Biomimetic Membranes *for* Water Purification

Sandia National Laboratories

2011

R&D 100

Submitting organization

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Role: Nanoporous Membrane Self-Assembly (Brinker) and Atomic Layer Deposition (Jiang)

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Product information

Biomimetic Membranes for Water Purification

Figure 1. Nanoporous biomimetic membrane on a nanostructured support used for water desalination testing.

Brief description

Selective high-flux desalination membranes based on self-assembled nanopores tuned with atomic layer deposition to mimic the structures of natural membrane-bound biological channels.

Product first marketed

Technical advance SD-1175/S-121507, "Biomimetic Membranes for Water Desalination," Susan Rempe, C. Jeffrey Brinker, David Michael Rogers, Ying-Bing Jiang, Shaorong Yang, disclosed October 5, 2010 (see Appendix D).

R&D 100 awards entry or previous winner

No, this is first-time submission for this product.

Principal investigator

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Product price

Interactions with the Dow Chemical Company have been initiated to license the biomimetic membranes technology at an undisclosed price.

Patents or patents pending

Provisional patent application Serial No. 61/390,041 filed October 6, 2010.
Full patent application is in preparation.

Product's primary function

Biomimetic membranes are designed for water purification using reverse osmosis (RO) technology, which removes impurities from water with applied pressure powered by electrical energy. These membranes reject salts and larger solution components, thus creating drinkable water. The nanoporous biomimetic design enables high salt rejection and faster water flow at lower driving pressures than competing membranes, thus reducing the energy cost of desalination. Specifically, at low pressures around 5.5 bar, the biomimetic membrane achieves an *order-of-magnitude improvement in membrane permeability to water flow* compared to commercial membranes and still maintains high salt rejection ratios. If the small-scale biomimetic membrane were embedded in a large-scale format, the improved performance would translate into a projected savings of 88% of the cost due to the membrane resistance to flow. Given the current cost of electrical energy, this enhancement in membrane performance represents a potential savings of $1.45 million per year for a modestly sized 100 ML/day desalination plant.

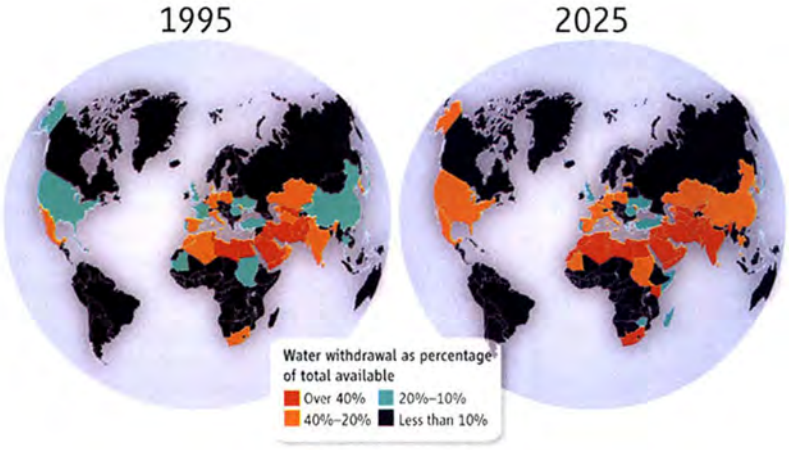


Figure 2: Spreading water shortages underscore the need for new solutions to clean water.

Why do we need desalination membrane technology?

A pervasive and growing problem afflicting nearly half of the world's population is inadequate access to clean, fresh water (Fig. 2). Scarcity of clean water underlies death, disease, and international tension. Furthermore, energy and water are inextricably linked, with the production of one requiring use of the other. For example, vast amounts of water used in mining, drilling, oil and coal refining, biofuels production, and in cooling systems for nuclear and electrical generation drive water use and further stress clean water supplies.

The **best** current solution to water purification relies on RO membranes that remove salts and larger components from water with applied pressure (Fig. 3). A survey by the U.S. National Research Council in 2004 revealed that more than half of the 15,000 desalination plants operating around the world utilize RO technology. In the U.S., RO membranes contribute to 96% of online desalination capacity. Since desalination by reverse osmosis is more efficient than the alternative evaporation technology, all new plants going into production are built on RO technology.

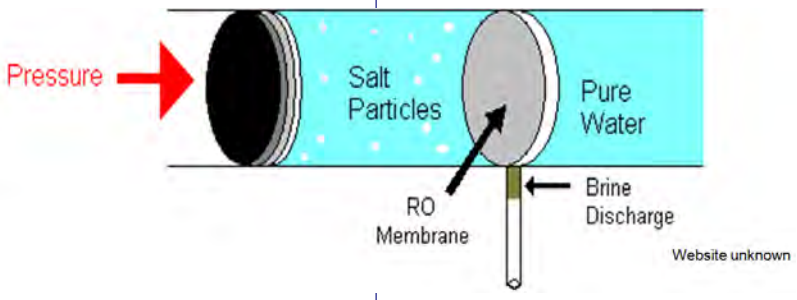


Figure 3: Reverse osmosis technology involves pushing water through a semi-permeable membrane that blocks dissolved salts. Thin film composite membranes first developed in 1977 are still used today in desalination plants.

Despite its success and widespread use, water desalination by RO is associated with tremendous energy costs. Expensive electrical energy accounts for the largest component of the operating cost for seawater desalination facilities. Using the Perth, Australia desalination plant as an example, more than half the energy budget is used

to establish the pressure drop needed to push water through the semi-permeable membrane that blocks dissolved salts. This energy requirement is far higher than the minimal thermodynamic cost associated with concentrating salt solutions because current membranes lack permeability to water and thus resist flow. Considering the cost of electricity needed to establish pressure gradients across the RO membrane, membrane resistance to flow carries a price tag of $1.6 M per year for a modestly sized 100 ML/day RO facility.

The challenge in designing membranes to reduce the cost of desalination comes from the two seemingly contradictory goals that must be accomplished simultaneously: excluding ions while facilitating fast transport of water. Traditional RO membranes are based on a non-porous thin-film composite design in which a dense polymer skin provides the active-site architecture responsible for ion rejection. The fundamental structure of these RO membranes has remained unchanged for over 30 years. While thin-film composite architectures perform well in terms of salt rejection, a breakthrough in materials research is needed to design new membranes that also achieve higher permeability to water, or, equivalently, reduced resistance to flow.

