Dead Sea Water 2019 Workshop

Nanomaterials at the water-energy nexus

February 4-7, 2019

Program
and
Abstracts

ISRAEL SCIENCE FOUNDATION
ISRAEL DESALINATION SOCIETY
Lawrence Livermore National Laboratory
THE STEPHEN AND NANCY GRAND WATER RESEARCH INSTITUTE
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nature nanotechnology

Schedule and Oral Program

February 4th – Monday	
15:00	Arrival, check-in, registration, and poster setup
19:00	*Dinner*
21:00	**Reception**

February 5th - Tuesday	
08:30-08:40	Welcome
08:40-10:10	Session A: Carbon nanofluidics and similar materials
8:40-09:15	**Gerhard Hummer:** Nanoporous Membranes of Densely Packed Carbon Nanotubes Formed by Lipid-Mediated Self-Assembly
9:15-09:50	**Rahul Nair:** Tunable graphene-based membranes
9:50-10:10	**Armin Golzhauser:** Functional Nanomaterials from Surfaces: 2D Membranes for Water Purification
10:10-10:40	*Coffee break*
10:40-12:30	Session A: Carbon nanofluidics and similar materials
10:40-11:15	**Maria Drndic:** Quasi-2D membranes with holes at the water-energy nexus
11:15-11:50	**Hyung Gyu Park:** Water Transport under Low Dimensional Confinement
11:5-12:10	**Serena Casanova:** Surface-Controlled Water Flow in Nanotube Membranes
12:10-12:30	**Laxmi Pandey:** Bio-functionalized Tungsten disulfide (WS2) membrane for water desalination
12:30-13:30	*Lunch*
13:30-17:30	Social activity: Hiking tour in Nahal David reserve (pre-registration) or spa

February 5th - Tuesday

17:30-19:05	Session B: Applications of carbon materials and nanofluidics
17:30-18:05	**Menachem Elimelech:** Transport and Selectivity in Membranes with Sub-1-nm Pores
18:05-18:25	**Andrea Schafer:** Nanomaterial-ultrafiltration composite membranes for micropollutant adsorption: from material characteristics to process design
18:25-18:45	**Andriy Yaroshchuk:** Dielectric exclusion of ions from nanopores
18:45-19:05	*Coffee break*
19:05-20:00	Session B: Applications of carbon materials and nanofluidics (continued)
19:05-19:40	**David Jassby:** Nano-Enabled Electrochemistry at the Membrane/Water Interface
19:40-20:00	**Christopher Arnush:** Laser-Induced Graphene Membranes for Water Treatment
20:00	*Dinner*
21:00	**Poster Session/Refreshments**

February 6th - Wednesday

08:00-09:15	Breakfast
9:30-11:00	Session C: Physics of nanofluidic transport and separation
09:30-10:05	**Lyderic Bocquet:** Fluid Transport at Nanoscale: Fundamental Challenges Beyond Navier-Stokes?
10:05-10:40	**Uri Sivan:** The Last Nanometer: the Way Water Meets DNA and Solid Surfaces at x10,000,000 Magnification
10:40-11:00	**Yun-Chiao Yao:** Ionic Transport through Carbon Nanotube Porins
11:00-11:30	*Coffee break*
11:30-:12:45	Session C: Transport and separation phenomena
11:30-12:05	**Narayana Aluru:** Proton Conduction Based Layered Materials for Energy-Water Nexus
12:05-12:25	**Yoav Tsori:** Reversible Pore Gating in Aqueous Mixtures via External Potential

February 6th - Wednesday

12:25-12:45	**Jeff Sokoloff:** Water Filtration in Carbon Nanotubes Resulting From Electronic Friction at the Walls
12:45-13:45	*Lunch*
13:45-17:00	Free time (optional short local tour)
17:05-18:20	Session D: Nanofluidic electro-separations
17:05-17:40	**Maarten Biesheuvel :** Physics-based modeling of pressure-driven and current-driven water desalination
17:40-18:00	**Gilad Yossifon:** Active electrokinetic control of the concentration-polarization layer in a microchannel-Nafion membrane system
18:00-18:20	**Barak Shapira:** Energy Extraction and Water Treatment in one System: The idea of Using a Desalination Battery in Cooling Tower
18:20-18:50	*Coffee break*
18:50-19:30	Session D: Nanofluidic electro-separations
18:50-19:10	**Louis de Smet:** Application of redox-active intercalation nanomaterials in Capacitive Deionization: Experiment and model
19:10-19:30	**Matthew Suss:** Capacitive deionization: leveraging the electric double layer for selective water desalination
20:00	Gala Dinner

February 7th - Thursday

08:00-09:00	Breakfast & Check-out
09:00-10:30	Session E: Novel nanofluidic materials
9:00-09:35	**Alexandra Radenovic:** A tale of single pore in quasi 2D membrane
9:35-10:10	**Chuanhua Duan:** Exploring Fundamental Water Transport in Nanoporous Membranes Using Single Nanopores and Nanochannels

February 7th - Thursday	
10:10-10:30	**Peter Berg:** One-dimensional model for electro-kinetic transport in deformable nanochannels
10:30-11:00	*Coffee break*
11:00-11:55	Session E: Novel nanofluidic materials
11:00-11:20	**Volker Abetz:** Novel Ways to Generate Isoporous Block Copolymer Membranes in Flat Sheet Geometry
11:20-11:55	**Mihai Barboiu:** Artificial Water Channels may be most innovative new idea for water purification membranes and aqueous separations
11:55-12:15	Summary and Closing Remarks,
12:15-13:15	Free lunchtime & Check-out
13:15-17:00	Organized departure

Oral Abstracts

List of Submitted Oral Abstracts
(in alphabetic order of presenting authors)

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Novel Ways to Generate Isoporous Block Copolymer Membranes in Flat Sheet Geometry

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A decade ago so-called „isoporous integral asymmetric membranes" from block copolymers have been reported for the first time. A block copolymer solution is cast on a porous non-woven as an approximately 200 μm thick film and after some time, which allows part of the solvent to evaporate, immersed into a precipitant (usually water).[1,2,3] This process is a combination of the self-assembly (S) of the block copolymer by microphase separation in the concentrating solution during evapration of solvent and a non-solvent induced phase separation (NIPS) when it is quenched in the precipitation bath and has been often abbreviated as SNIPS.

Most SNIPS studies reported so far have been carried out on polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) and therefore we also use this block copolymer in the studies presented here. SNIPS was so far mostly applied for the preparation of flat sheet membranes and one of the major draw backs is the relatively large consumption of block copolymer per area, which is a problem if the usually expensive block copolymer is not available on large scale. Here we report a novel casting technique, which reduces the block copolymer consumption in membrane production significantly (> 90%) by using a profile roller coating process.[4] Another challenge in fabrication of integral asymmetric membranes with an isoporous top layer is the alignment of the cylindrical pore forming microdomains in the top layer. Often the processing windows are rather small to obtain the desired structure. Here we present studies where an electric field was applied during membrane preparation and it is shown that such an external field enhances the formation of highly ordered isoporous membranes.

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4. Bucher, T.; Filiz, V.; Abetz, C.; Abetz, V., Formation of Thin, Isoporous Block Copolymer Membranes by an Upscalable Profile Roller Coating Process - A Promising Way to Save Block Copolymer. *Membranes* **2018**, *8*, 57.

Laser-Induced Graphene Membranes for Water Treatment

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Laser-induced graphene (LIG) is a three-dimensional porous electrically conductive graphene material generated by irradiation of polymer substrates with a 10.6 mm CO_2 laser. Here we show examples of LIG as membranes for advanced water treatment with variation of pore size and solute rejection. Variation of fabrication conditions can tailor both the surface chemical composition and the surface properties from superhydrophillic to superhydrophobic. LIG on dense and porous substrates exhibited an antifouling effect due to many factors including the unique surface structure of LIG. Specifically, on polyethersulfone porous substrates common to separation membranes, LIG surfaces were shown to strongly resist biofilm growth. Since the LIG-membranes are electrically conductive, an active antimicrobial action was seen using the LIG-membranes as porous electrodes during filtration of contaminated waters. Mechanisms of action will be explained. This method to "laser-print" electrically conductive graphene on membranes and dense substrates will enable many new applications in water treatment and separations.

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2. Singh, S. P.; Li, Y.; Be'er A.; Oren, Y.; Tour, J. M.*; **Arnusch, C. J.*** Laser-Induced Graphene Layers and Electrodes Prevents Microbial Fouling and Exerts Antimicrobial Action *ACS Applied Materials and Interfaces* **2017,** *9* (21), 18238-18247.

3. Li, Y.; Luong, D.X.; Zhang, J.; Tarkunde, Y. R.; Kittrell, C.; Sargunaraj, F.; Ji, Y.; **Arnusch, C. J.***; and Tour, J. M.* Laser-Induced Graphene in Controlled Atmospheres. From Superhydrophilic to Superhydrophobic Surfaces. *Advanced Materials* **2017**, 1700496.

4. Singh, S. P.; Ramanan, S.; Kaufman, Y.; **Arnusch, C. J.*** Laser-Induced Graphene Biofilm Inhibition: Texture Does Matter. *ACS Applied Nano Materials* **2018***, 1 (4)*, 1713–1720.

One-dimensional model for electro-kinetic transport in deformable nanochannels

Peter Berg, University of Alberta, Canada

We present a theoretical study of nonlinear coupling between wall deformation and water & counter-ion flows in a charged, deformable nanochannel. The Stokes-Poisson-Nernst-Planck equations are employed to describe the electro-kinetic flow inside the channel while the viscoelasticity of the surrounding medium is governed by a Kelvin-Voigt model.

