

## Membrane Science emerging as a convergent scientific field with molecular origins and understanding, and global impact

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Membrane separation science concerns the selective transport of chemical species across molecularly designed barriers that are effectively two-dimensional. This interdisciplinary field has become the focus of many scientific communities in recent years including researchers in supramolecular chemistry, materials science, environmental science, polymer science (chemistry and physics), colloid and interface science, nanofluidics, structural biology, and biophysics. The great attraction of membrane science is the connection and visibility of the broad impacts of the final application, which is even apparent while working at the smallest scales. The “big picture” challenges that membrane science seeks to address include water purification, wastewater treatment, desalination, carbon dioxide capture, food and dairy processing, removal of pathogens (including viruses), hydrocarbon processing, and resource recovery from wastes, among a wide variety of applications. These topics span many urgent societally relevant themes of clean water and air, public health, climate change, waste minimization, and energy production.

The assembled special issue of PNAS illustrates the convergence emerging in the field across scales (from molecular self-assembly to industrial scale separations), disciplines (from biophysics to industrial scale hydrocarbon separations), materials (from membrane proteins to graphene), and approaches (molecular analysis to economic analysis). The issue also highlights emerging areas of interest including biomimetics, ion-ion separations, membrane process residuals (brine) treatment, hydrocarbon separations using membranes, and technologies for wastewater resource recovery.

The papers are organized by applications, and within each application area by scale and approach. In general, this special issue is roughly divided into three main sections: biologically inspired ideas and applications to separation processes in aqueous liquids, gas and hydrocarbon separations, and improving current membranes and membrane processes.

The first section of this special issue is on biologically inspired ideas for designing more selective and energy efficient membranes. A unique feature of biological membranes is the exceptional ion selectivity seen in membrane proteins as exemplified by the potassium channel, which has a 10,000:1 selectivity of potassium over sodium.<sup>1</sup> These channels inspire the work presented by Warnock *et al.* on lithium/sodium discrimination mechanisms in crown ether ligand-enhanced membranes.<sup>2</sup> Using experiments and simulations of single and mixed ion systems, they highlight fundamental principles to guide the development of single ion selectivity in synthetic membranes. Critically, they demonstrate the influence of ion dehydration and ligand-ion coordination on sorption, diffusion, and selectivity mechanisms in hydrated membranes.

At an engineered membrane level, in the next paper, Lounder *et al.* show a scalable approach with zwitterionic amphiphilic membranes to demonstrate impressive fluoride/chloride separation factors  $>6$  under both single and mixed monovalent salt solutions.<sup>3</sup> The membrane architecture, which results from the self-assembly of a random copolymer combining zwitterionic and crosslinkable hydrophobic segments, consists of a relatively impermeable hydrophobic matrix with water and ion permeable sub-nm zwitterionic channels. Specific differential interactions between anions and the zwitterions lead to differential transport rates for different anions while monovalent counterion transport remains the same, leading to effective salt separations. These membranes are also expected to have superior membrane fouling resistance based on previous work on similar membranes<sup>4</sup>.

In the next paper in this section, Di Vincenzo *et al.* combine molecules created using supramolecular chemistry (Imidazole quartets) with traditional interfacial polymerization to demonstrate scalable thin film composite desalination membranes with tunable salt selectivity and permeability. While artificial channels have been demonstrated previously to create macroscale membranes, desalination membranes have not been reported using artificial water channels. This paper reports on creating truly scalable brackish desalination membranes by adapting traditional interfacial polymerization where an aqueous diamine monomer solution impregnated in a porous support is reacted with an acid chloride monomer solution in an organic phase. Di Vincenzo *et al.* first mixed an ethanol-based solution of the Imidazole quartets that form a colloidal solution with an aqueous solution of phenylene diamine, which was then impregnated into a porous ultrafiltration support.<sup>5</sup> The standard trimesoyl chloride monomer was then added to the membrane to create a highly effective interfacially polymerized membrane that exceeds the performance of current brackish water reverse osmosis membranes.