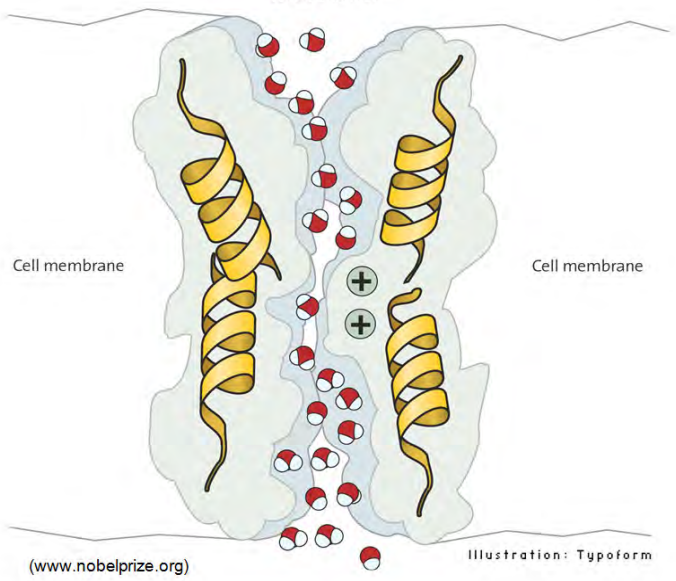


Figure 4: The biological aquaporin protein provides a working example of a membrane pore that filters salts from water far more efficiently than current reverse osmosis membranes. Pore dimensions are 4 nm in length and 0.3 nm at the smallest diameter.

Considerable research undertaken to improve the polymer-based thin-film composites has resulted in incremental progress only, motivating a search for alternative materials demonstrating both high flux and selectivity. Zeolite-based membranes have been considered, but these show high resistance to flow. Membranes composed of stacked, oriented-carbon nanotubes demonstrate high permeabilities around 5.5 cm/hr per unit of applied pressure, more than an order-of-magnitude improvement over thin-film composites, but fail in terms of salt rejection in solutions of relevant ionic strength and are complicated to fabricate.

Combined high flux and selectivity *is* achieved in natural systems by membrane-bound ion and molecular channels, whose pore size and chemistry is defined with sub-nanometer precision through protein folding and whose thickness is limited to that of the cellular membrane bilayer, only 4 nm (Fig. 4). Efforts to incorporate natural water

channels formed by *aquaporin* proteins into synthetic block copolymer membranes showed permeabilities two orders-of-magnitude higher than thin-film composite membranes, but the proteins lacked stability at room temperature.

Our research & development approach

In developing robust membrane designs capable of high flux and selectivity, we have pursued a different research strategy that benefits from the study of natural biological channels. Figure 4 shows an *aquaporin* channel. These channels, present in our kidneys and responsible for purifying 150 L of water daily, provide working examples of membrane nanopore structures that achieve high water flux and perfect salt rejection with only small pressure gradients. Other transmembrane channels, such as the potassium channels of nerve and muscle, present designs that facilitate rapid permeation of only select ions. Since people benefit from small amounts of minerals in their drinking water, these ion-selective channels provide working examples of membrane nanopore structures that produce mineral water efficiently.

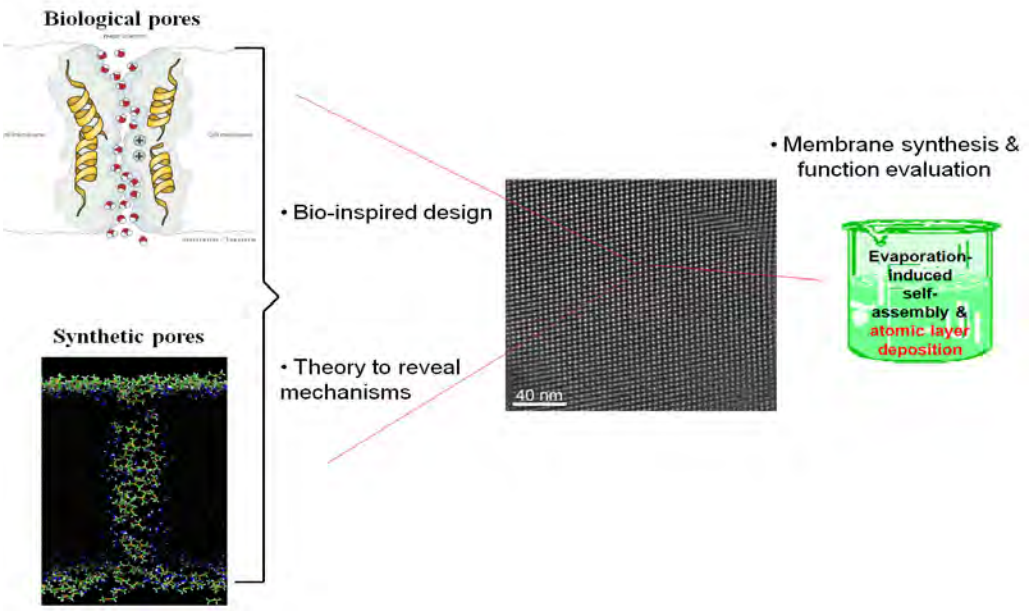


Figure 5: Research & development strategy: 1) Understand biological filtration mechanisms; 2) Translate designs to inorganic membranes; 3) Optimize for fast selective water transport.

We hypothesized that understanding and harnessing these biomimetic principles could potentially lead to robust solid-state membranes critical to lowering the cost of reverse osmosis technology. Synthetic strategies pioneered by us permit fabrication of highly ordered nanoporous membranes with tailor-made pore geometries and interior pore surfaces. Multi-scale modeling based on quantum descriptions of atomic interactions permit accurate assessments of pore structure *versus* function relationships. Thus, we used a combined experimental and multi-scale modeling approach to explore how structure correlates with function in nanopores pertinent to fast selective water transport (Fig. 5). In the resulting biomimetic membranes, we captured some structural features important to the function of biological water channels and produced membrane designs that maintain high salt rejection ratios while achieving an order-of-magnitude improvement in permeability compared to commercial membranes in small-scale tests.

How does it operate?

In contrast to thin-film composite membranes with polymeric skins, biomimetic membranes are designed to have a nanoporous architecture in which the engineered pores define the active sites that block ions and facilitate fast water permeation. Since ions and water molecules are similar in size, membrane pores cannot separate ions from water by size alone (Fig. 6 & Fig. 7). Instead, the surface chemistry and architecture of each membrane pore must be delicately controlled to tune chemical interactions with

Figure 6: How to design a hole for seemingly contradictory goals: fast water passage and dissolved salt rejection?

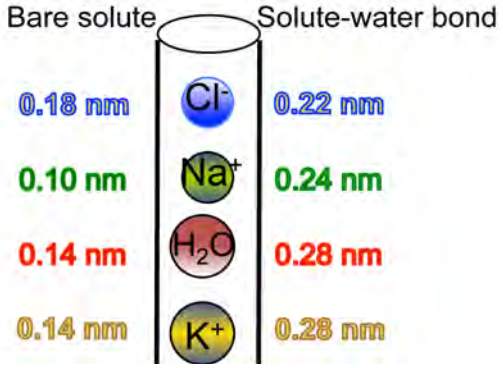


Figure 7: Water desalination by size exclusion in the traditional sense doesn't work because of the similarity in size between ions and water molecules.

water and ions that lead to efficient water purification. A challenge in the experimental and theoretical studies is to determine which molecular-scale structural features of the pore provide interactions that stabilize water molecules, without trapping them, and simultaneously exclude specific ions by destabilization (Fig. 8).