Following a dimensional reduction, the case of locally electro-neutral (LEN) channels is governed by a single, nonlinear ordinary differential equation, with closed-form solutions for small deformations. The quantitative response of the walls' relaxation dynamics and the channel's electro-kinetic transport is investigated in different charging regimes. Within the framework of non-equilibrium thermodynamics of electro-kinetic transport, closed-form formulae for Onsager coefficients are derived, yielding a symmetry breaking.

Furthermore, an extension of the model is presented for electro-actuators that operate through a coupling of electrical and mechanical responses in closed nanochannels in which LEN is violated near the electrodes. Numerical methods and results are presented, highlighting the significance of the fluid and charge redistribution for elastic deformations of the nanochannel.

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Surface-Controlled Water Flow in Nanotube Membranes

Serena Casanova and Davide Mattia – University of Bath, UK

A conspicuous strand of work in the past few decades has been dedicated to disclosing the existence of flow enhancement in carbon nanotubes and explaining the origin of the phenomena [1]. Following this effort, interest rose into exploiting fast water transport in materials different from ideal graphitic carbon, ranging from defected carbon nanotubes produced via chemical vapour deposition [2] to boron nitride nanotubes interesting for their rejection properties [3].

Hydrophobicity has been used as a means to correlate flow enhancement to surface properties [4], however this has sometimes been proved to be an oversimplified way to describe the phenomena, not explaining reported high flows in strongly hydrophilic nanochannels [5] and low enhancement in boron nitride nanotubes with carbon-like hydrophilicity [6, 7].

In this work, we aim at separately describing the effect that a change in carbon nanotube structure with the introduction of defects and a change in chemistry with the introduction nitrogen has on water permeance. This is achieved by combining experimental results and molecular dynamics.

Carbon nanotubes and carbon nitride nanotubes with a broad range of diameters (from ~ 10 nm to ~ 80 nm) are synthesized in the pores of anodic alumina templates and tested in a dead end filtration setup. A model true to the chemical structure of the synthesized nanotubes is built from the material spectroscopy results and used for molecular dynamic simulations of flow, which agreed well with the experimental findings.

Our approach explains the obtained drops in water permeance going from graphitic to defected carbon nanotubes and carbon nitride nanotubes as an effect of changes in solid-liquid interaction, and specifically the diffusion of water on the nanotube inner surface and the work of adhesion for the liquid-wall phase boundary.

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Application of redox-active intercalation nanomaterials in Capacitive Deionization: Experiment and model

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Abstract

Capacitive Deionization (CDI) is a water desalination technology in which electrodes in an electrochemical cell, connected to an external circuit, remove ions present in water. Conventionally, carbon has been the choice of material for the electrodes due to its low cost, high specific surface area, electronic conductivity, and ion mobility within pores. The ions are stored at the pore walls of these electrodes in an electrical double layer (EDL). Nanomaterials like Prussian blue analogs (PBAs), studied as a potential electrode material for sodium ion batteries, have a different ion storage mechanism, referred to as ion intercalation. Taking inspiration from the field of energy storage, we investigate one such PBA, nickel hexacyanoferrate (NiHCF), as an electrode nanomaterial for CDI.[1-3] It is of interest due to its low cost and low toxicity, open framework structure (resulting in facile (de)insertion of cations), high charge intake capacity (~ 60 mAh/g) and a size-based selectivity towards various cations. NiHCF nanoparticles are mixed with carbon and a polymeric binder and the resulting blend is rolled into 200 μm thin electrode sheets. The desalination performance of these electrodes, including the salt adsorption capacity (SAC), average salt adsorption rate (ASAR) and energy consumption are studied for operational variables like the applied current density and feed concentration.[4] A clear trend in the values of performance parameters is observed with changing operational variables. In addition, a definitive performance comparison between carbon and PBA electrodes is made to accurately assess the benefits and drawbacks of PBA electrodes in CDI. Finally, a simple predictive model, based on a continuous stirred tank reactor and Frumkin adsorption isotherm, is devised for a single salt solution. It describes the dynamics of the effluent salt concentration, resulting in SAC and ASAR estimations, as well as the cell voltage, leading to an evaluation of energy consumption.

References

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2) Theory of water desalination with intercalation materials, Singh, Bouwmeester, de Smet, Bazant, Biesheuvel *Physical Review Applied* **2018**, *9*, 064036.
3) Timeline on the application of intercalation materials in Capacitive Deionization, Singh, Porada, Biesheuvel, de Gier, de Smet – under review.
4) Application of redox-active intercalation nanomaterials in Capacitive Deionization: Experiment and modeling, Singh, Porada, Biesheuvel, de Smet – manuscript in preparation.

Exploring Fundamental Water Transport in Nanoporous Membranes Using Single Nanopores and Nanochannels

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Nanoporous membranes play important roles in a wide range of industrial applications including water desalination/purification, materials processing, batteries/fuel cells, and sensing. Further development of nanoporous membranes requires thorough understanding of their transport properties. However, the current approach of studying nanoporous membranes in their final applications , e.g. in the form of a membrane for water purification, limits our understanding of fundamental mass transport inside due to the structure complexities. An alternative approach to study nanoporous membranes is to study them in the form of their basic constituents, e.g. single nanopores/nanotubes/nanochannels. This new approach, now referred as the nanofluidic approach, opens new avenues to further develop nanoporous membranes and has attracted great attention over the last ten years.

In this talk, I will present two of our recent works on exploring new fundamental water transport in nanoporous membranes using single nanochannel/nanopores. First, I will present a study of fast water transport in graphene nanochannels. Graphene nanochannels are the basic components of graphene oxide (GO) membranes which hold great promise for water desalination and nanofiltration but has yet remained controversial. My group has developed a new flow measurement method based on capillary filling and a novel hybrid channel design that can accurately measure hydraulic resistance of single graphene nanochannels. I will show how we use this method to discover a wide range of water slippage in graphene nanochannels and explain what causes these variations.

Second, I will discuss how we can also use the hybrid channel design to explore kinetic-limited ultimate water evaporation from single nanochannels and nanopores. Single nanochannels/nanopores are the basic components of evaporative nanoporous membranes, which have found great applications in various membrane distillation technologies and electronic cooling. I will demonstrate that the ultimate evaporation fluxes from single nanochannels/nanopores can break down the kinetic limits predicated by the classical Hertz-Knudsen equation by an order of magnitude. The strong dependence of the kinetic-limited evaporation flux on nanochannel/nanopore size, shape, interval distance, as well as operation conditions (e.g. temperature and humidity) will also be discussed.

FUNCTIONAL NANOMATERIALS FROM SURFACES: 2D MEMBRANES FOR WATER PURIFICATION

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Clean water is a global challenge, and membrane filtration is a key technology to achieve it. There are growing research efforts to explore the use of 2D carbon materials as nanoconduits for molecular transport and separation [1]. Surface science plays a prominent role in these activities as molecular surfaces layers can serve as precursors in the fabrication of nanomembranes. Here, we report on the fabrication and application of carbon nanomembranes (CNMs) with sub-nanometer channels that prove to be excellent water filters, combining a high selectivity with an exceptionally high water permeance. The CNMs are fabricated via the electron induced cross-linking of self-assembled monolayers (SAMs) [2]. CNMs made from terphenylthiol SAMs result in a ~1.2 nm thick membrane perforated by sub-nanometer channels with diameters below ~0.7 nm and areal densities of ~10^{18} m^{-2}. When tested as filter membranes, it was found that the CNMs efficiently block the passage of most gases and liquids. However, water passes through with an exceptionally high permeance of ~1.0×10^{-4} $mol\cdot m^{-2}\cdot s^{-1}\cdot Pa^{-1}$ [3]. This suggests that water fast and cooperatively translocates through a channel with a rate of ~66 $molecules\cdot s^{-1}\cdot Pa^{-1}$. As the fabrication of CNMs is scalable, this finding can open new paths towards the use of 2D materials in water purification.

Keywords: Self-Assembled Monolayer, Carbon Nanomembranes, Filtration

References

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Tunable graphene-based membranes

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Keywords: Graphene, graphene-based membranes, van der Waals pressure

Permeation through nanometre-pore materials has been attracting unwavering interest due to fundamental differences in governing mechanisms at macroscopic and molecular scales, the importance of water permeation in living systems, and relevance for filtration and separation techniques. Latest advances in the fabrication of artificial channels and membranes using two-dimensional (2D) materials have enabled the prospect of understanding the nanoscale and sub-nm scale permeation behaviour of water and ions extensively. In particular, graphene oxide (GO) membrane containing 2D graphene capillaries shows unique permeation properties such as ultrafast permeation of water and molecular sieving. In my talk, I will discuss our recent results on molecular and ionic permeation properties of GO membranes and its prospect for several applications.

Reference

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Bio-functionalized Tungsten disulfide (WS2) membrane for water desalination

Laxmi Pandey, * Bedanga Sapkota, Meni Wanunu

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The fabrication of a semipermeable membrane which allows the passage of water with high flux, but no ions, is very crucial for water desalination. To overcome the limitations of currently used polymeric membranes, researchers have been focused on 2D materials because of their minimum material thickness since they can be exfoliated into single layers, high mechanical strength, and chemical robustness.

The membrane formed by layer stacking of 2D nanosheets consists of nanochannels. To sieve the ions utilizing both size exclusion as well as charge exclusion effect, the functionalization of nanochannels by appropriate charged molecules is very important. My research will be focused on formation of WS_2 (which is the most robust and the least studied 2D material for water desalination application) membranes which consists of bio-functionalized porous nanosheets.