The second section of the issue is focused on gas and hydrocarbon separations. The first paper in this section by Villalobos *et al.* is a unique demonstration of bottom-up synthesis with fine control of pore sizes in systems of only a few graphene layers to provide attractive selectivities between similarly sized gas pairs.<sup>6</sup> A challenge with creating scalable few-layer graphene membranes for separations has been engineering defects of controllable size to allow for size-based separation of gases. This is because complex post processing of intact graphene films by methods such as chemical/UV etching<sup>7,8</sup> and/or ion bombardment is needed. In this study, Villalobos *et al.* have achieved true bottom-up synthesis of polycrystalline graphene films with high pore density ( $10^{12} \text{ cm}^{-2}$ ) by controlled precipitation of carbon on nickel surfaces. The resulting membranes have very high gas permeances (H<sub>2</sub> permeance up to 38000 gas processing units and high gas pair selectivities for industrial important separations such as H<sub>2</sub>/CH<sub>4</sub>, H<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub>).

The second paper in the section is by Corrado *et al.*, where the free volume elements in polymeric gas separation membranes are engineered through the design of pentiptycene-based ladder polymers.<sup>9</sup> These membranes exhibit a unique trend of increased permeability over time with selectivity remaining relatively constant, contrary to aging-affected decreasing permeability commonly observed in current membranes. This counter intuitive trend is highlighted as a feature that is enabled by the concept of configurational free volume, where functional groups move out of the way of polymer free volume elements to provide additional access to these molecular microcavities, thus boosting permeability.

The next two papers in this section deal with the fascinating class of membrane materials known as Carbon Molecular Sieves (CMS) that are created by pyrolysis of high-aromatic content rich polymers. In the paper by Ma *et al.* the challenge of xylene isomer separations is tackled by creating a new type of CMS membrane based on a spirobifluorene-based polymer that provides a significant boost to membrane productivity relative to spirobisisindane-based polymers.<sup>10</sup> Moreover, these materials were observed to maintain high xylene isomer fluxes even under conditions of high xylene loading in the membrane, which contrasts with zeolite membranes that are known to have significant reductions in productivity under such conditions.

Next, Roy *et al.* provide an industrial perspective and a review of the current landscape of olefin-paraffin separations for petrochemical cracker operation.<sup>11</sup> They present a figure of merit for comparing various types of materials (including CMS membranes) and described design considerations with process modeling to enable sustainable and efficient olefin/paraffin separations. The paper provides a roadmap for development of implementable paraffin/olefin separations while considering practical, design and operational parameters in the context of scalability and long-term operation.

The final section of this special issue contains three papers on improving membranes and solving persistent challenges in operating membrane processes and in membrane synthesis. The first paper develops and applies new methods for valuing innovation in membrane systems. Recognizing that innovation in tightly coupled, multi-component systems can lead to unexpected changes in the value of improving a single component, Dudchenko *et al.* develop a probabilistic method for prioritizing innovation investments.<sup>12</sup> They demonstrate this method in an analysis of high salinity membrane-based desalination processes, helping researchers to develop key insights into the relative value of performance enhancements or cost reductions in key system components. They then apply their process-based cost optimization models to establish today's dominant technologies for high salinity brine concentration and set quantitative innovation targets for next-generation technologies seeking to displace the current state-of-the-art.

In the second contribution in this section, Scarascia *et al.* describe a unique method to prevent biofouling of anaerobic membrane bioreactors used for sustainable wastewater treatment and energy recovery.<sup>13</sup> They demonstrate the effectiveness of using a combination of bacteriophage treatment (akin to phage therapy proposed as medical antibiotic replacements) and UV disinfection. The authors show that the combined use of these two biofouling control strategies is indeed synergistic and represents a chemical free way of cleaning membranes.

Finally, a method is presented by Lu *et al.* to show how a simple additive (salt) during the interfacial polymerization process can be used to create thin film composite membrane polyamide nanofiltration (NF) with higher selectivity and permeability.<sup>14</sup> The authors illuminate the area of research of polyamide thin film composite membrane synthesis that has been in the domain of industrial art for the last few decades with low diffusion of knowledge to the general scientist even though these membranes are the poster children for the enormous impact membranes have already had on our society. For example, polyamide thin film composite RO membranes (featured on the cover of this issue) are used to treat over 60 billion gallons of water every year in many plants around the globe at an efficiency that approaches the thermodynamic limit of energy efficiency (for seawater desalination). Surprisingly, they are also among the least understood in terms of

chemistry-structure-function relationships. The science of these membranes and others reported in this issue are primed for what we think are explosive innovations in the service of the largest hurdles facing mankind in an increasingly resource constrained and polluted world.

