhi Wang | 14:00-14:30 | KL20-Jinping Li |
| | 14:30-15:00 | KL08- Liangyin Chu | 14:30-15:00 | KL21-Yong Wang |
| | 15:00-15:20 | Coffee Break | 15:00-15:20 | Coffee Break |
| | Chair: Liangyin Chu | | Chair: Zhongyi Jiang | |
| | 15:20-15:50 | KL09-Tongwen Xu | 15:20-15:50 | KL22-Rong Wang |
| | 15:50-16:20 | KL10- Xingang Li | 15:50-16:20 | KL23- Jian Jin |
| | 16:20-16:50 | KL11-Shaomin Liu | 16:20-16:50 | KL24-Huabing Xing |
| | Reception 18:30-21:00 | 16:50-17:20 | KL12-Xuefeng Zhu | 16:50-17:20 |

Scientific Program

(Abbreviation: PL--Plenary Lecture, KL--Keynote Lecture)

🚩 Friday, October 12

13:00-20:00 **Registration**
18:30-21:00 **Welcome Reception**

🚩 Saturday, October 13

Chair: Weishen Yang

8:20-8:30 **Opening Ceremony**

8:30-9:10 PL01 [Jürgen Caro](#)
Leibniz University Hannover
Smart membranes in gas separation and nano filtration: MOF, COF, MXene...

9:10-9:40 KL01 [Lijun Zhang](#)
China Petrochemical Corporation
乙烯分离技术研究进展

9:40-10:00 **Coffee Break**

Chair: Tongwen Xu

10:00-10:30 KL02 [Bo Wang](#)
Beijing Institute of Technology
Crystalline porous solids for separation


10:30-11:00 KL03 [Guangshan Zhu](#)
Northeast Normal University
Construction of porous aromatic frameworks with exceptional porosity via building unit engineering

11:00-11:30 KL04 [HJM Bouwmeester](#)
University of Twente
Mixed ionic-electronic conducting membranes: fundamentals and challenges

Chair: Chongli Zhong

13:00-13:30 KL05 [Gaohong He](#)
Dalian University of Technology
气体分离膜的制备与应用

-
- 13:30-14:00 KL06 [Wanqin Jin](#)
Nanjing Tech University
Ceramic-supported composite membranes: fundamental study and engineering application
- 14:00-14:30 KL07 [Zhi Wang](#)
Tianjin University
Development of CO₂ separation membrane materials with high performance
- 14:30-15:00 KL08 [Liangyin Chu](#)
Sichuan University
Control and intensification of mass transfer and separation processes with smart materials
- 15:00-15:20 **Coffee Break**
- Chair: Liangyin Chu**
- 15:20-15:50 KL09 [Tongwen Xu](#)
University of Science and Technology of China
Electronanofiltration (ENF)-novel membrane processes for separating ions with 1-2 valence
- 15:50-16:20 KL10 [Xingang Li](#)
Tianjin University
现代精馏技术
- 16:20-16:50 KL11 [Shaomin Liu](#)
Curtin University of Technology
Recent works in metal membrane reactors
- 16:50-17:20 KL12 [Xuefeng Zhu](#)
Dalian Institute of Chemical Physics
Mixed conducting membranes and membrane reactors

 **Sunday, October 14**

Chair: Jinping Li

- 8:30-9:00 KL13 [Qilong Ren](#)
Zhejiang University
Separation of natural bioactive homologues by molecular-recognition extraction
- 9:00-9:30 KL14 [Chongli Zhong](#)

Beijing University of Chemical Technology
计算引领下的新型分离材料设计与制备

9:30-10:00 KL15

[Xianfeng Li](#)

Dalian Institute of Chemical Physics

Ion conducting membranes in secondary batteries

10:00-10:20

Coffee Break

Chair: Qilong Ren

10:20-10:50 KL16

[Chusheng Chen](#)

University of Science and Technology of China

Dense ceramic oxygen-permeable membranes and fuel pre-reforming processes for solid oxide fuel cells applications

10:50-11:20 KL17

[Haihui Wang](#)

South China University of Technology

Electrochemical synthesis of MOF membrane for gas separation

11:20-11:50 KL18

[Jiepeng Zhang](#)

Sun Yat-Sen University

Reversed adsorption selectivity for efficient separation of alkenes/alkanes

Chair: Rong Wang

13:30-14:00 KL19

[Zhongyi Jiang](#)

Tianjin University

Bioinspired membrane separation processes

14:00-14:30 KL20

[Jinping Li](#)

Taiyuan University of Technology

MOFs 分离低碳烃的探识

14:30-15:00 KL21

[Yong Wang](#)

Nanjing Tech University

嵌段共聚物分离膜：从多孔到均孔

15:00-15:20

Coffee Break

Chair: Zhongyi Jiang

15:20-15:50 KL22

[Rong Wang](#)

Nanyang Technological University

Development of low-pressure nanofiltration (NF) hollow fiber membranes for water softening

15:50-16:20 KL23

[Jian Jin](#)

Suzhou Institute of Nano-tech and Nano-bionics

Precise control of membrane structure for high-performance separation

16:20-16:50 KL24

[Huabin Xing](#)

Zhejiang University

Anion-pillared hybrid microporous materials for hydrocarbon separation

16:50-17:20 KL25

[Zhiping Lai](#)

King Abdullah University of Science and Technology

Nanoporous carbon composite membranes for high-performance water desalination

Appendix I. Poster Presentations

 Saturday-Sunday, October 13-14

- PP01 [Huixia Luo](#)
Sun Yat-Sen University
High-flux dual-phase percolation membrane for oxygen separation
- PP02 [Congcong Chen](#)
China University of Petroleum(East China)
Preparation and modification of TPU pervaporation membrane for gasoline desulfurization
- PP03 [Mumin Wang](#)
China University Of Petroleum (East China)
Influence of polyethylene glycol on the deep desulfurization of catalytic cracking gasoline by polyurethane membranes via pervaporation
- PP04 [Fusheng Pan](#)
Tianjin University
High selective hybrid membranes by incorporating hollow crystalline porous nanospheres
- PP05 [Xiaoliang Zhang](#)
Jiangxi Normal University / China
Development of high-Rejection performance of metal-Doped microporous organosilica membranes for desalination
- PP06 [Yi Liu](#)
Dalian University of Technology
Fabrication of twin-free c-oriented NH₂-MIL-125(Ti) membranes with superior H₂/CO₂ selectivity by in-plane epitaxial growth
- PP07 [Ming Xue](#)
Jilin University
MOF membrane with underwater superoleophobicity for oil-water separation
- PP08 [Pengyuan Wang](#)
Dalian Institute of Chemical Physics
Ultrathin ZIF-8 film containing polyoxometalate as an enhancer for selective formaldehyde sensing
- PP09 [Yuan Peng](#)
Dalian Institute of Chemical Physics