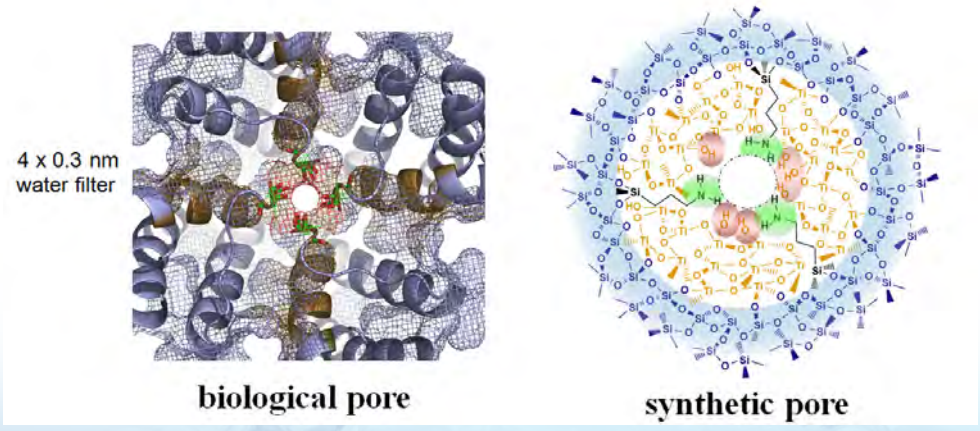


Figure 8: What molecular-scale structural features determine fast water transport and salt rejection for single pores?

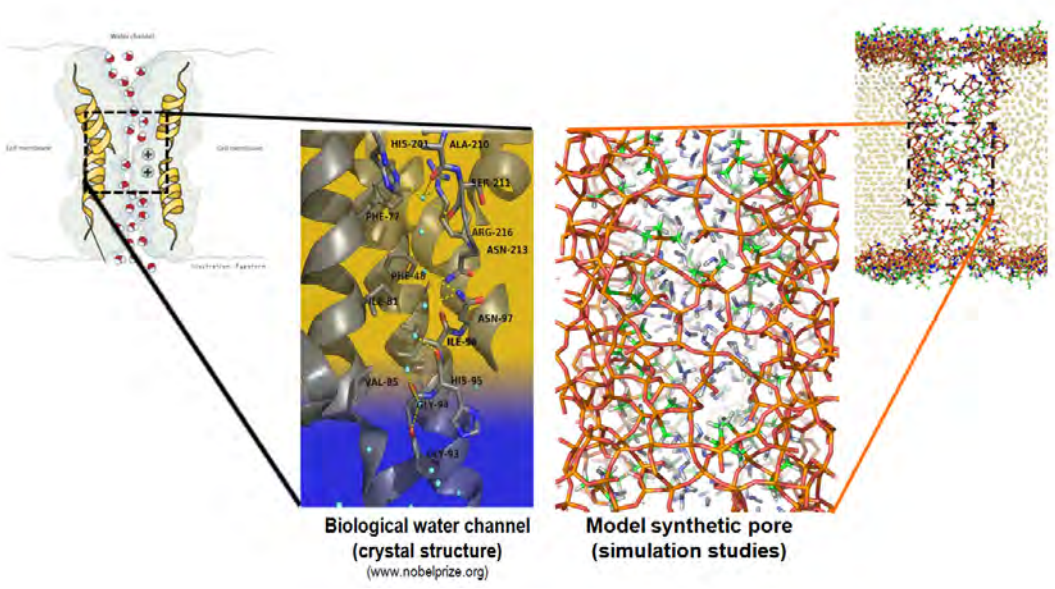
Inspection of the crystal structure of one of the biological *aquaporin* proteins reveals a complex pore design that underlies fast water transport rates and complete ion rejection (Fig. 9, left). Six trans-membrane alpha-helices form a *thin and narrow* passageway for waters only 3 Å in diameter in the narrowest segment and with a length limited by the thickness of the cell membrane bilayer, only 4 nm. One side of the interior pore wall is composed primarily of *hydrophobic* aromatic residues (phenylalanine, PHE). A series of *hydrophilic* carbonyl oxygens and amine groups form a staircase along the other side, with each polar group accepting or donating a hydrogen bond to water molecules permeating in single-file through the channel.

Figure 9: (Left) Complex structural features of biological pores:

- *short, narrow passageway for waters (green)*
- *repulsive hydrophobic walls (VAL, ILE, PHE)*
- *staircase of stabilizing polar groups (C=O, N-H)*

(Right) Synthetic pores require multiple structural elements for biomimetic filtration:

- *ions stabilized in pores wider than 1 nm*
- *narrow hydrophobic walls destabilize ions,*
- *but also limit water mobility*
- *symmetric dense polar groups stabilize ions*



To probe the significance of *aquaporin's* structural features and the potential functional outcome if these features were translated to an inorganic nanoporous membrane, we conducted molecular simulations of water-filled silica nanopores. We also synthesized nanoporous silica membranes with varied pore sizes and surface chemistries that mimic the biological channels. We investigated the effect of pore diameter and chemistry on water flux, ion exclusion, and ion permeation as functions of the pressure gradient across the membrane.

Experimental studies relied on the evaporation-induced self-assembly technique pioneered by us to direct the formation of nanoporous silica films with ordered arrangements of mono-sized pores on an underlying anodized alumina porous support (Fig. 5, membrane in middle.) Following calcination and UV/ozone exposure, the nanoporous film has fully hydroxylated 2.6 nm pores as measured by a surface acoustic wave-based technique. Both the pore interior and the thin film (membrane) surfaces can be functionalized to achieve specific structural designs.

Theoretical studies relied on atomistic models of water-filled silica nanopores constructed to mimic the experimental pores. (Fig. 9, right) Molecular simulations were performed using both classical force fields and *ab initio* techniques. The *ab initio* approach relies on highly accurate density function theory (DFT) calculations. DFT

explicitly accounts for the valence electrons of water, ions, and solid substrates and has proved successful in predicting chemical reactions in water as well as ion solvation properties. Thus we applied *ab initio* molecular dynamics techniques to examine the surface chemistry of narrow pores and ion-binding reactions. We used classical molecular dynamics to study water and ion transport through narrow pores and predict thermodynamic stabilities inside the pores. We also used *ab initio* simulations to examine the structural elements controlling selective ion binding in biological channels.