Porous WS2 nanosheets obtained from ultrasound treatment will be mixed with the solution containing positively charged peptides. Because of peptide-peptide interaction and solid-peptide interaction, the peptides will self-assemble on the WS_2 sheets. The positively charged WS_2 nanosheets thus obtained will be subjected for interaction with single stranded DNA and double stranded DNA separately. As a result, DNA will be sandwiched between two positively charged WS_2 sheets. Then, the solution containing bio-functionalized WS_2 sheets will be filtered to form a membrane which will contain nanochannels. The membrane thus prepared will be used for water desalination. The first hypothesis of the proposed research is that the charged surface of membrane and size of Nano-channels enhance salt rejection by ion exclusion and size exclusion effect. Second hypothesis is that the sandwiched DNA increases the interlayer spacing which can increase the water flux. The pores on nanosheets further help to increase the water permeance.

Process parameters for photocatalytic membrane as nanofluidic reactors

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Advanced water treatment technologies including membrane technology or oxidation processes can be an important contributor in the water-energy nexus due to the significant energy consumption [1]. The utilization of sunlight for the photocatalytic degradation of water contaminants can complement other treatment processes that cannot achieve effective micropollutant. Low concentration, low molecular weight and persistence pose significant challenges for treatment processes. Photocatalytic water treatment processes often face difficulties such as long reaction times, mass transfer limitations and requirement for high energy light of specific wavelengths [2]. Confining the photocatalytic reaction in membrane pores as nanofluidic reactors alters both mass transfer and apparent reaction kinetics, to the extent that the required reaction times are reduced to applicable values [3].

In this study anodic aluminium oxide (AAO) membranes (SmartMembranes FlexiPor 200 nm pore size) are coated with a photo-active TiO_2 thin-film, via atomic layer deposition (ALD). The process parameters of the degradation of methylene blue (MB) as a simple organic, used in the first instance for method development, are studied in a custom-built photocatalytic membrane system. The light source is a ultraviolet light emitting diode (UV-LED) with a wavelength of 365 nm. Influences of membrane flux, MB concentration, and light intensity are examined for single-pass flow-through conditions.

The here presented system shows the capability to remove significant amounts (30 - 90 %) of MB in a single-pass. The influence of membrane flux and MB concentration on the MB removal fit to trends reported for similar systems. However, the measured reaction rated differ from Langmuir-Hinshelwood kinetics, which are often applied for photocatalytic reactions in water. Insights into the rate determining parameters are presented in this work with an indication of pore dimension. In summary, the photocatalytic membranes have shown high activity even at low light intensities, comparable to the UV content of the sunlight (~50 % MB removal at 1 equivalent sun) and hence offer significant prospects for water treatment that may be able to effectively solve the micropollutant challenge.

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Energy Extraction and Water Treatment in one System: The idea of Using a Desalination Battery in Cooling Tower

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Abstract

The use of sodium manganese oxide as intercalation electrode for water treatment (referred as a "desalination battery" [] and "hybrid Capacitive Deionization"[]) was recently explored. Herein, we examine the feasibility of using a desalination battery, which consists of crystalline $Na_4Mn_9O_{18}$ as the cathode and $Ag/AgCl/Cl^-$ electrode as the anode, to extract energy from low-grade waste heat sources. The sodium manganese oxide electrode was produced via solid state synthesis and sprayed coated onto graphite foil. The sodium manganese oxide electrode shows temperature dependence of electrode potential, namely, $\partial E / \partial T$, of -0.63mV/K, (whereas, the Ag/AgCl mesh electrode shows much lower dependence of potential with respect temperature (<0.1 mV/K)). In order to demonstrate ion removal capabilities together with the feasibility of thermal energy conversion, a flow battery system was constructed. Thermally regenerative electrochemical cycles (TREC) were constructed for the flow battery cell. Thermal energy conversion, in this particular system, was shown to be feasible at relatively low C-rate (C/19) and temperature variation between 30 and 70 °C.

Water Filtration in Carbon Nanotubes Resulting From Electronic Friction at the Walls

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Abstract

In this talk, a mechanism for removal of salt from salt water is discussed, which is results from friction due to Ohm's law heating, resulting from motion of an electron charge induced in the tube walls by the water molecules' dipoles and the ions' charges. The filtration occurs because this friction is larger for salt ions than for water molecules. Friction due to Ohm's law heating might also provide an explanation for the observation by Secchi, et. al., that the flow velocity of water in carbon nanotubes increases rapidly as the tube radius decreases from 50 to 15nm, which does not occur for boron nitride nanotubes which are insulators. This friction has the right magnitude to produce the slip-lengths reported found by Secchi, et. al. One possibility is that the nanotubes in this experiment were metallic, whose conductivity becomes large as their radius decreases, due to ballistic conduction. Another possibility is that when the tube circumference drops below the electron mean free path, the wall switches from behaving as a two dimensional conductor to behaving as a one dimensional conductor for which the electrons are more strongly localized. For sufficiently small conductivity, small distortions of the localized states can provide the dominant contribution to the induced charge, rather than current flow, thus reducing the Ohm's law heating.

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Capacitive deionization: leveraging the electric double layer for selective water desalination

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Capacitive deionization (CDI) is a fast-emerging water desalination technology, most often applied to brackish water desalination and water softening.[1,2] CDI cells desalt feedwaters by storing ions in electric double layers within micropores of electrically charged carbon electrodes. CDI cells have demonstrated a size-based ion selectivity wherein smaller ions are preferentially electrosorbed over larger ions due to ion volume exclusion interactions.[3] Selective ion removal is a highly desirable feature in water treatment systems, as selectivity mechanisms can be leveraged towards preferential and energy efficient removal of toxins and other undesirable ions. We here demonstrate that the size-based selectivity exhibited by microporous CDI electrodes can be substantially boosted through addition of chemical charge to micropores via surface functionalization.[4] We develop a theory of size-based ion storage in micropores including the effect of chemical charge,[5] which predicts such enhancements and demonstrates they are a result of enhanced counterion crowding in functionalized micropores. Desalting an electrolyte consisting of competing potassium and lithium ions, we demonstrate that a surface functionalized (oxidized) cathode increases the selective removal of the smaller potassium ion. Contrary to model predictions, the largest enhancements are measured at lower cell voltages, for example from a selectivity factor of ~1 for typical electrodes to 1.8 for surface functionalized electrodes at 0.4 V charging voltage. This counter-intuitive result is demonstrated to be due to significant cathode chemical surface charge degradation occurring at higher cell voltages, a phenomenon which has not been previously reported upon in the CDI literature to our knowledge. Model results show that achieving stabilized surface groups at high electrode potentials can lead to further enhancements in size-based selectivity factors achievable by CDI electrodes.

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Reversible Pore Gating in Aqueous Mixtures via External Potential

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We examine theoretically porous membranes in aqueous mixtures. We show that the membrane's pores can be reversibly gated from `off' (co-solvent-rich, poor conductor of ions and other solutes) to 'on' (water-rich, good conductor) states by an external potential. The transition voltage or charge for switching depends on the membrane hydrophilicity/hydrophobicity, the salt content, the preferential solvation of the salt ions, and the temperature. These parameters also determine whether the filling transition is abrupt or gradual. We then look at how the pore-filling transition affects chemical reactions undergoing in the mixture. We find that pore-filling can dramatically accelerate the chemical kinetics. Such control of reaction kinetics by an external potential may be a useful new addition to the existing arsenal to control the temporal and spatial extent of reactions. This kind of control is especially suited for devices guiding reagents flowing in microfluidic channels adjacent to micrometer-scale electrodes.

Ionic Transport through Carbon Nanotube Porins

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Channels are the functional units for membranes used in separation technologies. To achieve fine control of molecules down to atomic level, confined water flow through the channels and selectivity of desired materials are critical. Carbon nanotubes (CNTs), whose diameters are comparable to protein pores (0.6-1.5 nm) and which have narrow hydrophobic inner channels that enable fast transport of water and ions, represent an attractive platform for building separating membranes. Moreover, the rigid structure and chemical robustness of CNTs allow well-controlled pore sizes for diverse *ex vivo* applications. In our group, we have established methods to create carbon nanotube porins (CNTPs)—ultrashort CNTs wrapped with phospholipids that are called. In this study, we quantify the ionic conductance and selectivity of CNTPs with diameters of 0.8 nm and 1.5 nm, respectively. We report the conductance of individual CNTPs, as well as the scaling of the conductance with the electrolyte concentration. We also use reversal potential measurements under different electrolyte concentration ratios to characterize CNTP ion transport selectivity. Comparison of transport efficiencies and selectivities of two different diameter CNTPs provide the insights for the mechanisms of nanofluidic transport in those pores. Our studies lay the groundwork for using these new materials in a variety of water technology applications such as desalination and reverse electrodialysis.

Active electrokinetic control of the concentration-polarization layer in a microchannel-Nafion membrane system

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The length of the concentration-polarization layer within a microchannel-permselective membrane system is indirectly prescribed by the complicated competition between several mechanisms which are primarily dictated by the system parameters and applied voltage [1]. In contrast, here we propose a novel mode of directly controlling the diffusion layer length, regardless of the dominating over-limiting-current mechanism and system parameters, via the embedding of an electrode array within the microchannel interfacing a permselective medium. With these electrodes, three different electroconvection mechanisms – Induced charge Electroosmosic (ICEO) [2], Alternating current electroosmosics (ACEO) [3] and Electrothermal flow (ET) [4] - can be activated, either separately or together, to control the diffusion layer length via the emergence of vortex structures that locally stir the fluid [5, 6]. The choice of which mode/s to activate depending on the desired result and relevant application. This electrokinetic-based spatio-temporal control of the diffusion layer may bring new functionalities to concentration-polarization based microscale applications, e.g. on-chip electro-dialysis, separation and preconcentration of analytes.