Two-dimensional metal-organic framework nanosheets for membrane-based gas separation

- PP10 [Yujie Ban](#)
Dalian Institute of Chemical Physics
Pore engineering of MOF membranes
- PP11 [Ang Guo](#)
Dalian Institute of Chemical Physics
MOF-based mixed matrix membranes
- PP12 [Yingwu Zhou](#)
Dalian Institute of Chemical Physics
Carbon molecular sieving membranes
- PP13 [Lili Cai](#)
Dalian Institute of Chemical Physics
Oxygen-permeable catalytic membrane reactors for hydrogen separation:
Membrane materials and catalysts
- PP14 [Rui Yao](#)
Dalian Institute of Chemical Physics
Ultrathin molecular sieve membranes
- PP15 [Wenping Li](#)
Dalian Institute of Chemical Physics
Novel reaction-separation coupling processes in oxygen-permeable membrane reactors
- PP16 [Yue Zhu](#)
Dalian Institute of Chemical Physics
Selection of oxygen permeation models for different mixed ionic-electronic conducting membranes

Appendix II. Abstracts of Invited Lectures

PL01: [Juergen Caro](#)

Smart membranes in gas separation and nano filtration:

MOF, COF, MXene...

Juergen Caro^{1,2}, Hongwei Fan^{1,3}, Yanying Wei^{2,1}, Haihui Wang^{2,1}

1) *Leibniz University Hannover,*

2) *South China University of Technology, Guangzhou,*

3) *Beijing University of Chemical Technology*

Abstract

Supported thin MOF layers are usually prepared by solvothermal crystallization. Also counter diffusion and interfacial growth, chemical vapor deposition, electrophoretic nuclei assembly, pseudomorphic replication or phase transformation, and layer-by-layer (l-b-l) techniques by dipping/spraying can be used. Recent developments in gas separation membranes such as switching of gas transport by external stimuli like electric fields [1] or light of a certain wavelength [2] are highlighted.

A new field of membrane research is the deposition of 2D nano-sheets to stacked membranes. In a pioneering paper, the top-down concept has been developed to decompose a 3D MOF into nano-sheets [3]. Recent examples are synthesis of MXene (Ti_3AlC_2) [4,5] and g- C_3N_4 [6] membranes with synthesis of the nano-sheets from the 3D materials (top down).

Novel COF membranes allow high water flux and good dye/drug retention in nano-filtration [7] as well as gas separation [8].

[1] A. Knebel, B. Geppert, K. Volgmann, D.I. Kolokov, A.G. Stepanov, J. Twiefel, P. Heitjans, D. Volkmer, J. Caro, Defibrillation of soft porous metal-organic frameworks with electric fields, *Science*, 358 (2017) 347.

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KL01: [Lijun Zhang](#)

乙烯分离技术研究进展

[Lijun Zhang](#)

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摘要

报告包括乙烯装置中分离技术的应用进展，包括传统的分离工艺、新型单元技术以及新方法的研究进展，传统分离工艺主要介绍深冷分离工艺，新型单元技术主要介绍浅冷油吸收、超临界萃取和反应精馏技术，新方法主要介绍膜分离、水合物分离以及 MOFs 的研究进展以及在乙烯分离的潜在应用。

Crystalline Porous Solids for Separation

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Abstract

Metal–organic frameworks (MOFs), with their well-defined pores and rich structural diversity and functionality, have drawn a great deal of attention from across the scientific community. However, industrial applications are hampered by their intrinsic fragility and poor processability. Stable and resilient MOF devices with tunable flexibility are highly desirable. We proposed a photo-induced post-synthetic polymerization (PSP) strategy to covalently assemble MOF crystals by flexible polymer chains, and thus endow the MOF powder with processability and flexibility. Further we presented a solvent- and binder-free approach for producing stable MOF coatings by a unique hot-pressing (HoP) method, in which temperature and pressure are applied simultaneously to facilitate the rapid growth of MOF nanocrystals onto desired substrates. This strategy was proven to be applicable to carboxylate-based, imidazolate-based, and mixed-metal MOFs. We further successfully obtained superhydrophobic and “Janus” MOF films through layer-by-layer pressing. These methods can be scaled up in the form of roll-to-roll production and may push MOFs into unexplored industrial applications.

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Postsynthetic Polymerization of a Metal–Organic Framework toward a Flexible Stand-Alone Membrane, *Angew. Chem. Int. Ed.* 2015, 54, 4259–4263.

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KL03: [Guangshan Zhu](#)

Construction of Porous Aromatic Frameworks with Exceptional Porosity via Building Unit Engineering

[Guangshan Zhu](#)^{1*}

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Abstract

Construction of excellent porous organic frameworks (POFs) with high surface areas and stability is always a tremendous challenge in synthetic chemistry.¹ The geometric configuration and reactive group of building unit are crucial factors to influence the structure and porosity of the resulting product. Recently, we report the design, synthesis, and characterization of two porous aromatic framework (PAF) materials, named PAF-100 and PAF-101, via a strategy of building unit engineering.² PAF-100 and PAF-101 present high Brunauer-Emmett-Teller (BET) surface areas exceeding 5000 m² g⁻¹ and uniform pore size distributions. Furthermore, PAF-100 and PAF-101 show high methane uptake with value of 742 cm³ g⁻¹ and 622 cm³ g⁻¹, respectively, at 298 K and 70 bar. The successful synthesis of PAFs with exceptional porosity from engineered building unit is powerful for constructing highly porous POFs.

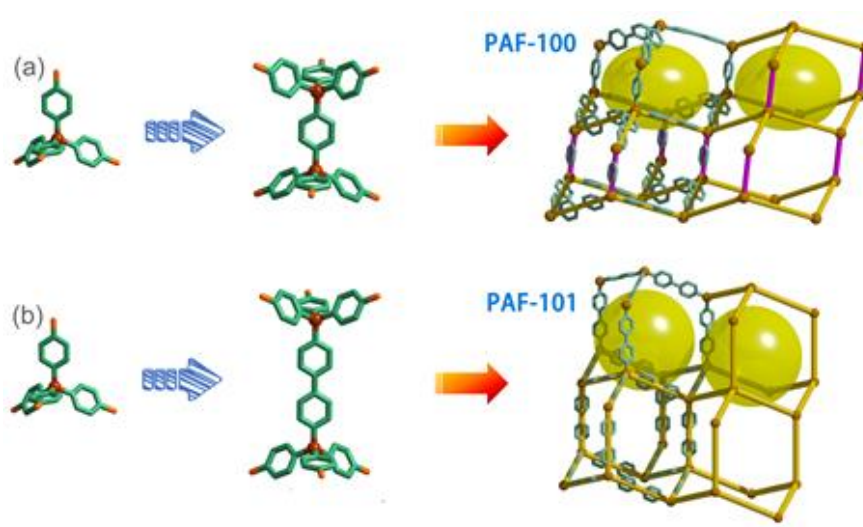


Figure 1: Synthetic route to PAF-100 (a) and PAF-101 (b)

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2. M. Li, H. Ren, F. Sun, Y. Tian, Y. Zhu, J. Li, X. Mu, J. Xu, F. Deng, G. S. Zhu, *Adv. Mater.* **2018**, accepted.