The combined experimental and theoretical studies revealed important lessons about how molecular structure correlates with function in water-filled nanopores:

- *Narrow pores* restrict entry to naked solutes that lack stabilizing electrostatic interactions with hydrating water molecules. Then the chemical composition and architecture of the channel walls plays a primary role in determining which solutes permeate fast, stick, or get rejected. In *wider* pores, ions can be stabilized by their accompanying waters of hydration and thus may permeate regardless of pore wall composition (Fig. 10).

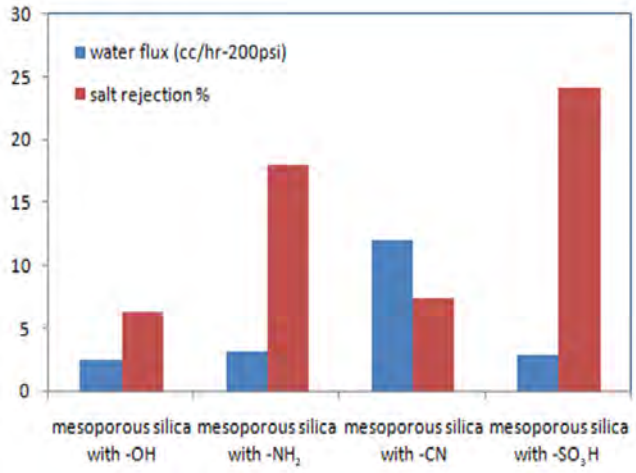


Figure 10: Pores of 2.6 nm diameter and functionalized with varied surface chemistries show high water flux, but low salt rejection. In large pores, waters of hydration stabilize ions and promote permeation.

- *Narrow hydrophobic pores* destabilize ions due to lack of electrostatic interactions from nearby polar groups, making *hydrophobic* surfaces good for salt rejection. But they also reduce water mobility and lower water occupancy, which increases resistance to water flow and thus reduces water permeability (Fig. 11).

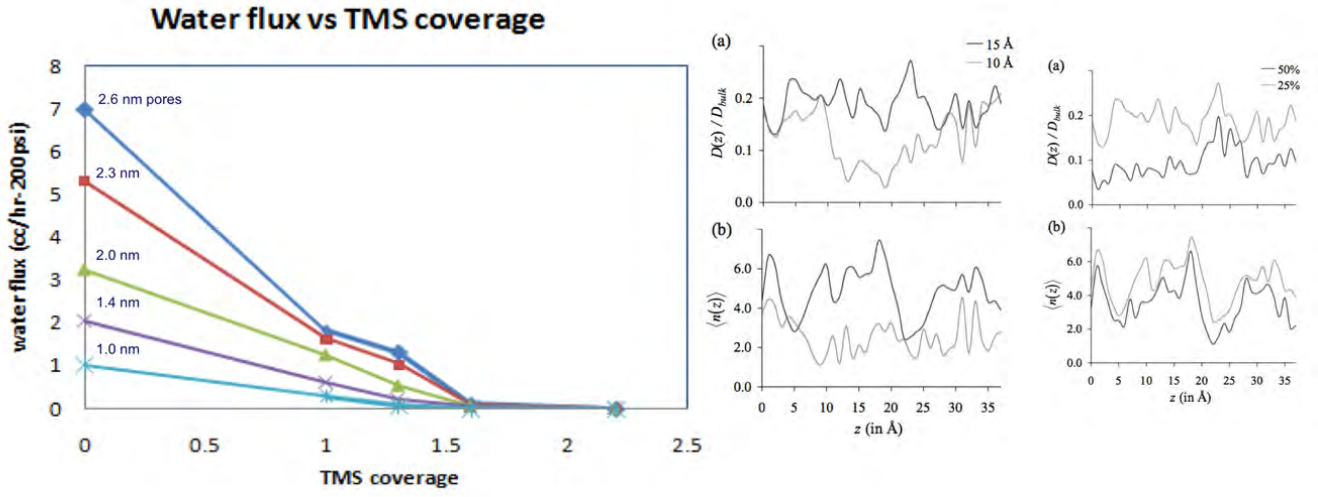


Figure 11: Increasingly more narrow and hydrophobic surfaces lack water binding sites, and thus lower water flux (lower left) by reducing water mobility (right, top) and occupancy of the pores (right, bottom). Gradients of hydrophobicity were achieved by varying trimethylsilyl (TMS) coverage on the silica nanopore surface.

- *Narrow hydrophilic pores* with dense symmetric arrangements of polar groups stabilize ions due to binding sites formed by electrostatic interactions. Strong interactions trap ions while moderate ones can facilitate ion permeation. Alternating stretches of dipolar/nonpolar regions in the pore interior can block ion transport due to dominating ion-pore dipole interactions over ion-ion interactions (Fig. 12).

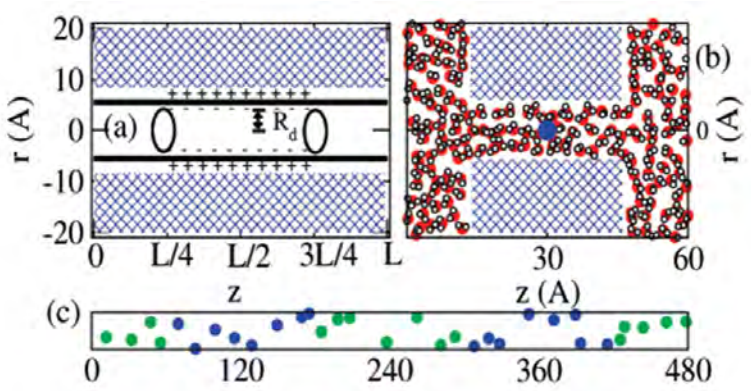


Figure 12: Different membrane geometries modeled to study effects of surface dipoles on ion stability in water-filled nanopores: A) infinite pore geometry, B) membrane geometry, C) alternating dipolar and nondipolar regions in infinite geometry. In C, dipole-ion interactions are unscreened by water, leading to charge-segregated behavior that can block ion transport (Na^+ and Cl^- depicted as blue and green spheres).

Thus the *aquaporin* structure promotes fast water transport and complete ion rejection with *hydrophilic* functional groups inside the pore that stabilize water while greasy *hydrophobic* functional groups prevent trapping of water and ions. Since resistance scales linearly with membrane thickness, a *thin* pore facilitates fast transport while a *narrow* passageway restricts entry to small naked solutes, which lack stabilizing interactions with hydrating water molecules. Altogether, the walls of the narrow channel must provide the same amount of thermodynamic stability to the permeating waters as provided by bulk water solution for optimal water transport, yet destabilize ions due to an absence of ion binding sites.