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Poster Abstracts

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Dehydration assisted selective ion permeation through Graphene Oxide Membranes

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Membranes made of graphene oxide laminates show exceptional permeation properties. However, their use in ionic sieving and desalination is limited by a cut-off diameter of 9 Å, defined by their ≈ 14 Å interlayer capillary width. A smaller, yet tunable, interlayer spacing in graphene oxide membranes would result in a finer and controllable ionic sieving. Nevertheless, this control has proved to be a challenge due to swelling of the inter-layer capillaries. Here, we control the interlayer capillary width of graphene oxide membranes from ≈ 9.8 Å to ≈ 6.4 Å by physical confinement and show that precise ionic sieving can be achieved. Unlike the size exclusion mechanism, ion permeation through graphene oxide membranes with sub-nanometre channels is governed by the energy barrier for the ion to enter the capillary, which is dictated by the strength of interactions between the ion and surrounding water molecules. The measured energy barrier values for K^+ ion are 72.3 kJ/mol and 20.2 kJ/mol for graphene channels with spacing 7.9 and 9.8 Å respectively. The observed ion permeation rate decreased exponentially with decreasing capillary width, whereas water permeation rate only decreased by a factor of 2 maximum. The relatively small impedance for water permeation is explained by the smaller energy barrier for water molecules entering the channels due to the weaker water-water interaction and enhanced water transport through graphene nano channels. In addition, we have also demonstrated an easy and scalable method to obtain swelling controlled graphene oxide membranes with 99.7% NaCl salt rejection.

Theory of simultaneous desalination and electricity generation via an electrodialysis cell driven by spontaneous redox reactions

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Abstract

In recent years, the expanding demand of society for clean water and energy has become a global concern. Moreover, the interrelationship between these two commodities, known as the ‘water-energy nexus’[1,2], has become an increasingly complicated economic problem. Energy production process, such as fuel extraction and processing and electricity generation such as thermoelectric, hydroelectric and other renewable technologies consume tremendous amount of water. Oppositely, reverse osmosis and electrodialysis[3] water desalination, purification and softening, and wastewater remediation can require a substantial portion of the energy supply.

Many studies name electrochemical desalination systems as a leading candidate technology for economical water desalination. Such techniques as capacitive deionization,[4,5] desalination batteries,[6–11] and desalination redox flow batteries[12,13] operate in energy consuming charging/discharging cycle. In 2018, the Suss lab proposed a desalination fuel cell (DFC) which requires only chemical energy as input and desalinates water continuously while simultaneously producing electricity.

So far, this device has been demonstrated experimentally as a proof-of-concept. Developing the theory underpinning such a device will contribute to improved understating crucial and underpin future development and optimization of desalination fuel cells and desalination flow batteries as well.

We present a mathematical model for the desalination fuel cell. We propose a transport model describing electromigration of salt ions through non-ideal ion-exchange membranes driven by spontaneous redox reactions at the electrodes. To our knowledge, such a cell, which basically performs electrodialysis driven entirely by chemical energy, has never before been modeled. We further highlight key mechanisms underpinning desalination performance and elucidate potential optimization strategies.

How Graphene and Hexagonal Boron Nitride get electrified in water?

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The recent emergence of nanofluidics has highlighted the exceptional properties of graphene and its boron-nitride counterpart as confining materials for water and ion transport [1-4]. Surprisingly ionic transport experiments have unveiled a considerable electrification of the water-BN surfaces, with a contrasting response for its water-carbon homologue [1]. This surface charging was conjectured to originate in the differential hydroxide adsorption at the surface of these twin materials, but the considerable challenge of simulating the elusive hydroxide ion has precluded a proper explanation up to now.

In this talk, we report free energy calculations based on *ab initio* molecular dynamics simulations of hydroxide OH^- ions in water near graphene and hexagonal boron nitride (h-BN) layers. Our results disclose that both surfaces get charged through hydroxide adsorption, but via strongly different mechanisms. The hydroxide species shows strong chemisorption on the h-BN surface, but only weak physisorption on the graphene surface [5].

Interestingly OH^- is accordingly shown to keep a very fast lateral dynamics and interfacial mobility in the physisorbed layer on graphene. This behavior sheds new lights on the experimental results on ionic transport in carbon channels. Taking into account the resulting large ionic surface conductivity, an analytical transport model allows to reproduce quantitatively the experimental data [5].

Our results offer new foundations for the chemical reactivity of carbon and BN materials in water and suggest new perspectives in the context of advanced membrane technologies for water purification and energy harvesting [6].

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Multiterminal 2D nanopore device

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The complete understanding of ionic transport through solid-state nanopores can open new pathways to applications. Particularly, a detailed mechanism of conduction in ion channels would provide insight into signal transmission within the neuronal network. The Coulter counter scheme that is often used to study ionic transport through a 2D nanoporous membrane does not allow active modulation of epy nanopore charge since it relies on the variation of the solution pH.

Recent progress in fabrication of the sub-nanometer pores in 2D materials has revealed interesting nonlinear current-voltage characteristics[1] (CVC), including a Coulomb blockade that is defined by the nonlinear CVC of MoS2 nanopores manifesting as a suppressed conductance area around $V \leq 0.4V$. This suppression becomes stronger with growth of ion valence z but it is also strongly linked to charges hosted inside the pore. The Coulomb blockade effects observed in single ion junctions in sub-nm nanopores act analogously to quantum dots–the first observation of mesoscopic many-body effects in an ionic system.

Here suggested is the use of a field effect transistor-based system which integrates a nanopore in a conductive channel in order to study the correlation between the in- plane DC electronic transport and the ionic transport through the pore simultaneously in sub-nanometer pores and active charge modulation.

This method will allow us to achieve a highly sensitive and reliable read-out method for the characterization of ionic transport through the nanopore.

This work was supported by the ESKAS (nr 2017.0247), Eurotech Postdoc Programme (Project 'Electronic read-out of ionic transport through the solid-sfafe nanopore').

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Biomimetic carbon nanotube-containing membranes for water purification

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A common practice nowadays for obtaining fresh water is the desalination of seawater using membrane-based methods. Cell lipid membranes, containing highly selective proteins, provide superior levels of differentiation and transport control compared to industrially available reverse osmosis (RO) membranes. Biomimetic membranes can theoretically achieve such exceptional permeability and selectivity by harnessing the benefits of nature's design in the architecture of synthetic membranes. Our hypothesis is that we can realize the advantages of biological membranes in a synthetic biomimetic membrane using carbon nanotube porins (CNTPs) of tunable diameter, embedded within a barrier membrane affixed to a robust support.

Preliminary results of our collaborators show the possibility of successfully incorporating a single CNTP into a lipid layer as well as implanting several CNTPs into liposomes. Our goal is to upscale the setup by developing a macroscopic array of pore-spanning lipid or polymer membranes with embedded CNTPs. Following earlier strategies researched in our group, we developed a micro-setup to assemble macroscopically large membranes and investigate their characteristics. We tested several types of commercially available porous supports, such as ultrafiltration membranes, to assemble reproducibly a pore-spanning lipid-like matrix membrane on top of the support. The matrix membrane was tested in terms of adhesion to the support and integrity (defect rate). We will present updated proof-of-concept results assessing water permeability, ion permeability, and electrical properties of the pore-spanning membranes to verify integrity and selectivity before and after incorporation of CNTPs. Such measurements are performed in a dedicated micro-cell using osmotically-driven transport regime.

Developing and exploring this novel system serves two main purposes. First, it highlights preparation challenges and limitations (such as concentration polarization) not apparent in nano-scale systems. Second, we assess the performance and potential of the biomimetic membranes as a future alternative to the currently used membranes.

Water filtration with inch-sized carbon nanomembranes

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Energy-efficient water treatment is among the highest priorities of the modern society. In this context, novel nanostructured materials hold an attractive potential to provide better performance at a lower price. Particularly, multiple nanocarbons, such as CNT and graphene, have been proven to be promising with regard to facile and selective water permeation. Herein, we report for the first time on water filtration experiments with supported carbon nanomembranes (CNM) of several centimeters in diameter. The material of interest represents ultrathin porous films which are formed out of polyaromatic molecules upon electron-induced carbonization.

This study focuses on hybrid membranes comprising a 10-nm thick CNM as an active layer and a commercial Microlon© membrane as a carrier. As shown by pure water flux measurements, its permeability coefficient in the support is two orders of magnitude greater compared to that in the composite, indicating no disturbance to the properties of CNM. Ion rejection tests with NaCl, Na_2SO_4, $MgCl_2$, and $MgSO_4$ revealed that the sulfates are rejected more readily than the corresponding chlorides, whereas in all cases the salt passage grows with concentration. These observations point to the Donnan's effect and suggest that CNM is negatively charged.

We performed further experiments with solutes possessing bulkier anions, and Fig. 1 summarizes the output. As evidenced, the filtration characteristics of the CNM composites exhibit a clear size cut-off which means rather narrow size distribution of their pores. In fact, there are a few variable parameters in the CNM synthesis, and the results obtained demonstrate the possibility of using CNM as a platform for designing water purification membranes. For instance, 1-nm thick CNM based on densely packed self-assembled monolayers seem to be intriguing in terms of osmotic processes.