KL04: [HJM Bouwmeester](#)

**Mixed ionic-electronic conducting membranes:
fundamentals and challenges**

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Abstract

Mixed oxygen ionic-electronic conducting (MIEC) oxides hold promise for use as oxygen separation membrane to produce high-purity oxygen. Such membranes may also be integrated in ceramic membrane reactors, e.g., for natural gas conversion to syngas. In addition to long-term stability under operating conditions, the challenge to researchers is to develop membrane materials showing fast oxygen diffusion and surface exchange kinetics. The present paper surveys theory and research on oxygen transport in the MIEC materials, with emphasis on defect chemistry and surface exchange kinetics; progress, problems and perspectives in the development of membrane materials; and identifies directions for future research.

气体分离膜的制备与应用

贺高红

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摘要:

气体膜分离具有高效和低能耗等突出优点, 在石油化工、环境保护等领域的应用越来越广泛。提高分离膜的性能和对过程的优化设计是气体分离应用的关键。

气体膜的分离层是致密的, 因此其性能的取决于膜材料的分子结构, 侧链与透过物质的相互作用, 决定了本征的透过性和选择性, 主链的稳定性决定寿命, 我们设计侧链功能基团促进气体的溶解, 以及膜的微相分离等, 提高膜的气体分离性能和耐溶胀性等; 我们通过选择主链增加耐溶胀能力等; 膜的最终性能取决于制备工艺, 我们从分子层面设计铸膜液相分离和界面润湿, 优化制备工艺。

气体分离的对象往往是多组分的, 回收目标也是多样的, 系统是复杂的, 对膜分离为核心的流程提出了更高的要求。围绕多源化工气体的膜分离资源化和尾气达标排放, 建立了多源组分非理想膜过程的快捷、准确模拟, 新型耦合多技术整体协同设计, 在耦合协同资源化和 VOCs 减排等领域展开了系统研究, 并取得了系列研究成果和工程应用。如通过膜与变压吸附耦合工艺, 实现了高纯度、高收率回收炼厂气中的氢气。研发的具有自主知识产权的工艺包, 成功用于中石油大连石化 80000Nm³/h 多源富氢气体中氢气和轻烃的综合处理, 是目前国内规模最大的炼厂气综合回收利用装置, 经济效益近 2 亿元/年; 开发以膜为核心, 结合冷凝和吸附等分离单元优势的循环级联工艺设计方法和具有自主知识产权的系列工艺包; 该技术通过协同强化, 较美、德等同类技术节能 10~40%, 聚烯烃单耗降低 0.3~1.0%, 已经占有 90% 以上国内烯烃回收市场, 并多次在国际、国内竞争中击败美国 MTR 和德国 BORSIG, 并批量出口到日本等国外高端化工市场。

KL06: [Wanqin Jin](#)

Ceramic-supported Composite Membranes: Fundamental Study and Engineering Application

Wanqin Jin

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Abstract

By combining advantages of organic and inorganic materials, organic-inorganic composite membranes are regarded as a hot research interest in fields of membrane technology and chemical engineering. This presentation will review our recent progress in ceramic supported composite membranes, covering from fundamental study to engineering application. It aims to give an overview of design, preparation and application of the composite membranes used for molecular and ionic separation. Various membrane types with different materials will be involved in the talk, including ceramic-supported polymer composite membranes, mixed matrix membranes, and graphene-based membranes. Meanwhile, the presentation will illustrate typical examples of the composite membranes applied in fields such as bio-fuels production, volatile organic compounds (VOCs) recovery, and so on. In addition, large-scale production and industrial implementation of the organic-inorganic composite membranes will also be introduced.

Keywords: organic-inorganic composite membranes; molecular separation; industrial implementation

KL07: [Zhi Wang](#)**Development of CO₂ separation membrane materials with high performance**

Zhi Wang

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Abstract

A high-performance membrane should be of high permeability and selectivity, good stability and favorable resistance to potential impurities. Several methods have been developed to enhance the membrane performance for practical application. (1) Modification of membrane structures at multiple levels which can enhance multiple membrane performance. Piperazine (PIP) used as a cross-linking agent was fixed steadily in the PVAm-PIP/PSf membrane by the intermolecular hydrogen bonds between secondary amine group of PIP and primary amine group in PVAm which can largely improve the effective carrier concentration^[1]. The introduction of 2-aminoterephthalic acid (AA) into PVAm can restrain the polymer chain mobility and increase the effective carrier content which can be used to enhance membrane performance especially in relatively high temperature^[2]. (2) Introduction of multi-permselectivities into membrane which can make full use of the distinctions between CO₂ and other gases in size, condensability and reactivity. The multi-permselective membrane can efficiently separate CO₂ from various gases (H₂, CH₄, and N₂). The interfacial polymerization method was used to fabricate membranes of multi-permselectivities. Crosslinked polyamide with both EO groups and tertiary amino groups was formed after polymerization. The diffusivity-selectivity is enhanced by covalent crosslinking. The solubility-selectivity and the reactivity-selectivity are introduced by EO groups and tertiary amino groups, respectively^[3]. (3) Construction of high-speed CO₂ facilitated transport channels. Hydrotalcite (HT) with the hydrated carbonate anions at interlayer make it possess excellent CO₂ facilitated transport properties which can be grafted with polymer to prepare CO₂ separation membrane^[4]. Highly permeable montmorillonite (MT) layers bonded and aligned with the chain stretching orientation of polyvinylamine are immobilized onto a porous PSf substrate to fabricate mixed matrix membranes (MMMs) for CO₂ separation. High-speed gas-transport channels are formed by the aligned interlayer gaps of the modified MT, through which CO₂ transport primarily occurs^[5]. Metal-induced ordered microporous polymers (MMPs) are synthesized from aminated polymers, small organic linkers and divalent metal ions by using a facile polymer-directed chemical synthesis (PDCS) process. In comparison with conventional microporous materials, the MMPs show a significant improvement in both framework size and crystal size controllability, and in hydrolytic stability which is beneficial to the fast transport of CO₂^[6].