Of the many nanoporous membranes synthesized during studies of pore structure versus function, the best desalination performance was observed with the polypeptide membrane. Similar to *aquaporins*, the polypeptide membranes contain key structural elements important to high water flux and ion rejection: multiple chemical functionality in asymmetric arrangements of *hydrophilic* amide and *hydrophobic* aromatic chemical groups; a narrow and thin pore architecture. Our expectation is that perfect translation of the *aquaporin* structural features would yield two orders-of-magnitude increase in water permeability over conventional thin-film composites.

Our biomimetic membrane fabrication process has achieved partial translation of this biological architecture in an inorganic membrane format, accompanied by high salt rejection and an order-of-magnitude improvement in water permeability over traditional RO membranes.

Building blocks

The synthetic nanoporous membrane employs a hierarchy of oriented, cylindrical channels within channels to achieve acceptable material strength at high surface coverage. At the smallest level, 2.6 nm diameter pores are functionalized by a chemical deposition process called atomic layer deposition (ALD). We restrict ALD to the mouth of the pore using plasma activation. As a consequence, a narrow and thin constriction region forms near the surface of the membrane. After depositing polypeptides in this constriction region, the resulting dimensions of the passageways and asymmetric patterns of *hydrophobic* and *hydrophilic* functionality in the pore active sites mimic structural features of natural water channels (Fig. 13).

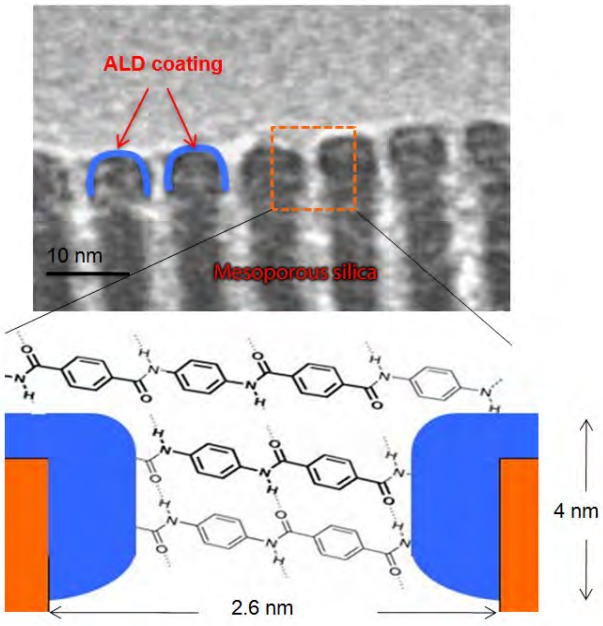


Figure 13: Translating the biomimetic design: Image from transmission electron microscopy (TEM) shows pore geometry modifications achieved by atomic layer deposition targeted to the pore mouth (top). Further ALD of polypeptide groups modifies internal pore chemistry to produce pore active sites with dimensions and chemical functionality similar to natural biological pores (bottom).

More specifically, to achieve a delicately tuned biomimetic structure in an inorganic membrane format, we start with an anodized alumina support having 20 nm pores aligned normal to the support surface. A regular nanoporous silica substructure is then assembled within the pores using an evaporation-induced self-assembly technique pioneered by us. Following calcination and UV/ozone exposure, the nanoporous substructure has fully hydroxylated 2.6 nm diameter pores as measured by a surface acoustic wave-based technique. We further tune the pore size and surface chemistry using ALD—a process for fabricating materials one atomic layer at a time that is used in the semiconductor industry. Within a pore, this allows pore size tuning with sub-nanometer precision.

ALD is a self-limiting layer-by-layer thin film deposition technique composed normally of successive steps of adsorption and hydrolysis/activation of metal halide or metal alkoxide precursors. Our previous research introduced plasma-assisted (PA)-ALD as a means to deposit dense oxide films on the immediate surface of a nanoporous film. In PA-ALD, exposure to a remote oxygen plasma, rather than hydrolysis, is used to activate the immediate mouth of the pore through formation of hydroxyl groups. Because both the plasma Debye length and the radical mean free path exceed the pore diameter (~3 nm), deposition does not occur deep within the pore interiors.

Gas permeance measurements after 32 polypeptide ALD cycles confirm the retention of porosity in the membranes with pore diameter of 2-3 Å (Fig. 14). Measurements of water flux and salt rejection ratios after successive polypeptide ALD cycles show that desalination performance changes with addition of polypeptide chemistry to the pore walls and reductions in the size of pore permeation pathways (Fig. 15). As expected, larger pores permit faster water flux. Surprisingly, pore surface chemistry becomes significant to ion rejection after only two polypeptide cycles. The biomimetic membranes are formed after 32 polypeptide ALD cycles.

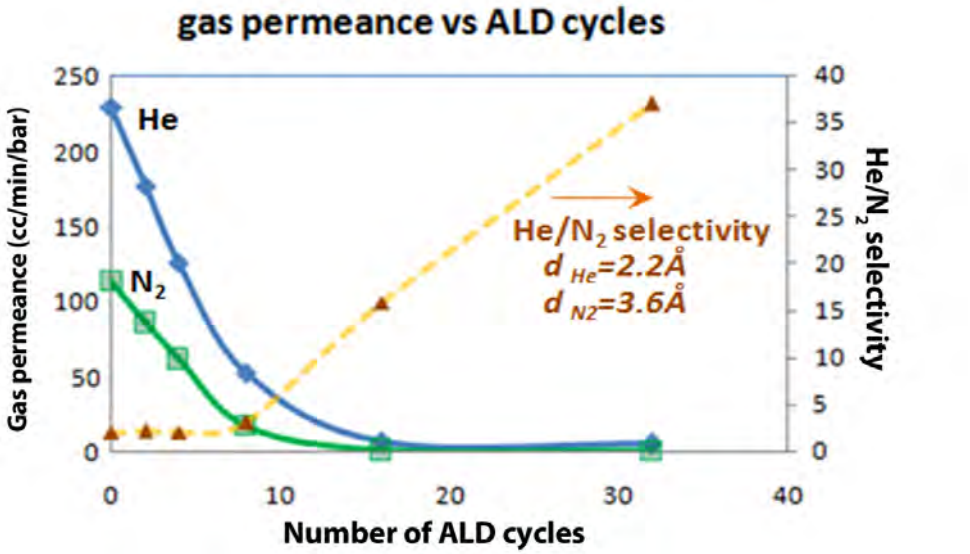


Figure 14: Gas permeance measurements probe progressive pore size reduction with number of polypeptide ALD cycles. After 32 cycles, the He/N_2 selectivity increases substantially and He still permeates (4.8 cc/min/bar), showing that the membrane retains some porosity with pore diameter around 2-3 Å.