This work was kindly supported by the Minerva Fellowship Program.

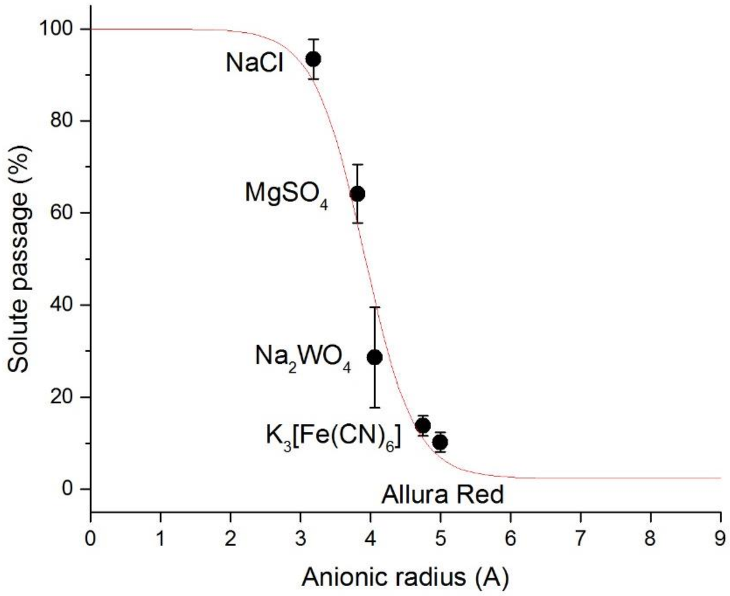

Figure 1. Ion rejection in CNM-based composite membranes. Hydrated radii of anions are plotted.

A Maxwell-Stefan approach to probe sensitivity of flux coupling in Forward Osmosis

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The goal of this study is to quantify the interactions between fluxes of different components in forward osmosis (FO). Specifically, the interactions of the draw solute with water and feed solutes is interesting because the draw solute flux is oppositely directed, and could thus potentially hinder water and/or feed solute flux (Xie et al. 2012).

To this end, FO is studied in silico using a Maxwell-Stefan model. The Maxwell-Stefan theory explicitly relates interparticle friction to thermodynamic gradients (Krishna and Wesselingh 1997; Fornasiero, Prausnitz, and Radke 2005; Paul 2004). The model is first calibrated using experimental data to yield realistic water and draw solute fluxes for a given set of driving forces. Subsequently, the sensitivity of the water and feed solute fluxes towards the binary Maxwell-Stefan diffusion coefficients and solute partitioning coefficients was assessed.

It was found that feed solute rejection is generally not sensitive towards draw solute flux due to the low partitioning of draw solutes in membranes. Only in the unrealistic case of exceedingly high friction between feed and draw solutes does the impact become noticeable. In contrast, feed solute partitioning and feed solute – membrane friction had a profound impact on feed solute rejection. The observed differences between FO and RO solute rejection can be explained by partitioning and pressure-induced diffusion.

This study is the first to systematically investigate solute transport interactions in FO, starting from a firm theoretical basis.

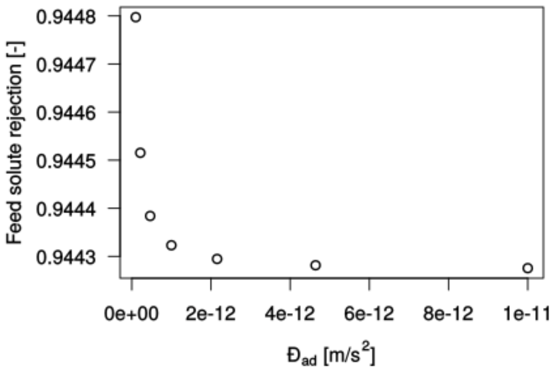

Illustration 1: Influence of feed solute - draw solute friction on feed solute rejection. Note the Y-scale.

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Highly Permeable and Selective Reverse Osmosis Membranes using Artificial Water Channels

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The current market of Reverse Osmosis - RO membranes for desalination is dominated by thin-film composite membranes comprising an active layer of polyamide (PA) fabricated by interfacial polymerization (IP) of m-phenylenediamine with trimesoyl chloride, giving rise to fully aromatic films. However, traditional PA membranes, used predominantly for high-pressure membrane applications, suffer from inherent limitations which reduce their performance.

Biological membranes with highly selective pores for energy efficient separations can be used as inspiration to overcome these problems. Producing defect-free bio-inspired membranes of large areas remains the most critical challenge.

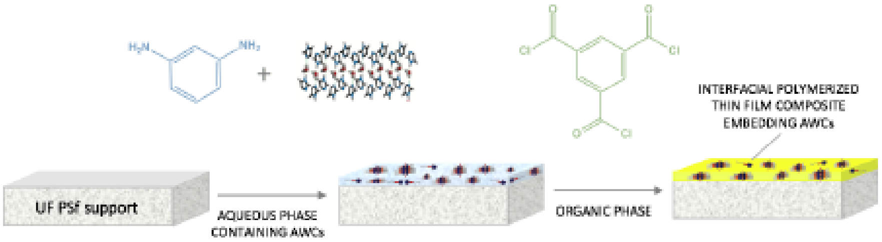
In the framework of this project, we report the development of several approaches to upscale the molecular/supramolecular Artificial Water Channels (AWCs) systems to generate defect-free highly selective membrane materials to be applied in RO applications [1-3].

Bio-inspired desalination membranes are prepared by using an IP approach, contacting an aqueous phase containing polyamine and alkyureido-imidazole monomers with an organic solution comprising an acyl halide, to fabricate bio-inspired PA-AWCs hybrid polymers, whose structures present the same microscale morphology of classic TFC-PA layers but with a different roughness that includes supramolecular aggregates of highly selective I-quartet AWCs.

Results show that our bio-inspired AWCs-PA layers can enhance the selective water transport through the polymer. Their performances are evaluated by cross-flow filtration of solutions containing 3.500-35.000 ppm NaCl at 18-65 bars of applied pressure under RO conditions.

The resulting thin-layers, embedding densely packed Å-scale bio-mimetic channels, overcome the perm-selectivity trade-off of current commercial PA membranes, achieving a large improvement of 200% up to 4.2 LMH/bar in water permeance while maintaining excellent NaCl rejection (observed rejection > 99.5%).

The proposed strategy represents a possible highly efficient route to further advance desalination strategies.



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The Role of Ion Exchange Membrane Type in Ion Exchange Membrane Bioreactor Treatment of Groundwater Contaminated with Oxyanions

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Perchlorate contamination of ground water is a worldwide concern. At several sites in Israel's coastal aquifer, hundreds of ppm of perchlorate were found accompanied with significant concentrations of nitrate and chlorate as well consequently preventing water production from wells in the area.

The ion-exchange membrane bioreactor (IEMB) [1] is a hybrid process for safe treatment of groundwater highly contaminated with oxyanions (perchlorate, nitrate, and chlorate). By Donnan dialysis anionic contaminants migrate across an anion exchange membrane (AEM) from a feed-water compartment to a bio-compartment. Once in the bio-compartment, the anions undergo microbial reduction to safer species such as chloride ions and nitrogen. The AEM acts as a barrier and keeps both compartments completely separate. Glycerol is used as an exogenous carbon and electron source for the biodegradation process [2]. This arrangement keeps the carbon source, reaction byproducts and bacteria confined in the bio-reactor thus preventing the contamination of the treated water. The IEMB process is significantly less energy intensive than pressure-driven or electrically driven processes for removal of these contaminants.

The present study examines the role of ion exchange membrane type in performance of the IEMB in removing perchlorate and other anions (nitrate and chlorate) at levels of hundreds mg L^{-1} from ground water with a mixture of high levels of oxyanions. This was based on Donnan dialysis studies and was studied initially for synthetic and actual ground water fed to the water side while feeding 0.1 N of NaCl to the bio-compartment. To understand the results, conductivity and selectivity measurements were carried out on the different membranes. The anion exchange membranes examined included ACS (Tokuyama Soda), PCA-100 (PC-Cell GmBH), and AMI-7001 (Membrane International).

For ACS membrane and at all experiment conditions studied here, perchlorate dominates the flux across the AEM and fluxes deviated from linear dependence on the driving force at less than 0.5 mM. Even though perchlorate concentration is considerably lower than nitrate and chlorate, its flux is greater than the sum of the other anion fluxes. At an effective perchlorate driving force (EDF) value above 0.7 [mM] perchlorate had a negative effect on the other anions resulting in a decrease in the flux for both nitrate and chlorate while its own flux only increased.

On the other hand, experiments with PCA-100 membranes showed a linear dependence of flux on driving force to much higher levels and much less interference of the perchlorate on the transport of nitrate and chlorate (Figure 2). Tests of membrane conductivity and recovery after perchlorate exposure supported the improved results with the PCA-100 membranes. Another type (AMI-7001) also showed promise based on conductivity but may be problematic in terms of polymer structure. The membrane selectivity for perchlorate and the other oxyanions over chloride was clearly lower for the PCA-100 membranes than ACS. The selectivity of the different membranes will be related to the differences in ion exchange membrane structure. An adaptation of the Donnan transport model of Velizarov [3] and Blaedel [4] will be proposed to explain the connection between selectivity and perchlorate flux.