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KL08: [Liangyin Chu](#)**Control and intensification of mass transfer and separation processes with smart materials**

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Abstract

Mass transfer and separation processes are important processes in many industrial fields such as chemical engineering, biomedicine and so on. The regulation and intensification of mass transfer and separation processes play a key role in the transformation of traditional technology and the development of new technology. By introducing the response behaviors of smart materials, it is possible to achieve the environmental regulation and intensification of mass transfer and separation processes, and it is one of the frontiers and hotspots in the interdisciplinary researches of chemical engineering and materials, chemistry, medicine and so on. How to construct novel smart responsive drug delivery systems and membrane separation systems to break through the diffusion theory and enhance the membrane separation processes is still challenging in this field. By designing molecular-level structures and microstructures, we constructed responsive controlled release systems and smart membrane systems with smart materials, and pioneered the development of novel efficient smart membrane separation systems, responsive self-regulatory controlled release drug carriers with novel modes with the assistance of responsive smart materials. Thus, the difficult problems of molecular desorption in affinity membrane separations and the limited mass transfer momentum in carrier systems have successfully solved, and the regulation and intensification of drug separation and mass transfer processes have been achieved. The results provide novel ideas for the innovation of membrane separation systems and the regulation and intensification of mass transfer processes in drug controlled release systems.

KL09: [Tongwen Xu](#)**Electronanofiltration (ENF)-novel membrane processes for separating ions with 1-2 valence**

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Abstract

The hurried expansion and growth of so many industrial production houses like metal finishing, electroplating, mining and steel processing industries produced an excessive amount of metal ions contained wastewaters, which is regarded as the major trepidation from the environmental stance. Worldwide most nations, by now established a huge number of waste water industries plus processing plants to get rid of this concern. The available well-known methods to treat such wastes include crystallization, neutralization, extraction or membrane technologies such as electrodialysis, nanofiltration and diffusional dialysis, etc. Generally, membrane-base technologies show advantages over traditional ones due to the convenient operation and less energy cost and widely accepted by the industries. However, they also show some disadvantages. For example, electrodialysis was limited by the lack of monovalent -selective ion exchange membrane, nanofiltration is limited by the concentration polarization and treating ability for diffusional dialysis is very low. The objective of this presentation is to develop a new membrane process-electronanofiltration or electrodialysis with nanofiltration like membrane for treating metal ions contained wastes. Both the membrane formation and the process detail will be investigated.

Biography

Prof. Tongwen Xu is currently a full professor in the School of Chemistry and Material Science at the University of Science and Technology of China (USTC) and has been joining USTC since 1997. He received his Master in Hefei University of Technology and PhD degrees in Tianjin University. Prof. Xu has been a short-term visiting scientist of University of Tokyo and Tokyo Institute of Technology in 2000, 2001 respectively. He received a Brain Pool Program from Korea (2006) and worked one year in Gwangju Institute of Science and Technology. Prof. Xu was awarded Outstanding Youth Foundation of China in 2010, selected as FRSC in 2013 and as Changjiang Scholars Program Chair Professor in 2014. He is serving as execution/guest editors and editorial boards of 11 international journals. He has held 60+ patents, edited 5 technical books, and published over 350+ SCI journal articles with H-index 55. His research interests cover membranes and the related processes.

KL10: [Xingang Li](#)

现代精馏技术

KL11: [Shaomin Liu](#)

Recent works in metal membrane reactors

Mixed conducting membranes and membrane reactors

混合导体透氧膜及膜反应器

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膜分离与膜过程是当代新型高效的共性技术, 是多学科交叉的产物, 满足现代工业对节能、环保、高效、经济新技术发展的要求, 成为实现经济可持续发展战略的重要组成部分。混合导体透氧膜是一种能够同时传导氧离子和电子的混合导电无机陶瓷膜。利用混合导体透氧膜分离技术替代传统的高能耗深冷精馏技术、发展空气分离与催化氧化反应一体化技术, 对解决当今的能源短缺问题和改善日益严峻的环境压力具有重要意义。本人通过对透氧膜材料的深入研究, 提出膜材料设计原则, 优化膜材料; 通过对膜渗透机理的深入理解建立可靠的氧渗透模型; 在此基础上, 通过系统实验和理论模型研究, 实现对膜材料构效关系的科学认知; 进而发展适用于特定反应的膜材料和催化膜反应器, 实现化学反应和膜分离过程的耦合强化, 揭示膜反应器中反应-分离耦合的基本规律。

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KL13: [Qilong Ren](#)

Separation of natural bioactive homologues by molecular-recognition extraction

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Abstract

The selective separation of natural bioactive homologues plays a key role in many fields including pharmaceutical-chemical industry, food industry, biomass utilization, and so on. However, the difference of homologues' molecular structure is as slight as 1-2 groups, leading to very similar molecular sizes and properties, thus the separation of homologues is very challenging. The widely-used chromatographic technologies suffer from several problems such as low capacity, slow mass-transport, large solvent consumption, or high energy cost. Molecular-recognition extraction technique can identify the slight difference in the physicochemical properties of natural bioactive homologues, and it also has the benefits of large capacity, low mass transport resistance, restricted emulsification, process continuity, and easy scale-up. It has been successfully applied to the efficient separation of various types of natural bioactive homologues including polyphenols, flavonoids, terpenes, sterols, and so on, with significantly lower solvent consumption and energy cost than conventional chromatography techniques. Hydrogen-bonding recognition, π - π recognition and synergistic interactions are essential to the highly-selective separation of homologues molecules.

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计算引领下的新型分离材料设计与制备

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摘要

吸附与膜分离为新型的分离技术，其基础为材料的设计与制备。材料的研发经历了由经验指导实验向理论指导实验的转变，目前，基于材料基因组学的“理论预测-实验验证”新模式已成为材料研发的前沿与热点。本报告结合报告人团队的研究成果，介绍了基于构效关系的理论指导实验和最新的材料基因组学的研究进展（以 COF 材料为例），充分说明了计算与实验研究相结合的重要性，指出“计算引领下的新材料设计与制备”为材料研发的高效模式。

Ion conducting membranes in secondary batteries

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Abstract

Electric energy storage technologies can solve the intermittence and instability of renewable energy sources when using them to generate electricity. Therefore, electric energy storage technologies are very important to accelerate the utilization of renewable energy sources. Among variable electric energy storage technologies, the research and development of secondary batteries, like lithium-ion batteries, lithium-sulfur batteries and flow batteries, can facilitate the wide use of portable mobile electronic equipments and electrical vehicles. Besides, the investigations on secondary batteries are significant for the development of the large-scale energy storage technologies.

A membrane is one of the key materials of a secondary battery, playing the role of separating the anode and cathode to prevent the occurrence of short circuit, while allowing the transport of charge carriers to achieve a complete circuit. The properties of membranes commonly determine the performance of secondary batteries. Ion conducting membranes with various structures can be prepared by many methods, thus meeting diverse requirements of different secondary batteries (Figure 1).^[1-2] In this presentation, the author will illustrate the research and utilization of ion conducting membranes in secondary batteries.