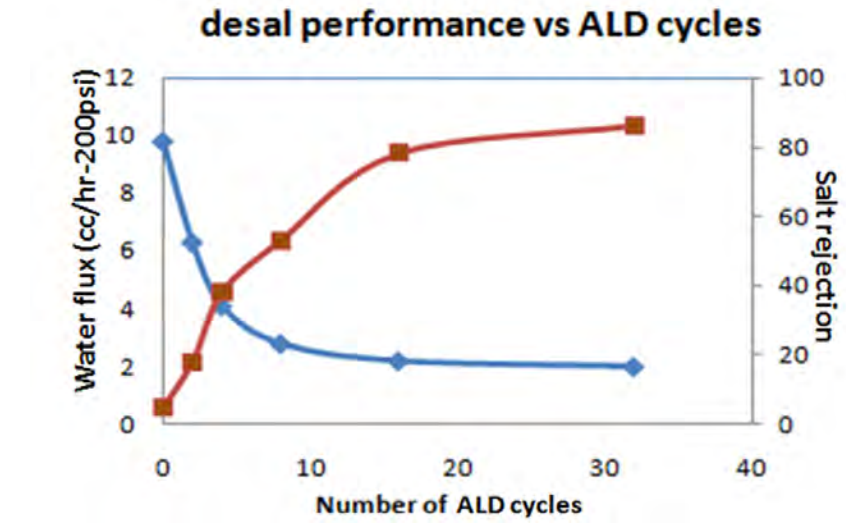


Figure 15: Measurements of water flow and salt rejection probe desalination performance with progressive deposition of polypeptide by ALD. After only 2 cycles, salt rejection increases substantially, from 4.7 to 18%, while water flux remains relatively high. This shows the high impact of polypeptide surface chemistry on salt rejection.

The resulting biomimetic membranes, fabricated with polypeptide ALD (Fig. 16), mimic key structural and chemical characteristics of biological water channels: 1) *hydrophilic* polar groups that form binding sites for water (C=O/N-H); 2) *hydrophobic* aromatics to prevent trapping of waters and ions; 3) no binding sites for ions; and 4) narrow and thin water passageways within the nanoporous architecture. As a consequence of this novel design, the biomimetic membranes achieve highly efficient desalination via a mechanism similar to natural biological channels.

Key Innovations

The novel and differentiating design of the biomimetic membrane lies in its nanoporous architecture. In contrast, traditional thin-film composite membranes first designed more than 30 years ago contain random pathways for water percolation, greatly increasing resistance compared to the regular, oriented channels we have developed.

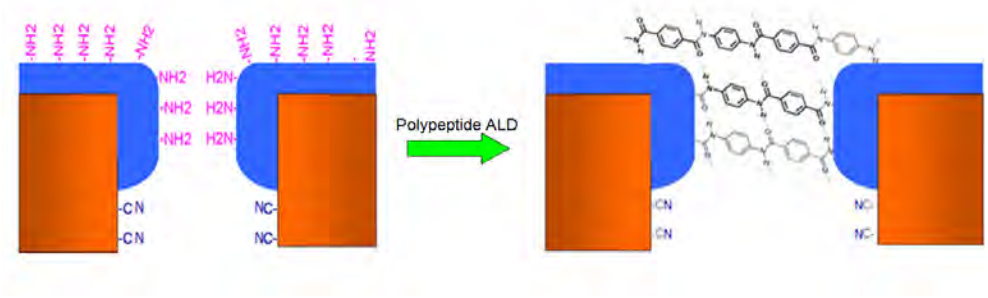


Figure 16: Translation of multiple biomimetic structural features to synthetic pores is achieved by evaporation-induced self-assembly of uniform pores with geometry and chemistry tuned by atomic layer deposition. After polypeptide deposition, the resulting narrow passageways and asymmetric patterns of hydrophobic and polar groups mimic natural water channels and facilitate fast water flux and high salt rejection.

In pursuit of the nanoporous design, we developed an innovative research strategy. Biological transmembrane channel proteins that demonstrate far more efficient water filtration than commercial membranes provided inspiration and informed the nanoporous design of the biomimetic membranes. Recent advances in nanofabrication techniques based on evaporation-induced self-assembly and targeted atomic-layer deposition were used to fabricate aligned mono-sized pores with tailor-made interiors. Combined experimental and multi-scale modeling investigated the science of the interface between waters, ions, and pores to determine molecular structure-function relationships pertinent to desalination. Guided by new insights gained by our scientific investigations of structure-function relationships, we transcribed key molecular design principles of natural porous systems into robust synthetic membranes using our nanofabrication techniques.

To summarize, our approach to biomimetic membrane design and fabrication using self-assembly and atomic layer deposition represents a revolutionary advance in the field of membrane technology for water filtration.

Product comparison

Nearly all commercially manufactured membranes are based on the traditional polymeric thin-film composite (TFC) design developed in 1977. In this non-porous membrane, the active-site architecture responsible for membrane resistance to flow and ion rejection consists of a thin, dense polymer skin layer. The skin may be constructed of polyamide, which is coated onto an underlying porous support. Companies producing polyamide TFC membranes include The Dow Chemical Company through its subsidiary, FilmTec Corporation; Toray Membranes; and a Japanese company called Nitto Denko.

For a head-to-head performance comparison between our nanoporous biomimetic membrane design and a non-porous design, we obtained the FILMTEC SW30HRLE polyamide thin-film composite membrane from Dow. The SW30HRLE membrane is the gold standard in large saltwater purification applications.

Performance Measurements and Efficiency Calculations

Water flow and salt rejection ratios were measured for our nanoporous biomimetic polypeptide membrane and the FILMTEC SW30HRLE thin film composite membrane under equivalent conditions for a variety of imposed membrane pressure drops. Results from these measurements are plotted in the graph (Fig. 17) and in Table 1 (Comparison Matrix), with data points at the 5.5 and 10.3 bar of applied pressure. Note that no water flux was observed for the thin-film composite below an applied pressure of 10 bar.

To assess the consequence of water flow and salt rejection performance on membrane efficiency, we modeled the membrane as a simple resistor and applied Onsager's linear transport theory to define membrane permeability. The work required to push a volume of water through the membrane depends directly on the pressure differential needed to accomplish the task: the difference in pressure applied to force water through the membrane compared to the lower pressure of water when it emerges on the other side. Some of this work goes toward concentrating salts on the input side—this reflects the minimal thermodynamic energy cost for water desalination. The rest of the work goes toward heating the membrane, which accounts for energy lost due to membrane resistance. Improved membrane permeability reflects a decrease in its inverse property, the membrane resistance to fluid flow.

Once membrane permeability is calculated, we can predict the cost savings to a desalination plant if it were outfitted with membrane designs that feature higher permeability. Cost is directly related to membrane resistance to fluid flow. The estimate in savings is based on the cost of electricity (6 cents per kW-hr), which is used to establish the pressure gradients required for reverse osmosis desalination.