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### **References**

- (1) D. A. Doyle, J.M. Cabral, R. A. Pfuetzner, A. Kuo, J. M. Gulbis, S. L. Cohen, B.T. Chait, R. MacKinnon, The structure of the potassium channel: molecular basis of K<sup>+</sup> conduction and selectivity. *Science*. 280, 69-77 (1998).
- (2) S. J. Warnock, R. Sujanani, E. S. Zofchak, S. Zhao, T.J. Dilenschneider, K. G. Hanson, S. Mukherjee, V. Ganesan, B. D. Freeman, M. M. Abu-Omar, C. M. Bates, Engineering Li/Na Selectivity in 12-Crown-4-Functionalized Polymer Membranes. *Proc. Natl. Acad. Sci. U.S.A.* this issue, xxxx-xxxx (2021).
- (3) S. J. Lounder, A. Asatekin, Interaction-Based Ion Selectivity Exhibited by Self-Assembled, Cross-Linked Zwitterionic Copolymer Membranes. *Proc. Natl. Acad. Sci. U.S.A.* this issue, xxxx-xxxx (2021).
- (4) Lounder, S. J.; Asatekin, A. Zwitterionic Ion-Selective Membranes with Tunable Subnanometer Pores and Excellent Fouling Resistance. *Chemistry of Materials* 33, 4408–4416 (2021).
- (5) M. Di Vincenzo, A. Tiraferri, V-E Musteata, S. Chisca, M. Deleanu, F. Ricceri, D. Cot, S.P. Nunes, M. Barboiu, Tunable membranes incorporating artificial water channels for high performance brackish/low salinity water reverse osmosis desalination. *Proc. Natl. Acad. Sci. U.S.A.* this issue, xxxx-xxxx (2021).
- (6) L. F. Villalobos, C. Van Goethem, K-J Hsu, S. Li, M. Moradi, K. Zhao, M. Dakhchoune, S. Huang, Y. Shen, E. Oveisi, V. Bureau, K.V. Agrawal, Bottom-up synthesis of graphene films hosting atom-thick molecular-sieving apertures. *Proc. Natl. Acad. Sci. U.S.A.* this issue, xxxx-xxxx (2021).
- (7) S. P. Koenig, L. Wang, J. Pellegrino, J. S. Bunch, Selective molecular sieving through porous graphene. *Nature Nanotechnology* 7, 728-732 (2021).
- (8) Huang, S.; Dakhchoune, M.; Luo, W.; Oveisi, E.; He, G.; Rezaei, M.; Zhao, J.; Alexander, D. T.; Züttel, A.; Strano, M. S. Single-layer graphene membranes by crack-free transfer for gas mixture separation. *Nature Communications* 9, 1-11 (2021).
- (9) T. Corrado, Z. Huang, D. Huang, N. Wamble, T. Luo, R. Guo, Pentiptycene-based Ladder Polymers with Configurational Free Volume for High Gas Separation Performance and Physical Aging Resistance. *Proc. Natl. Acad. Sci. U.S.A.* this issue, xxxx-xxxx (2021).
- (10) Y. Ma, N. Bruno, F. Zhang, M.G. Finn, R. Lively, Zeolite-like performance for xylene isomer purification using polymer-derived carbon membranes. *Proc. Natl. Acad. Sci. U.S.A.* this issue, xxxx-xxxx (2021).
- (11) A. Roy, S. Venna, G. Rogers, L. Tang, T. Fitzgibbons, J. Liu, H. McCurry, D. Vickery, D. Flick, B. Fish, Membranes for Olefin-Paraffin separation- An Industrial perspective. *Proc. Natl. Acad. Sci. U.S.A.* this issue, xxxx-xxxx (2021).

(12) A. Dudchenko, T. Bartholomew, M. Mauter, High impact innovations for high salinity membrane desalination. *Proc. Natl. Acad. Sci. U.S.A.* this issue, xxxx-xxxx (2021).

(13) G. Scarascia, L. Fortunato, Y. Myshkevych, H. Cheng, T. Leiknes, P-Y. Hong, UV and bacteriophages as a chemical-free approach for cleaning membranes from anaerobic bioreactors. *Proc. Natl. Acad. Sci. U.S.A.* this issue, xxxx-xxxx (2021).

(14) Y. Lu, R. Wang, Y. Zhu, Z. Wang, W. Fang, S. Lin, J. Jin, 2D Fractal Nanocrystals Templating for Substantial Performance Enhancement of Polyamide Nanofiltration Membrane. *Proc. Natl. Acad. Sci. U.S.A.* this issue, xxxx-xxxx (2021).