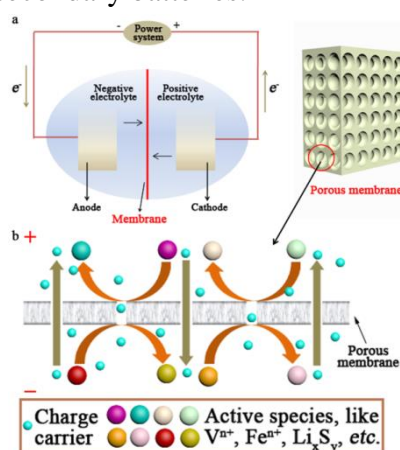


Fig. 1 (a) Schematic diagram of a normal secondary battery and (b) the ion conducting membrane.

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KL16: [Chusheng Chen](#)**Dense Ceramic Oxygen-permeable Membranes and Fuel Pre-reforming Processes for Solid Oxide Fuel Cells Applications**

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Abstract

Solid oxide fuel cell (SOFC) is an emerging clean and efficient power production technology. It is best operated with hydrogen as fuel in terms of anode activity. The use of hydrogen fuel is however limited by the lack of infrastructure for production, distribution and storage of hydrogen. Therefore, it has been proposed to directly use methane and other hydrocarbon as fuel for SOFC. The primary problem in using carbonaceous fuels is the deposition of carbon on the Ni-based anode of SOFC. One way to avoid this problem is to reform the carbonaceous fuel into syngas, a mixture of hydrogen and carbon monoxide. Steam reforming (SR) is the main route for fuel reforming, but due to its highly endothermic nature, a large quantity of heat needs to be fed into the reactor. Consequently, it is not economically feasible to operate a SR reactor at a size required by SOFC. Partial oxidation (POX) is an alternative process to SR. Owing to its exothermic nature, POX can be thermally self-sustained and allows for fast start-up. The main difficulty with POX lies in the consumption of pure oxygen that is currently produced by cryogenic air separation process. This difficulty may be overcome by making use of oxygen-permeable dense ceramic membrane. The membrane is made of mixed oxygen ionic and electronic conductor, allowing oxygen to permeate through while being impermeable to nitrogen and other gaseous species. With the membrane, the POX reaction and separation of oxygen from air can be integrated in a single space. A challenge for this approach lies in that the membrane must exhibit both high oxygen permeability and stability under stringent operation conditions with one side of the membrane exposed to oxidative atmosphere (air) and the other side highly reducing atmosphere containing H₂ and CO. In the present talk, it will be demonstrated that the dual-phase composite membrane made of oxygen ionic conductor Zr_{0.84}Y_{0.16}O_{1.92}(YSZ) and electronic conductor La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-δ} (LSCrF) with phase-inversion derived asymmetric structure can meet both the oxygen permeation and stability requirement under the POX conditions. It will also be shown that the catalytic POX reactor built with the YSZ-LSCrF membrane can effectively convert methane, propane and ethanol into syngas, and SOFC can run on the as-reformed carbonaceous fuel efficiently.

Electrochemical synthesis of MOF membranes for gas separation

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Abstract

Membrane separation is considered to be the most promising technology for industrial separation and purification due to the low energy consumption. Currently, metal-organic frameworks (MOFs) exhibit great potential in separation process owing to the tunable pore size associated with their highly designable structures and particular adsorption abilities, which are considered to be promising membrane materials. In recent years, supported MOF membranes have attracted increasing attention for separation. Inspired by electrochemical application, a novel electro-deposition assisted strategy is proposed to modify the substrate to build a versatile platform for in situ growth of various MOF membranes. In the last decades, electro-deposition has drawn great attention in the application of electrochemistry. Owing to the wide range of metals in choice and the accelerated formation rates of metal precursors by the addition of small current, electro-deposition is normally utilized as a facile and effective method to prepare different kinds of metal oxides/hydroxides on conductive substrates. In this work, the stainless steel nets (SSN) are chosen as the substrates allowing for the low cost and easy-welded property in industry. The preparation concept briefly goes as illustrated in Figure 1, the metal oxide/hydroxide with particular morphology, exactly corresponding to the metal centers of targeted MOFs, can be introduced onto SSN via electro-deposition. For example, ZnO nanorods, Co(OH)₂ nanosheets and Cu₂O nanocubes can be electro-deposited onto the substrates quickly and be further expected to provide active sites for the crystallization of Zn-ZIF-8, Co-ZIF-67 and Cu-HKUST-1, as well as their following in situ growth to form continues MOF membranes.

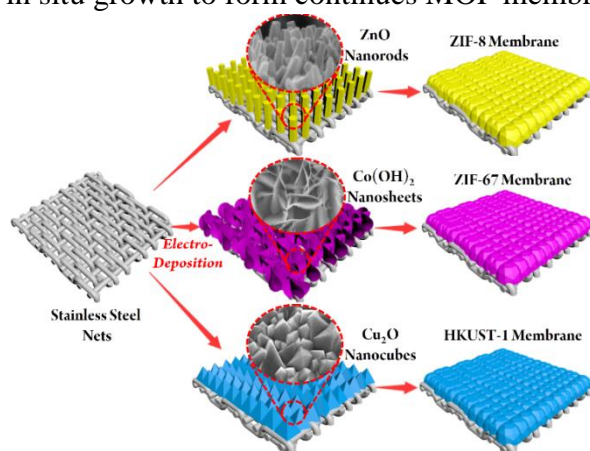


Fig.1 Schematic illustration of in situ growth of three different kinds of MOF membranes on the supports modified by electro-deposition.

KL18: [Jiepeng Zhang](#)**Reversed adsorption selectivity for efficient separation of alkenes/alkanes**

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Abstract

Separation alkanes/alkenes and purification of alkenes play a key role in industry and consume massive energy due to the lack of efficient methods/materials. Differential physical adsorption of gas is a promising approach in replacing the conventional distillation process. Porous coordination polymers (PCPs), also well known as metal-organic frameworks (MOFs), possessing diversified and designable pore structures, have demonstrated many advantages compared with classic adsorbents such as zeolites and activated carbons, but existing adsorption mechanisms/behaviors are not efficient for separation of alkene/alkane mixtures and purification of alkenes. Here, we show that hydrophilic ultramicropores can play key roles in strengthening host-guest interactions especially for alkanes with smaller polarity and larger flexibility, giving abnormal/reversed alkane/alkene adsorption selectivities and highly efficient purification of alkenes.