Competitive Matrix

The following considerations were made in constructing the plot and matrix. Water flow and salt rejection properties were measured using a high-pressure liquid chromatography (HPLC) water pump, with a constant input feed at 5 g/L NaCl solution, and varied imposed membrane pressure drops. These results are plotted in Figure 17. Using two sample data points from the measurements, membrane permeability (flow rate per unit of pressure drop) is tabulated in the top part of Table 1. In the lower part of Table 1, we calculate permeability using published data for commercial membranes operating under their optimal conditions of large pressure drops needed for high salt rejection.

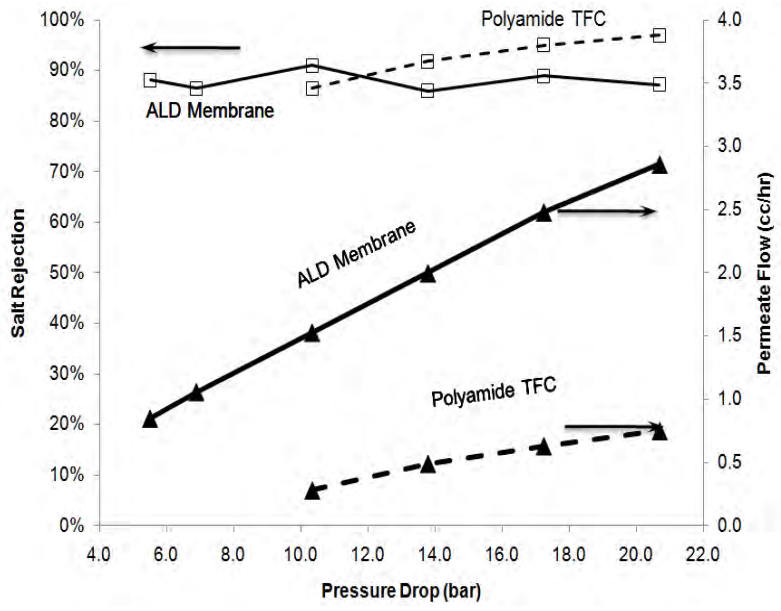


Figure 17 . Biomimetic membrane outperforms commercial membrane. The biomimetic (ALD) membrane has almost 4x's faster flow compared to the commercial thin film composite (TFC) membrane at 21 bar; this ratio increases with decreased driving pressure. Salt rejection for the biomimetic membrane is slightly lower at high applied pressures, but stays high independently of pressure. Thus, the biomimetic membrane performs well at applied pressures as low as 5.5 bar, giving rise to an order-of-magnitude improvement in permeability that could translate into a savings of $1.45 M/yr for a 100 ML/day desalination plant.

Table 1: Biomimetic membranes show more than an order-of-magnitude improvement in water flux per unit of pressure drop and still maintain comparable salt rejection ratios compared to commercial thin-film composite membranes.

Membrane	Permeability	Salt Rejection
	cm/hr-bar	%
BIOMIMETIC (ALD)†	2.42	88
BIOMIMETIC (ALD)††	1.18	91
DOW SW30HRLE††	0.21	87
DOW SW30HRLE◊	0.11	99.8
DOW SW30ULE◊	0.17	99.7
TORAY TM800S◊	0.14	99.8
NITTO SWC-4014◊	0.13	99.4

†*Measured at 5.5 bar of applied pressure.*

††*Measured at 10.3 bar of applied pressure.*

◊*Reference data reported on company datasheets for high applied pressure of 55.2 bar needed for high salt rejection.*

At lower pressures, the biomimetic membrane performs particularly well, achieving an order-of-magnitude improvement in membrane permeability to water flow compared to commercial membranes and still maintaining high salt rejection ratios.

How Product Improves upon Competition

In the head-to-head comparison with the Dow FILMTEC SW30HR thin-film composite membrane (see Fig. 17 and Table 1), we find that the nanoporous biomimetic ALD membrane outperforms the commercial membrane at all driving pressures. For example, at higher driving pressures of 20 bar, the biomimetic membrane purifies water with nearly *four times* the water flux compared to the commercial membrane, and this ratio *increases* with lower driving pressures. In contrast to the commercial membrane, high salt rejection is maintained independently of driving pressure in the biomimetic ALD membrane. Furthermore, water flux changes linearly with driving pressure. Thus at lower pressures, the biomimetic membrane performs particularly well, achieving an order-of-magnitude improvement in membrane permeability to water flow compared to commercial membranes and still maintaining high salt rejection ratios. The improved performance translates into a projected savings of 88% in energy cost from membrane resistance to flow for a single pass, a savings of $1.45 million per year for a modest 100 ML/day desalination plant. Finally, the nanoporous architecture and ALD fabrication strategy applied to construct the biomimetic membranes enable separate chemical functionalization of internal pore surfaces, which are critical to desalination function, from membrane surfaces, which are critical to avoiding fouling by biological species.

To summarize, the advantages of the nanoporous biomimetic membrane design include:

- Order-of-magnitude improvement in membrane permeability, which reflects a reduction in membrane resistance to flow.
- High salt rejection maintained independently of driving pressure.
- Water flux increases linearly with driving pressure.
- Separate chemical functionality can be implemented in internal pore surfaces, to control desalination performance, and membrane surfaces, to avoid biofouling.
- Projected reduction in excess energy cost due to membrane resistance to flow is 88%, a savings of $1.45 M/yr for a 100 ML/day desalination plant.

Scale-Up Considerations for Commercial Applications

Cost savings projections assume that the biomimetic ALD membrane design can be scaled up into large membrane format without loss in efficiency. Currently, the biomimetic membrane is constructed on a porous ceramic support, which is brittle. Ideally, a membrane should be embedded in a flexible format so that it can be folded in practical applications to achieve a large surface area within a small volume. Our team is working on constructing biomimetic membranes on alternative flexible supports to enable scale-up. The self-assembly and ALD processing steps are scalable and transferable to large-scale fiber-based membrane platforms.

Cost savings projections are based on salt rejection ratios achieved for a single pass across the membrane. The higher salt rejection ratios observed in commercial membranes can be achieved with two passes across the biomimetic membranes. Accounting for a double pass, the reduction in excess energy cost due to membrane flow resistance is 63% compared to the best competitor, Dow SW30ULE.

Lowering the cost of water purification will enhance access to clean fresh water, thus improving public health worldwide, easing international tension over water rights, and reducing the cost of energy production involving water use.

Product use

Principal Applications

Biomimetic membranes are designed to filter salts and larger constituents from water *efficiently* using reverse osmosis technology. Biomimetic membranes achieve efficiency by increasing water flux by an order-of-magnitude for the same pressure drop across the membrane. More efficient membranes reduce energy consumption, thus lowering the cost of clean water and lessening demands on electrical energy production used for desalination. Lowering the cost of water purification will enhance access to clean fresh water, thus improving public health worldwide, easing international tension over water rights, and reducing the cost of energy production involving water use.