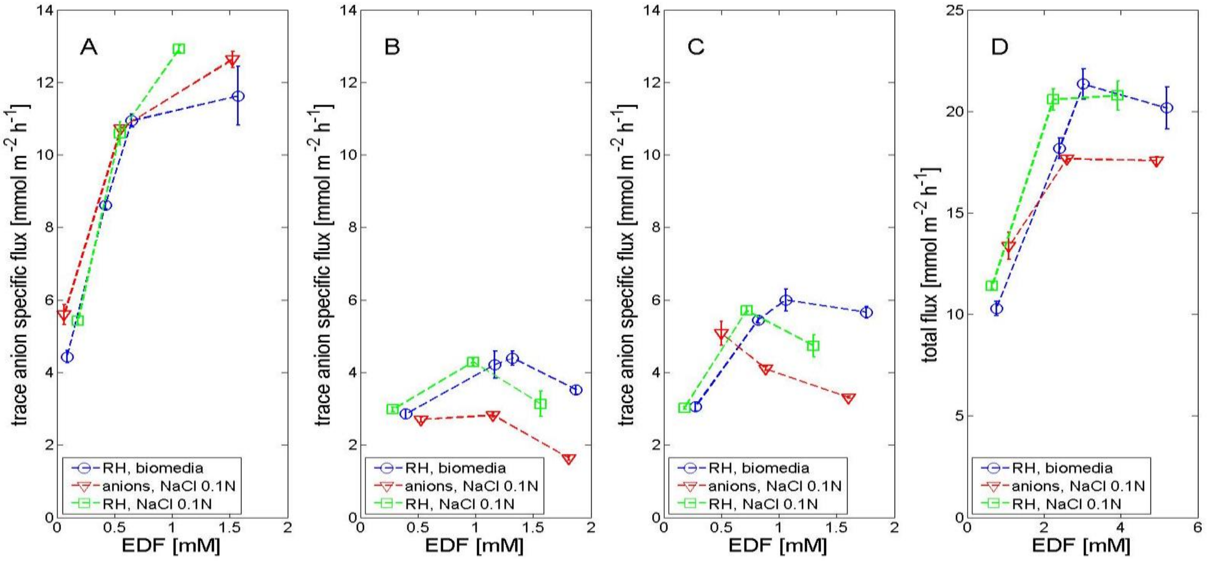

Figure 1 – Results of Donnan dialysis on ACS membrane. Oxyanions specific flux vs. the Effective Driving Force (EDF) of (A) perchlorate, (B) chlorate, (C) nitrate and (D) anions total flux vs. the total EDF, for IEMB Donnan dialysis experiments fed with (○) RHGW and bio media, (▽) synthetic anions solution and NaCl 0.1N and RHGW and NaCl 0.1N (□) into the water compartment and bio-compartment, respectively.

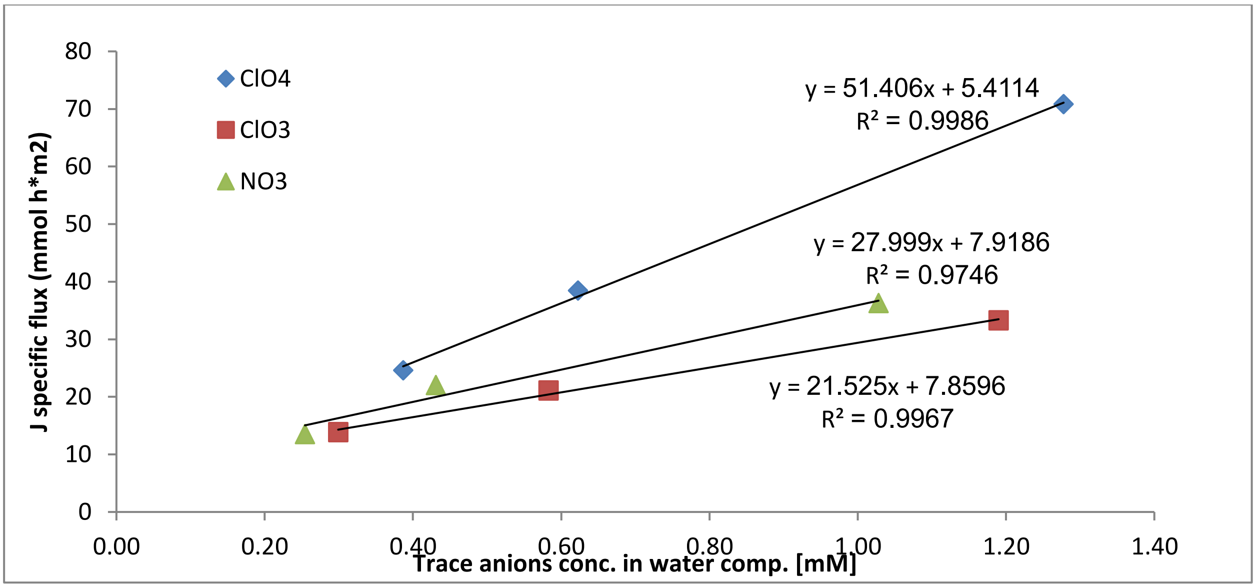

Figure 2: Specific flux in Donnan dialysis on synthetic mixture of oxyanions using PCA-100 anions exchange membrane. Bio-side contained 0.1 N NaCl.

The implications of these findings for operating the IEMB as a plug flow reactor will be outlined.

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Light Enhanced Blue Energy Generation using MoS2 Nanopores

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Abstract

Blue energy relies on the osmotic pressure generated between solutions of high and low ionic strength and would provide a sun-and-wind independent energy source at estuaries around the world. Converting this osmotic energy through reverse-electrodialysis relies on ion-selective membranes. A novel generation of these membranes is based on atomically thin MoS_2 membranes to decrease the resistance and increase power output. Typically, to achieve good ion permeability ratios, alkaline conditions are used to boost the surface charge in solution. By exploiting the photo-excitability of MoS_2 membranes, we are able to rise the ion selectivity of the membrane by a factor of 5 while staying at a neutral pH. We carefully investigate the different spurious effects such as heat which could explain this behavior and concluded that the observed effect is due to a change in the surface charge caused by light-induced charge generation. Furthermore, we find that the behavior of small nanopores is dominated by surface conductance and thus displays a reduced osmotic potential. We introduce a formalism based on the Dukhin number to quantify these effects in the case of a concentration gradient system.

Enhancing the ion size-based selectivity of capacitive deionization electrodes

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Capacitive deionization (CDI) is a fast-emerging water desalination technology, most often applied to brackish water desalination and water softening.[1] CDI cells desalt feedwaters by storing ions in electric double layers within micropores of electrically charged carbon electrodes. CDI cells have demonstrated a size-based ion selectivity wherein smaller ions are preferentially electrosorbed over larger ions due to ion volume exclusion interactions.[2] Selective ion removal is a highly desirable feature in water treatment systems, as selectivity mechanisms can be leveraged towards preferential and energy efficient removal of toxins and other undesirable ions. We here demonstrate that the size-based selectivity exhibited by microporous CDI electrodes can be substantially boosted through addition of chemical charge to micropores via surface functionalization.[3] We develop a theory of size-based ion storage in micropores including the effect of chemical charge,[4] which predicts such enhancements and demonstrates they are a result of enhanced counterion crowding in functionalized micropores. Desalting an electrolyte consisting of competing potassium and lithium ions, we demonstrate that a surface functionalized (oxidized) cathode increases the selective removal of the smaller potassium ion. We observe that the largest enhancements occur at lower charging voltages, from a separation factor of ~1 for untreated electrodes to 1.8 for functionalized electrodes at 0.4 V. Our model predicts this trend by using a fitted cathode chemical charge density of -0.4 M, but underprediction at low voltages and overprediction at high voltages suggests cathode chemical charge degradation is occurring at higher cell voltages, a phenomenon which has not been previously reported upon in the CDI literature to our knowledge. Model results show that achieving stabilized surface groups at high electrode potentials can lead to further enhancements in size-based selectivity factors achievable by CDI electrodes.

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Measures to improve in-line coagulation for NOM-removal with HFUF membranes – results from pilot-plant tests at Ringsjöverket, Sweden

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Natural organic matter (NOM) and color content of surface waters are increasingly becoming an issue for artificial groundwater recharge plants. Water from Lake Bolmen, in southern Sweden had 2017 an annual average NOM and color content of 8.6 mg/L TOC and 57 mg Pt/L respectively, and values ranging from 7.8-9.6 mg/L TOC and 50-70 mg Pt/L. Since water from Lake Bolmen will be used at Womb Water Works, an artificial groundwater recharge plant, the high NOM-content of Lake Bolmen must be reduced prior to aquifer recharge. From experiences of full-scale operations of chemical flocculation and sedimention using ferric chloride, one proposed solution was to pre-treat the lake water utilizing Fe(III)-assisted coagulation in combination with ultrafiltration (UF). In this study, a hollow fiber membrane (MWCO of 150 kDa) with a pore size of around 20 nm was used with two coagulant dosage configurations; 90 seconds and 14 minutes dosage contact times. The results showed the possibility to reduce NOM equal to conventional treatment at a stable flux of 50 L/(m^2, h) with CEB interval of 12 hours. However, coagulant demand was similar to conventional treatment, and higher flux resulted in irreversible fouling.