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KL19: [Zhongyi Jiang](#)**Bioinspired membrane separation processes**

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Abstract

Bioinspiration has become a powerful and versatile platform for the rational design of diverse kinds of innovative separation membrane materials and the efficient intensification of membrane processes. A variety of bioinspired membranes with high separation performance have been fabricated by imitating the delicate element compositions, tunable hierarchical structures, mild formation conditions, efficient mass transfer mechanisms, and exceptional multiple functions of biological materials. These membranes have found promising applications in the separation of liquid or gas mixtures. Bioinspired membranes have been fabricated by biomimetic, biomimetic, bioadhesion, and self-assembly methods in pursuit of the efficient, facile, controllable, generic, and green goal. These membranes have played critical roles in sustainable utilization of resources and energy, and could occupy an increasingly important position in the membrane area. This presentation will briefly summarize the recent advances in bioinspired membrane separation processes, primarily including hybrid membranes and composite membranes for carbon dioxide separation, antifouling membranes for water purification.

低碳烃高效分离的绿色化工过程研究

摘要

能源资源是人类社会最重要的物质资源，控制着经济发展、社会进步和现代文明的命脉。低碳烃（C1-C4）化合物作为能源资源的重要组成部分，是工业中重要的生产原料。例如，甲烷是天然气的主要成分，与化石能源相比，被认为是更清洁、便宜、全球均匀分布的燃料。乙烯是石油化工的基本原料，是世界上产量最大的化学产品，其下游产品占石油化工总产品的75%以上。目前，全球对乙烯的年需求量已经超过1.5亿吨，并且以4.5%的年增长率持续增长，乙烯的生产能力已经成为衡量一个国家石油化工工业发展水平的标志。丙烯是全球第二重要的化工原料，其主要用于生产丙烯腈、环氧丙烷、丙酮等。近年来，乙烯和丙烯等烯烃下游产品的发展迅速，使得国内对烯烃的需求量明显增加，超过了烯烃生产能力的增长速度，存在明显的供需缺口。

低碳烃主要来源于石脑油的蒸汽裂解，烷烃脱氢，甲醇制烯烃（MTO）等方式，在其生产过程中，这些化合物多以混合物形式存在，且这些化合物通常具有相似的分子结构，仅在碳数和不饱和度上存在微小差异。因此各组分之间沸点、酸碱性等物理化学性质非常接近，分离难度较大，工业界中均以巨大的能耗物耗以及高昂的设备投资作为代价。

工业生产中，低碳烃的分离工艺主要包括深冷分离、吸收分离、选择性反应技术等。深冷分离技术是大规模应用比较成熟的气体分离技术，能获得高纯度的产品。但是由于低碳烃化合物具有相似的沸点和相对挥发度，因此存在设备投资成本高、运行能耗大的问题。而吸附分离技术具有能耗少，操作简单，环境友好等优点，引起了广泛关注。吸附技术的核心是吸附剂，因此选择成本低、效果好、稳定性高的吸附剂是重中之重。

本报告以低碳烃的高效分离为目标，选择不同的金属-有机框架（MOFs）展开工作：通过从孔道尺寸调控到功能化修饰，构建不同的刚性、柔性结构探索，详细分析低碳烃分子与MOFs材料的相互作用以及分离机理，通过对目标分离组分制定针对性的分离策略，得出提高分离性能的方法，为低碳烃吸附分离吸附剂的设计制备以及工艺开发提供参考。

嵌段共聚物分离膜：从多孔到均孔

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摘要

相转化是制备聚合物分离膜最为常用的方法，半个多世纪以来，取得了巨大成功。但是，相转化制膜过程中需要大量使用有机溶剂，产生难处理废水。而且，由于分相与成孔同步发生，相转化制备的分离膜孔径分布较宽，分离精度有待提高。本课题组致力于发展分离膜的清洁制备方法，开发高分离精度的膜材料。

嵌段共聚物是两个或多个均聚物经共价键连接起来的聚合物，在一定的热力学条件下，可发生微相分离，形成纳米尺度的规整分相结构。将其中的分散相通过物理或化学方法转变为孔道，即可得到纳米孔膜材料。

我们提出选择性溶胀的嵌段共聚物成孔方法。将两亲嵌段共聚物置于极性溶剂中，极性嵌段形成的分散相发生选择性溶胀，体积膨胀，并在后续脱除溶剂过程中，极性链段收缩，形成孔道；而非极性嵌段形成的连续相则保持膜材料的整体稳定性。以聚苯乙烯基嵌段共聚物为模型体系，我们证实了嵌段共聚物选择性溶胀成孔制备超滤膜的可行性。而且，极性链段在溶胀过程中在孔壁和表面富集，得到的膜材料具有自发永久亲水特性。

选择性溶胀成孔以嵌段共聚物为起始原材料，不需要使用添加剂，得到干膜，工艺极为简便，且溶胀剂可以直接循环使用。与相转化的成膜方法相比，选择性溶胀是一种更为清洁的制备聚合物分离膜的方法。我们实现了低成本、高强度的嵌段共聚物的规模化合成和薄膜的连续化加工，推进选择性溶胀制备嵌段共聚物的放大制备。

嵌段共聚物直接进行选择性溶胀，得到的尚不是单分散膜孔。如对嵌段共聚物先进行预取向，再溶胀处理，可获得孔径单分散的直通孔。孔道均一化可同时提升膜分离的选择性、渗透性和稳定性。我们将孔径均一、孔道直通的分离膜定义为均孔膜。改变退火条件，我们制备了不同构型（垂直取向和平行取向）的均一孔道。在保证分离选择性的前提下，对比孔道不规整的分离膜，均孔膜渗透性有数量级上的提升。

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KL22: [Rong Wang](#)**Development of Low-Pressure Nanofiltration (NF) Hollow Fiber Membranes for Water Softening**

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Abstract

Water softening is a process to remove the water hardness from various water streams. The lime-soda ash treatment and ion exchange resin are the commonly used conventional methods [1], but the former produces a large amount of waste sludge and the latter increases sodium chloride content in the treated water. Nanofiltration (NF) membrane offers a promising alternative with higher efficiency and lower operating cost in the softening process of groundwater, brackish water and drinking water as well as in the pretreatment for seawater desalination.

However, it is challenging to develop NF membranes, which could achieve competent permeation flux at ultrafiltration (UF)-range low operating pressure in order to reduce energy consumption and membrane fouling tendency. In this presentation, three approaches for fabricating novel composite hollow fiber membranes with low operating pressure will be reported, which include dual layer hollow fiber fabrication followed by chemical cross-linking [2], layer-by-layer polyelectrolyte deposition [3] and interfacial polymerization [4]. The scale-up of the NF membrane production was also explored and succeeded, suggesting the great potential of the developed NF hollow fiber membranes for commercialization.