Based on the performance observed in small-scale studies, the order-of-magnitude improvement in water flux demonstrated by the biomimetic membrane is projected to have a significant beneficial impact on the worldwide water purification market. The improved water flux observed in the biomimetic membrane reduces the excess energy cost due to membrane resistance to flow by 88%, which translates into a savings of $1.45 M/yr for a modest-sized 100 ML/day desalination plant. Given that more than half of the 15,000 desalination plants around the world utilize RO technology, according to a 2004 survey by the U.S. National Research Council, and that *all* new plants going into production since then use RO technology, the potential economic benefits arising from the improved efficiency of the biomimetic membranes amounts to a possible savings of billions of dollars in electrical energy costs annually, along with an associated reduction in greenhouse gas production and improved quality of life.

Other Applications

The biomimetic membrane fabrication process and research strategy can be applied generally to design membranes for efficient liquid and gas separations. Besides tuning nanoporous architectures for salt rejection, they can also be tuned to reject toxic boric acid and arsenic while simultaneously facilitating water transport for efficient water purification. Carbon dioxide capture and removal could potentially be mediated by transport through selective porous membranes delicately tuned for the task with atomic layer deposition. Furthermore, the energy-efficient, highly selective membrane-based separation technology developed here is also pertinent to electrical energy storage applications in lithium-ion batteries.

Summary

Why this product should receive an R&D 100 Award

Commercial RO membrane technology has advanced only incrementally over the last 30 years. Our approach to biomimetic membrane design and fabrication using self-assembly and atomic layer deposition represents a revolutionary advance in the field of membrane technology for water filtration. Because of the nanoporous design, biomimetic membranes produce clean water far more efficiently than traditional non-porous membranes, thus significantly lowering the cost of water purification. Access to clean water improves as the cost goes down. The need for access to clean water may be the most important issue facing people worldwide because of its critical importance to public health, agriculture, and energy production.

Why is it important to have this product?

- Biomimetic membranes increase access to clean water by significantly lowering the cost of water desalination compared to traditional membrane systems.
- Cheaper, clean water benefits public health, agriculture, and energy production, and eases international tensions over water rights.

What technology benefits will it provide?

- The novel approach to membrane design and fabrication using self-assembly and atomic layer deposition represents a revolutionary advance in membrane technology that can be applied to develop efficient membranes for applications in toxin removal from water, carbon dioxide capture and sequestration, and electrical energy storage.
- The biomimetic membrane system is easily scalable to smaller sizes needed for domestic use or use by military in the field.

What financial benefits will it provide?

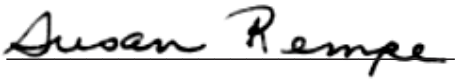
- Implemented at large scale, the order-of-magnitude improvement in water permeability demonstrated by biomimetic membranes is projected to translate to a savings of $1.45 M/yr annually for one desalination plant.
- The projected savings gained by one desalination plant due to the high efficiency of biomimetic membranes sums to a potential savings of billions of dollars in electrical energy costs annually, with an associated reduction in greenhouse gas production.

Wow! Factor

- By mimicking the nanoscale design features of natural water purification channels in a man-made membrane, we realized an order-of-magnitude improvement in water purification efficiency compared to state-of-the-art RO membranes.

Affirmation

By submitting this entry to *R&D Magazine* I affirm that all information submitted as a part of, or supplemental to, this entry is a fair and accurate representation of this product.



Susan Rempe

Appendices

Appendix A: Submitter Information

Appendix B: Development Team Information

Appendix C: Articles about Biomimetic Membranes for Water Purification

Appendix D: Technical Advance and Patents Pending

Appendix A: Submitter Information

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Appendix C: Articles about Biomimetic Membranes for Water Purification

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   a. "Access to clean water is increasingly becoming the most important issue facing people around the world."

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Appendix C: Articles about Biomimetic Membranes for Water Purification

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Appendix C: Articles about Biomimetic Membranes for Water Purification

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Appendix D: Technical Advance and Patents Pending

In re. Rempe, et al. Attorney Docket No. SD-11775PRO

BIOMIMETIC MEMBRANES FOR WATER DESALINATION

STATEMENT OF GOVERNMENT INTEREST

The United States Government has rights in this invention pursuant to Contract No. DE-AC04-94AL85000 between the United States Department of Energy and Sandia Corporation, for the operation of the Sandia National Laboratories.

BACKGROUND and SUMMARY

We have invented nanoporous materials that achieve a breakthrough in membrane design for pressure-driven water filtration. In a head-to-head performance comparison with commercially available reverse osmosis (RO) membranes, our membranes demonstrate production of drinking water from brackish input streams with three times higher water flux.

In contrast to traditional membranes that require high flux to maintain acceptable salt rejection, our membranes demonstrate high salt rejection even at low applied pressures, thus enabling production of purified water with doubled efficiency. We estimate that the improved efficiency of our membranes would lead to a 67% drop in energy loss due to membrane resistance in reverse osmosis desalination plants.

In traditional polymeric membrane technology, the active-site architecture responsible for ion rejection consists of a thin dense polymer coating on a porous support. In other words, the membrane is non-porous and thus requires high applied pressure to force salty water into the membrane for filtration and production of purified water on the other side. This thin-film composite membrane design has remained unchanged for 25 years.

In contrast to the traditional design of non-porous membranes for nano-filtration and reverse osmosis applications, we have pursued a novel design based on a porous architecture. Our nanoporous membrane design is inspired by cell membranes that contain nano-channels composed of proteins that catalyze higher water flux than conventional RO membrane technology and perfect ion rejection, all at small driving pressures. Our theoretical analysis shows that the biological protein channels that catalyze pure water transport lack binding

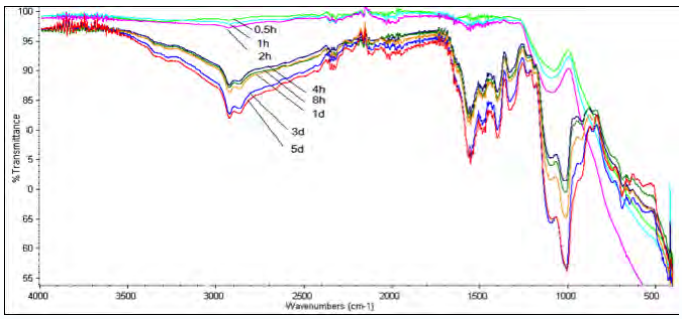

FIG. 1

EXCERPT: Filed provisional application and filed drawings

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND2011-2061P
Designed by the Sandia Creative Group (505)284-3181 SP (03/11)

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