Ionic Coulomb blockade as a fractional Wien effect

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Ionic transport is key to numerous processes from neurotransmission to ultrafiltration. The recent advances in nanofluidics have allowed tremendous progress in the exploration of ionic and fluid transport at the ultimate scales. However, artificial porins are still far from reaching the considerable richness and subtlety of the biological ionic machinery, which exhibits advanced functionalities such as high selectivity, ionic pumping, and electrical and mechanical gating. A key step towards such functionalities is achieving active control of ionic transport. In particular, the realisation of single ion transport that is tuneable by an external gate – the ionic analogue of the famous electronic Coulomb blockade (CB) – would open considerable new avenues in this pursuit. Despite several claims of ionic CB signatures in experiments and simulations, the understanding of this effect has never gone beyond the electronic analogy, ignoring the particularities of electrolyte systems at room temperature.

We explored theoretically the many-body dynamics of ions confined in a charged nanochannel and obtained analytical predictions demonstrating that ionic conduction is allowed only at discrete values of a gating charge. This result is analogous to the electronic CB, and it is in full agreement with numerical simulations. Surprisingly, this classical quantisation of ionic transport takes its root in the dissociation of 'Bjerrum pairs', through a mechanism reminiscent of Onsager's Wien effect. Our findings open the way to novel nanofluidic functionalities at the single-ion level. As a proof-of-concept, we demonstrate an ionic-CB-based ion pump inspired by its electronic counterpart.

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Ionic Current Control Through Si3N4 Surface Manipulation Techniques

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Techniques of ion transport manipulation have been of interest in many different applications such as water filtration, chemical separations, and biological selectivities. Many of these techniques rely upon the effects of surface charge and wettability in the nanoscale regime. In this work we have set focus on two of these methods: hydrophobicity and ionic circuit elements. We have prepared single nanopores, which contained a junction between a region that was hydrophobic due to the presence of aliphatic chains, and a zone containing polyelectrolyte. We show that the hydrophobic/hydrophilic junction leads to hydrophobic gating i.e. when the voltage reaches a threshold value, polarity dependent current openings and closings are obtained. The gating effect was observed in salts with small anions, such as KCl and NaCl; the gating did not appear for those with larger anions, like KBr and KI. These phenomena are consistent with the computational findings that large polarizable anions are attracted to the surface-vapor layer of hydrophobic surfaces. In addition to hydrophobic modification, ionic circuit elements also apply surface characteristic control toward regulation of ion species transport. These elements emulate diodes or transistors by combining regions of positive, negative, and neutral surface charge. This project uses the native surface charge of Si_3N_4 along with ion selective membranes to create regions of varying charge. The created individual components can then be combined to produce amplifiers or other similar known electronic components. At the nanoscale these elements can be realized and applied towards amplification of low current biological signals or building synthetic equivalents of biological systems such as neurons.

Self-assembly of block copolymers in isoporous hollow fiber membranes

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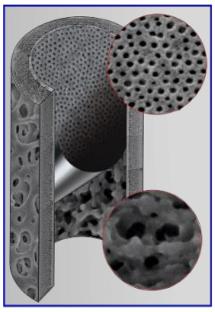
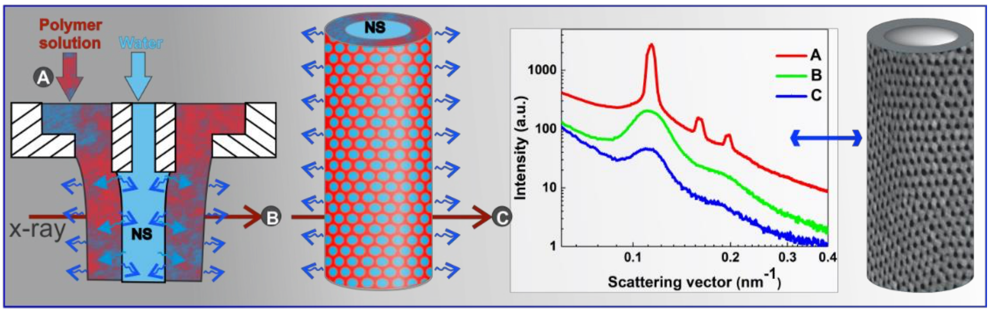
Isoporous block copolymer membranes are promising candidates for ultrafiltration applications by providing tunable pore-size along with high surface porosity and narrow pore size distribution. The membranes are fabricated via self-assembly of block copolymers in combination with non-solvent induced phase separation (SNIPS) in both flat sheet and hollow fiber geometries.[1-2] In particular, the self-sustainable geometry and high active surface area per unit volume make hollow fiber membranes (HFM) a fascinating tool for separations.

The fabrication of isoporous HFM is possible by both spinning and coating methods. In our recent works, the isoporous structure is developed on the lumen side of HFM with a diameter of ca. 1 mm, in order to achieve technologically more relevant inside-out HFM configuration. Polystyrene-*block*-poly(4-vinylpyridine) diblock copolymer solutions were used for the fabrication of wholly integral asymmetric and composite isoporous HFM, by the dry-jet wet spinning method and coating on the inner surface of support HFM, respectively. The key to this development is the ability to control the kinetics of ordering of macromolecules on the lumen side by using gas flow for controlled evaporation of solvents. SEM and TEM were used for microscopical characterization and primary results of water flux and retention tests are presented.[3-4] Furthermore, the self-assembly and influence of spinning parameters has been investigated by conducting *in situ* SAXS experiments during HF spinning of the block copolymer solution. These SAXS data are compared with the morphology of fabricated HFM. The emerging membranes offering high selectivity and permeability can be applicable for numerous ultrafiltration applications, mainly water filtration.





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Theoretical Models of Water Desalination by Capacitive Deionization

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Capacitive Deionization (CDI) is an emerging water desalination and purification technology[1], where two or more conductive porous electrodes are used to remove ions from aqueous solutions. The ions are attracted to the electrodes' surfaces, and are stored by forming electric double layers (EDLs), which screen the potential difference between the electrode and the bulk solution. The complicated porous structure of the electrodes poses difficulties for modelling the charge and salt dynamics during the operation of a CDI cell. To overcome these difficulties, further simplifications are required, and the use of volume averaging is most common[2].

Typically, in the volume averaging method, several mathematical terms are usually neglected or adjusted. In this work, we analyze the importance of these neglected terms. Two constraint have been found to be significant, a geometrical constraint which usually holds for conventional porous materials, and a time constraint governed by the local diffusion timescale, which holds for most DC CDI cells. However, further investigation of AC systems is recommended.

In most CDI models, the phenomenon of surface transport (ST) is neglected. ST refers to the movement of ions in EDLs tangential to the charged interface. ST is usually neglected due to the high ionic conductance of the bulk solution compared to the EDL conductance. However, in CDI cells, the bulk concentration reaches very low values, and therefore ST should not necessarily be neglected. In this work, ST effects on CDI charging dynamics have been investigated, and counter-intuitively predict slowing down of the process under some conditions[3]. Further work should be done to understand ST effects in multi-scale porous structures, common to CDI cells.

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Potential-dependent, switchable ion selectivity in aqueous media using titanium disulfide

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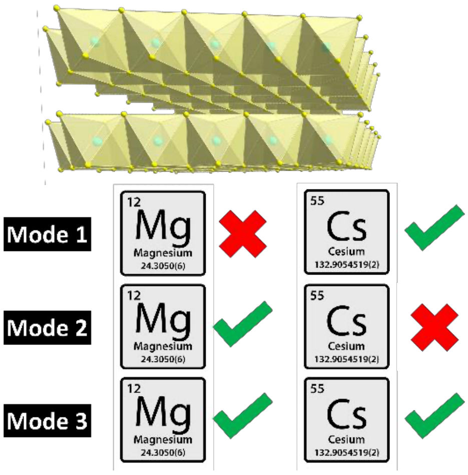
The development and utilization of energy efficient water treatment technologies remain a crucial challenge for a sustainable future of humanity. The ability to control the concentration of water-dissolved ions is critical for producing potable water, ensuring process stability in chemical and pharmaceutical production, accomplishing purification of polluted environmental water. The core aspect of separation technologies is the development of process engineer, and materials. Accordingly, a wealth of different technologies has appeared in literature, including reverse osmosis (RO), thermal adsorption processes, pH-dependent ion-exchange methods, and electrochemical processes. The latter potentially unlock high energy efficiency and performance longevity.

Selective removal of ions by electrochemical processes is a promising approach to enable various water treatment applications such as lithium-ion harvesting. Ion intercalation materials have been investigated for their intrinsic ability to prefer one specific ion over others, showing a preference for (small) monovalent ions over multivalent species.[1] In this work, we present for the first time a fundamentally different approach: tunable ion selectivity not by modifying the electrode material, but by adjusting the operational voltage. We used titanium disulfide which shows distinctly different formal potentials for the intercalation of different cations. Capitalizing on this potential difference, we demonstrate controllable cation selectivity by online-monitoring the effluent stream during electrochemical operation by inductively coupled plasma optical emission spectrometry for an aqueous mixture of 50 mM CsCl and $MgCl_2$. We obtained a molar selectivity of Mg^{2+} over Cs^+ of 31 in a specific potential range. By adjusting the second potential window, Cs^+ is preferred over Mg^{2+} by 1.7-times.



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Electrotreated Multi-Walled Carbon Nanotubes Membranes for oil-water separations

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Efficient oil-water separation is an important challenge in water and wastewater treatment applications. Conventional methods don't answer high separation efficiency and/or suffer from high operation cost. Nonwoven multi-walled carbon nanotubes (CNT) mats, which are thermally, mechanically and chemically stable, seem to act as membrane for oil-water separation due to low pore size (□ 30 nm) and high oil breakthrough pressure.