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KL23: [Jian Jin](#)**Precise Control of Membrane Structure for High-Performance Separation**

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Abstract

In this presentation, I will present two research works. One is the fabrication of a TFC NF membrane with a crumpled polyamide (PA) layer via interfacial polymerization on a single-walled carbon nanotubes/polyether sulfone composite support loaded with nanoparticles as a sacrificial templating material, using metal-organic framework nanoparticles (ZIF-8) as an example. The nanoparticles, which can be removed by water dissolution after interfacial polymerization, facilitate the formation of a rough PA active layer with crumpled nanostructure. The NF membrane obtained thereby exhibits high permeance up to $53.5 \text{ lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ with a rejection above 95% for Na_2SO_4 , yielding an overall desalination performance superior to state-of-the-art NF membranes reported so far. Another work is about the design of ultralarge free-standing single-layer protein nanosheets for precise nano-size separation *via* a Cu^{2+} catalyzed disulfide-bond cross-linked reaction along 2D orientation. The protein adopted in this work is tobacco mosaic virus (TMV), a typical cylinder-shaped protein with a diameter of 18 nm, a height of 4.7 nm, and more importantly a 4-nm-diameter pore in the protein center. Such an inner pore could be used as a well-defined channel for the selective passage of target molecules with suitable size. By such a design, single-layer TMV nanosheets extending over tens of micrometers in width and with well-defined nanopores were successfully developed. A ~ 40 -nm-thick ultrafiltration membrane laminated by the single-layer TMV nanosheets accomplished precise separation of ~ 4 -nm-sized substances with size difference only around 1 nm. Meanwhile, the membrane exhibited water permeability up to $\sim 7000 \text{ L m}^{-2}\text{h}^{-1}\text{bar}^{-1}$, which is an order-of-magnitude improvement comparing to traditional ultrafiltration membranes with similar rejection profile.

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KL24: [Huabin Xing](#)**Anion-pillared hybrid microporous materials for hydrocarbon separation**

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Keywords: gas separations; porous materials; ionic liquids; adsorption; hydrocarbons.

Abstract: That society increasingly depends upon gases as commodities and fuels means that the “age of gas” has dawned, creating with it an urgent demand for designing energy-efficient porous materials to address challenges in gas separations, sensing and storage. However, that there is in general a trade-off between uptake capacity and selectivity of porous materials creates a major barrier toward gas separation/purification through physisorption. Our study addresses this challenge in the context of alkyne capture from olefin, a critical step in the production of olefins including ethylene and propylene, the largest bulk commodity of the petrochemical industry by mass. Others include C4 olefin separation, sulfur dioxide and carbon dioxide capture. We reveal that pore chemistry and pore shape control in anion-pillared hybrid ultramicroporous materials enables the exploitation of supramolecular chemistry of gases to set new benchmarks for selectivity and that these benchmarks are accompanied by high uptake. The separation performances of anion-pillared hybrid ultramicroporous materials were evaluated by static gas adsorption and dynamic breakthrough experiments. The interaction mechanism between gas molecules and hybrid porous materials were investigated by experiments and modeling studies.

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Nanoporous Carbon Composite Membranes for High-Performance Water Desalination

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Keywords: Carbon membranes, desalination, membrane distillation, reverse osmosis, forward osmosis

Introduction

Water scarcity has been an increasing worldwide challenge due to climate change, ground water pollution and population growth. Water desalination is one of the few options that can provide additional water supply under no effect of climate change. Membrane technology has been the dominate method for water desalination, which mainly include three processes, i.e. reverse osmosis (RO), forward osmosis (FO), and membrane distillation (MD). These processes are often complementary. For example, RO is often the best of choice for brackish and seawater desalination, but cannot be used in high salinity water, while MD is capable to recovery water up to 100%. FO may have advantage in systems easy to foul. From the energy point of view, RO has the lowest energy consumption, but it requires high pressure and electricity, while FO and MD have potential to use renewable energy. The desalination mechanisms of RO and FO are typically based on solution-diffusion, while MD relies on capillary force to stop the transport of water in liquid form. Hence, the membranes used in these processes typically have different membrane properties and structures and are not compatible with each other. The membranes used in RO and FO are typically hydrophilic and dense, while the membranes used in MD are hydrophobic and microporous. Regardless of these differences, most membranes used in these three processes have high salt rejection enough to meet practical needs, but the discovery of the superfast water transport through carbon nanotube^[1] and aquaporin^[2] channels order of magnitude faster than that of the existing membranes indicates that there are still plenty of room to improve the membrane flux.

Here we report the synthesis of a nanoporous carbon fiber membranes supported on

yttrium stabilized zirconia (YSZ) hollow fiber support that showed excellent salt rejection and water flux in all the three membrane-based desalination processes.^[3]

Experimental

YSZ hollow fibers were fabricated from YSZ nanoparticles (30 to 60 nm from Inframat Advanced Materials Co.) through a phase-inversion/sintering process^[4, 5]. The inner and outer diameters of YSZ hollow fiber were about 0.91 mm and 1.4 mm with average pore size of 100 nm and porosity of 40%. A uniform layer of nickel nanoparticles was coated on the outer surface of YSZ hollow fiber by sputter deposition in argon plasma. A carbon nanowire layer was grown on the nickel deposited YSZ hollow fiber through a catalytic chemical vapor deposition (CVD) process. Acetylene was used as carbon source in the presence of hydrogen (acetylene to hydrogen volume ratio 1:10). The growth was conducted at 700 °C for 1 to 3 minutes. After that, the CVD chamber was quickly cooled down to room temperature under argon flow. The color of the YSZ hollow fiber turned from white to black, indicating successful growth of a carbon layer on the surface.

The setup of membrane distillation is illustrated in Figure 1a. The container filled with salt water was placed on a hotplate to control temperature. A carbon composite hollow fiber membrane was sealed in one end and immersed inside the salt water. The other end of the hollow fiber was connected to a condenser, and then a liquid nitrogen trap, and finally to a vacuum pump. The temperature of the cooling water used for the condenser is around 2 °C and the pressure of the vacuum pump is around 800 Pa. The weight and the salt concentration of the water collected in the liquid nitrogen trap was recorded after running for about 48 hours. The setup of RO and FO is illustrated in Figure 1b. The carbon composite hollow fiber membrane was mounted inside a glass tube and sealed from both ends. In the RO process, 2000 ppm salt water was cycled between the glass tube and a salt water bath. The water bath was pressurized by nitrogen gas to provide driving force. Fresh water was cycled between the carbon hollow fiber channel and the freshwater bath. In the FO process, 10% salt water was cycled between the hollow fiber channel and the salt water bath, while fresh water was cycled between the glass tube and the freshwater bath. The change in the volume as well as the salt concentration of the freshwater bath was monitored with time. The salt concentration was determined by electrical conductivity measured at 20 °C.