CNT mats surface should be modified in order to make it more hydrophilic for better oil rejection. Here we report on electrochemical oxidation of CNT mats. Electrochemical oxidation treatment converts natively hydrophobic CNT mats to efficient filtration membranes, whose 30 nm mesh size favorably compromises between the hydraulic permeability and oil breakthrough pressure and allows complete and robust removal of dispersed oil (including surfactant-stabilized) down to its solubility in water.

Laser induced graphene/polymer composite membrane for water treatment

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Laser-induced graphene (LIG) is a three-dimensional porous carbon material prepared by direct laser writing with a CO_2 laser on various polymers in an ambient atmosphere, leading to porous separation filters with electrically conductive and low fouling coatings. Low fouling LIG coatings in water technology have been reported, however, the mechanical strength and the separation properties of LIG coated membranes are limited. Concurrently, graphene oxide (GO) has emerged as a promising 2D nanomaterial to coat porous or non-porous polymer membrane supports resulting in separation membranes with enhanced separation. On the other hand, poly (vinyl alcohol) (PVA) is a nontoxic and biocompatible polymer with good film-forming properties and outstanding physical and chemical stability that has been widely used in many applications. Here, we report a hybrid LIG-GO membrane and mechanically robust electrically conductive LIG-PVA composite membrane with tailored separation properties suitable for ultrafiltration processes. Compared to LIG coated filters, the LIG-PVA composite and LIG-GO membranes exhibited 63- 69% increased bovine serum albumin rejection and up to ~99.9% bacterial rejection, which corresponded well to the measured molecular weight cutoff ~ 90 kDa. The hybrid membranes showed excellent antifouling, anti-biofilm and antibacterial capability compared to a typical polymer ultrafiltration membrane: Noteworthy is that the LIG supporting layer maintained its electrical conductivity and the LIG-PVA and LIG-GO used as electrodes showed complete elimination of bacterial viability with potent antimicrobial killing effects when treated with mixed bacterial culture.

A PDMS-stamp based deterministic transfer of MoS2 for nanopore devices.

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Abstract

Single-layer molybdenum disulfide (MoS_2) nanopores are 'blue-energy' nanopower generators that can act as an ion-selective membranes for osmotic-power generation [1]. To achieve this, the silicon-based MoS_2 nanopore devices require extensive microfabrication that comprise of three major steps: substrate fabrication, transfer of MoS_2 and nanopore-drilling in MoS_2 [2]. Transferring monolayer MoS_2 (_ 6.5 Å thickness) is a challenging step in device fabrication as it needs to be clean, precise and deterministic for making viable nanopore devices. Usually polymer-based transfer method is used especially poly(methyl methacrylate) (PMMA) which is time-consuming, require post-transfer cleaning steps and introduce detrimental effects in MoS_2 [3]. Here we demonstrate an alternative improved transfer method based on polydimethylsiloxane (PDMS)-stamps which aid in the transfer of MoS_2 from growth substrate (sapphire) to an arbitrary substrate (e.g. silicon nitride). We show that the unlike other PDMS-based methods [4-5] which either rely on transferring exfoliated samples or capillary-assisted transfer, the current method is more efficient, selective and offer a precision (_ 10 _ m) under an optical microscope and avoids using etching solutions (e.g. KOH). The highlights of the method are that it is transfer is achieved within 5-6 minutes, capable of transferring on _ 10 devices/stamp, and require no-post transfer cleaning. Furthermore, the method can be used to transfer single-to-multi-layer transfer of MoS_2 and can be extended to heterostructures.

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Angstrom-Size Pore Creation and Ionic Transport through in Single-Layer MoS2

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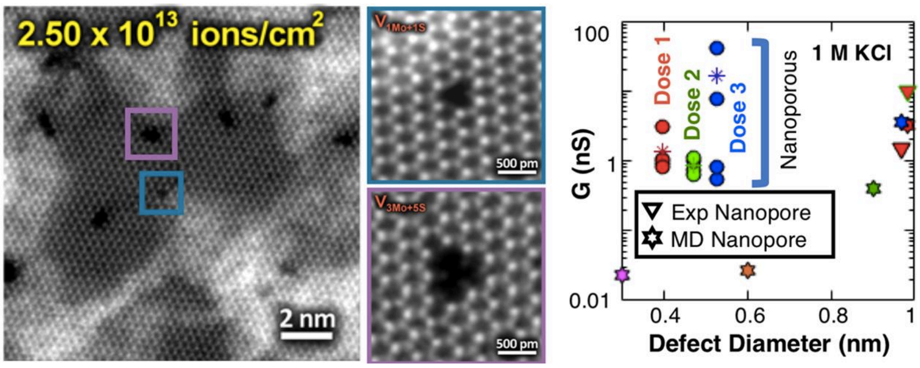

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Atomic-defect engineering in thin membranes provides opportunities for ionic and molecular filtration and analysis. While molecular-dynamics (MD) calculations have been used to model conductance through atomic vacancies, corresponding experiments are lacking. We create sub-nanometer vacancies in suspended single-layer molybdenum disulfide (MoS2) via Ga+ ion irradiation, producing membranes containing ~300 to 1200 pores with average and maximum diameters of ~0.5 and ~1 nm, respectively. Vacancies exhibit missing Mo and S atoms, as shown by aberration-corrected scanning transmission electron microscopy (AC-STEM). The longitudinal acoustic band and defect-related photoluminescence were observed in Raman and photoluminescence spectroscopy, respectively. As the irradiation dose is increased, the median vacancy area remains roughly constant, while the number of vacancies (pores) increases. Ionic current versus voltage is nonlinear and conductance is comparable to that of ~1 nm diameter single MoS2 pores, proving that the smaller pores in the distribution display negligible conductance. Consistently, MD simulations show that pores with diameters <0.6 nm are almost impermeable to ionic flow. Atomic pore structure and geometry, studied by AC-STEM, are critical in the sub-nanometer regime in which the pores are not circular and the diameter is not well-defined. This study lays the foundation for future experiments to probe transport in large distributions of angstrom-size pores.

Quaternization of a Polystyrene-block-poly(4-vinylpyridine) Isoporous Membrane: An Approach to Tune the Pore Size and the Charge Density

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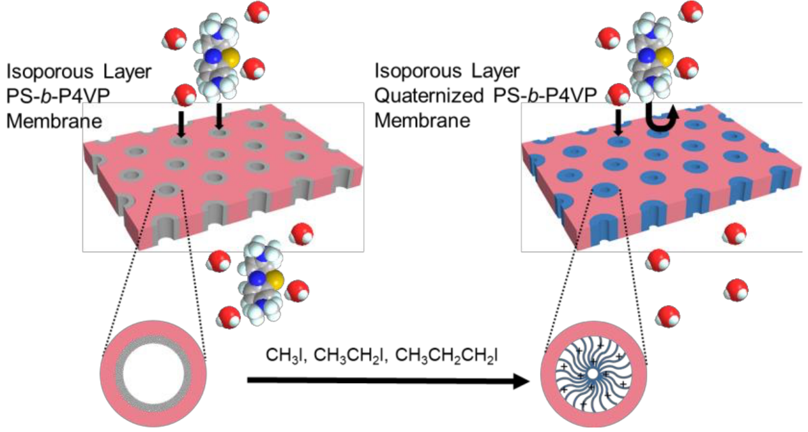
Isoporous integral asymmetric membranes derived from the self-assembly of block copolymers combined with the non-solvent induced phase separation (SNIPS) have gained great attention because of their potentially good selectivity, high permeability and scalable fabrication process.[1-3] To extend their utility, a good control over pore size and surface functionality in a facile manner is highly desirable. Here an approach is proposed to achieve this by quaternization of the poly(4-vinylpyridine) (P4VP) moiety of polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) SNIPS membranes using alkyl iodides via a scalable gas-solid heterogeneous reaction. By changing the size of the alkyl groups of the quaternization agent and the degree of quaternization the effective pore size and charge density of the membrane is tailored in a wide range. The membrane fabrication and post-modification method presented in this work is promising for the production of next generation nanofiltration membranes. As a first result on the separation of an ionic molecule from water, membranes with a quaternization of approx. half of the 4VP repeating units with methyl iodide, ethyl iodide, or 1-propyl iodide were tested and led to a retention of methylene blue (MB) from a 10 mg L^{-1} aqueous solution of 96%, 87% and 83%, respectively. Future research should be directed towards improving the fundamental understanding of transport and rejection behavior of these membranes for water purification, wastewater treatment, biomolecule separation etc.



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Optical sensing of ion flux through biomimetic carbon nanotube channels

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Increasing demands for cheaper and more efficient water treatment methods have never been higher, as shortages in fresh water have become a growing problem in many regions worldwide. In both research and simulations, sub-nm carbon nanotubes have demonstrated great potential in water treatment, desalination and energy conversion with high ion selectivity and enhanced water transport. In this work, we present an approach to investigate fluid transport across each single carbon nanotube channel by visualization of the ion and water flux under a Total Internal Reflection Fluorescence Microscopy (TIRF). Using a droplet interface bilayer (DIB) technique, we place an aqueous droplet (~ 200 nanoliter) on an oil-agarose hydrogel interface, which brings together the lipid monolayers on the droplet and the interface to form a bilayer that mimics a cell membrane. We then incorporate the carbon nanotube channels in this bilayer. Ion and mass fluxes in each channel are characterized through the optical image of ion-sensitive fluorescence, which enables tracking of the flux through a large number of nanoscale channels individually instead of averaging them. The evanescent excitation wave from TIRF also made it possible to eliminate background noise by confining the illuminated region. we envision that novel methods for water treatment can thus emerge via a better understanding of fundamental transport properties through biomimetic carbon nanotube porins.

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