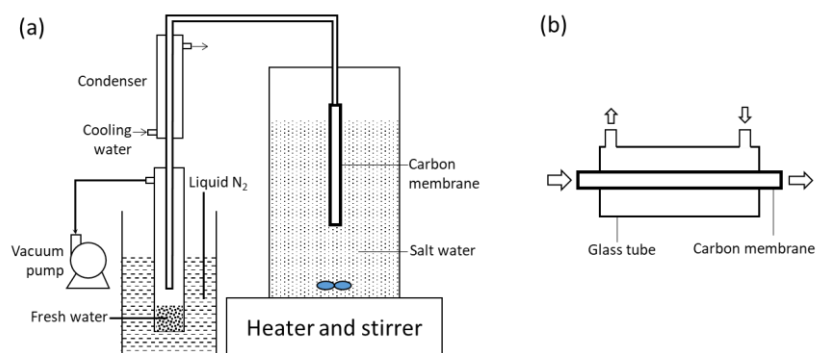


Figure 1: Illustration of the setup of (a) membrane distillation, (b) RO and FO.

Results and discussion

Figure 2a and 2b show the YSZ hollow fiber before and after carbon growth. The color of the pristine hollow fiber is white, while after growth the color changes to black. The magnified SEM image (Fig. 2c) focused on the outer surface of the hollow fiber shows a layer of carbon wires grown on the surface. The growth is along the vertical direction, but not well aligned. The top part of the wires is curled, forming a loose layer. The total thickness of the carbon wire layer depends on the growth time. For 2 minutes growth, the thickness is about 10 μm . The average pore size of the carbon layer was probed by gas permeation, which gave a value around 30 to 50 nm depending on the nickel sputtering conditions which control the density of the nickel particles on the surface. The average pore size matches very well with the liquid entry pressure based on the water contact angle of 93° on carbon surface. Therefore, we realized that the loose layer on the top surface is not the separation layer, while the structure at the interface between the carbon layer and the ceramic support plays a key role, which is shown in Figure 2d. The interface layer shows a nanoporous structure with pore size similar to the measured pore size. The structure of individual carbon wires was inspected by TEM (Figure 2e). The carbon wires have the multiwall carbon nanotube structure which is further confirmed by the Raman spectra in Figure 2f. However, a careful inspection of more than 100 wires indicates that all wires have the bamboo-knot-like structures, as enhanced by the black lines in Figure 2e, in the inner channel of the carbon nanotubes. Hence, although the carbon wires have the carbon nanotube structure, the inner channels are not available for transport. Therefore, the transport through the carbon layer must go through the gaps between the wires.

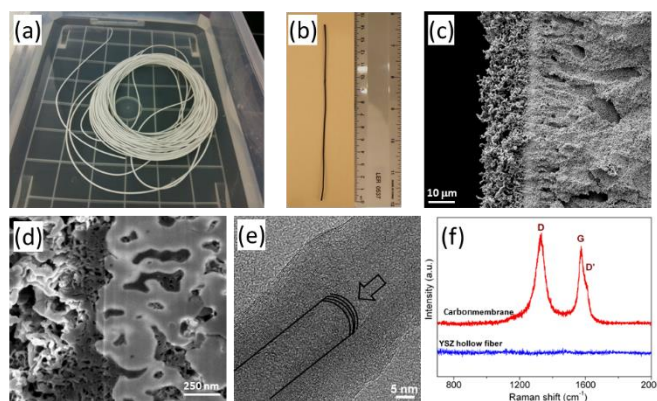


Figure 2: membrane characterization. (a) photo of the pristine YSZ hollow fiber; (b) photo the YSZ hollow fiber after carbon layer growth; (c) SEM of the carbon layer; (d) FIB SEM of the interface between the carbon layer and the support; (e) TEM of a single carbon wire; (f) Raman spectra of the carbon layer.

The performance of the membrane distillation is shown in Figure 3a. As expected, the water flux increased with temperature. At 90°C , the water flux of fresh water reached as high as 400 LMH. The water flux decreased with salinity. When 5% salt water used, the water flux at 90°C dropped almost to half of the fresh water value. Even though, the flux was 10 times higher than what was predicted from the Knudsen diffusion model. It was also much higher than the highest value reported from polymer

membranes (< 80 LMH), although the pore size of the reported polymer membranes were much larger (> 1 micrometer) than the carbon composite membranes.

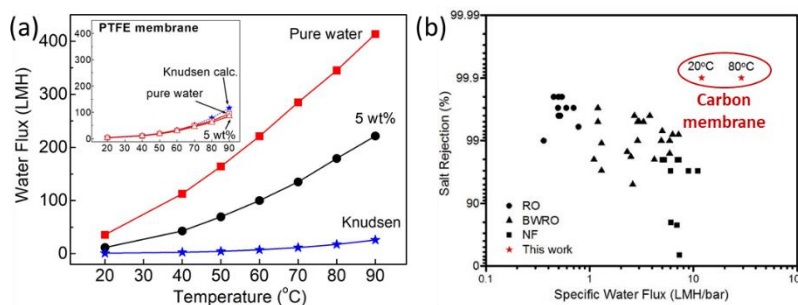


Figure 3: Membrane desalination performance. (a) MD water flux at different temperature and different salt concentrations; (b) the specific water permeance vs. salt rejection trade-off diagram of RO performance of different membranes.

The performances of RO and FO at 20 °C and 80 °C were listed in Table 1. The conductivity measurement of the fresh water after 48 h operation for all RO and FO processes indicate that the salt concentration is less than 1 ppm. Although the use of the water bath reduces the resolution of the salt concentration measurement by 10 times, the salt rejection was predicted to be larger than 99.9%. The comparison of the RO performance with other reported membranes is shown in Figure 3b. The overall performance at both 20 °C and 80 °C are order of magnitude higher than that of the polymer membranes. As for the performance of FO, the water flux of a commercial high flux membrane (HTI CTA) is around 9 LMH/bar with only 90% salt rejection. Hence, the flux of the carbon composite membrane even at 20 °C improved more than 5 times.

Table 1: Desalination performance of RO and FO of the carbon composite membranes.

The salt concentration for RO test is 2000 ppm, and for FO is 10%.

| Flux | 20 °C | 80 °C |
|--------------|-------|-------|
| RO (LMH/bar) | 15 | 29 |
| FO (LMH) | 58 | 74 |

Conclusions

A nanoporous carbon composite membrane supported on ceramic hollow fiber support was successfully developed. The membrane was applied to three membrane-based desalination processes including membrane distillation, reverse osmosis and forward osmosis. In all three processes the membrane achieved almost 100% salt rejection and 4~10 higher water flux than existing polymer membranes.

Acknowledgements

The work was supported by KAUST URF/1/1723 grant, KACST RGC/3/1614 grant, KAUST Special Partnerships Award number UK-C0016, SA-C0040, HKUST grant SRFI 11/SC02, and William Mong Institute of Nanoscience and Technology grant G5537-E.

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