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External Control of Ion Transport in Nanoporous Membranes with Surfaces Modified with Self-Assembled Monolayers

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We investigated the effect of external pH, ionic strength, and applied voltage to control the transport of ions through porous PCTE/Au/acid thiol membranes with pore radii of 4.0−5.9 nm. Electroless gold was deposited on the inside surfaces of the nanopores of the membrane. The thiols 11-mercaptoundecanoic acid ($HSC_{10}H_{20}COOH$) and 3-mercapto-1-propanesulfonic acid ($HSC_3H_6SO_3H$) were used to form self-assembled monolayers (SAMs) on the gold surfaces of the pores. The ionic permeant through the pores of the membranes was the organic ion benzene sulfonate (BS). The transport of benzene sulfonate in porous membranes modified with SAMs of the $HSC_{10}H_{20}COOH$ weak acid thiol was highly affected by external variation of the pH; the BS flux could be changed by a factor of 100. However, transport of benzene sulfonate in membranes modified with SAMs of the $HSC_3H_6SO_3H$ strong acid thiol was influenced less by external pH than transport in membranes modified with SAMs of the $HSC_{10}H_{20}COOH$ weak acid thiol. Increasing the ionic strength of the bulk solution caused the flux of benzene sulfonate to increase due to the decrease of the Debye length. Application of a voltage to the membrane has a significant influence on the benzene sulfonate flux through the porous membrane. Controlling the pH and the applied potential can lead to flux changes as large as a factor of 170.

Introduction

Nanoporous membranes have been investigated for a variety of applications in mass separation.[1−7] Several researchers have reported on pH-responsive or pH-switchable membranes, which have capabilities of passing cations at high pH and anions at low pH.[8,9] Liu et al.[8] have designed and synthesized a new type of pH-responsive film that contains amphoteric polyamine dendrimer units attached to an amphoteric random coil polymer via covalent bonds. Jimbo et al.[9] studied both theoretically and experimentally the passive transport of cationic, anionic, and neutral drugs through porous membranes with grafted-polymerized weak polyelectrolytes. The transport phenomena of amino acids, proteins, and ionic drugs in pH-responsive membranes have been studied in membranes with pH-responsive fixed charges.[10−12]

Martin and co-workers reported on the electroless deposition of gold on pore walls of polycarbonate track-etched (PCTE) membranes to achieve electrically tunable charge selectivity.[13] They devised ion-exchange membrane systems consisting of nanoscopic metal tubules with surface potentials which can be manipulated to either pass or exclude anions and cations by applying an electrical potential to the membrane.

In our previous work, we demonstrated the modification of surface properties of the pore walls in PCTE membranes by formation of self-assembled monolayers (SAMs) from ω-substituted thiols onto electroless gold deposited on the pore walls of the membrane.[14] We found that SAMs formed from a carboxylic acid functionalized thiol on gold impart to the porous membrane pH dependence of the ionic fluxes across the membrane.

In this work, we describe the effects of external pH, ionic strength, and applied electrical potential on the ionic transport in porous membranes with two different self-assembled monolayers covering the pores. The porous membranes were made by electroless gold deposition of gold on porous PCTE membranes followed by self-assembly of the two different acid-functionalized thiols. We show that external factors such as pH, ionic strength, and applied potential can be used to modulate the ionic transport in these porous membranes. The membranes can be useful for controlling protein separation, fabricating barriers, and devising controlled delivery systems.

Experimental Section

Materials. Commercial PCTE membranes (Poretics, Inc.) were used as received as substrates for electroless plating of gold. The membranes have a hydraulic pore radius of 28 nm, a pore density

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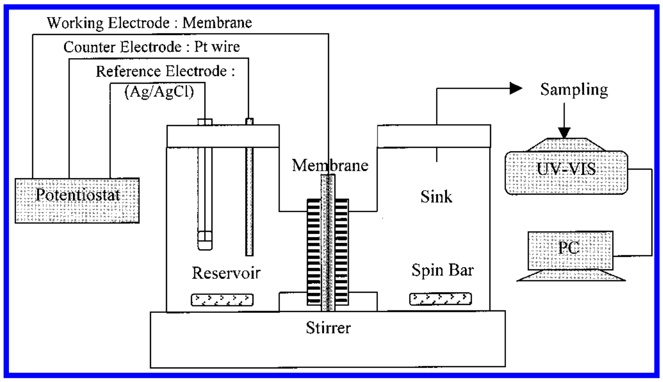

Figure 1. Diffusion experiment with applied potential to the membrane.

of 6 pores/μm^2, and a thickness of 6 μm.[14] The PCTE membranes have parallel cylindrical pores with a narrow distribution of pore sizes.[15]

The compounds $SnCl_2$ (98%), $AgNO_3$ (99+%), Na_2SO_3 (98+%), NH_4OH, trifluoroacetic acid (99%), formaldehyde, methanol (HPLC grade), and ethanol (HPLC grade) were obtained from Aldrich and used as received. A commercial gold-containing solution of $Na_3Au(SO_3)_2$ (Oromerse Part B, Technic Inc.) was used after dilution with water (40 times). The thiols 11-mercaptoundecanoic acid (95%) and 3-mercapto-1-propanesulfonic acid (sodium salt, 90%) were used to form SAMs on the gold surfaces. Milli-Q water (18 MΩ) was used for rinsing and preparation of all solutions.

Preparation of Membranes. We deposited electroless gold on the pore walls and both faces of the PCTE membranes using the procedure reported by Jirage et al.[16] The temperature of the gold-containing solution was maintained at 1 °C. After plating, all membranes were thoroughly rinsed with water. The PCTE membranes with electroless gold were immersed in an aqueous solution of 25% HNO_3, stored overnight, and then rinsed with water. This treatment is necessary to clean the membranes with the electroless gold without delaminating the gold from its substrate.[17] To form thiol monolayers on the gold surface, the gold-coated membrane was thoroughly rinsed with ethanol and then immersed in ethanolic solution of alkanethiol (5 mM) for 24 h.

Diffusion Experiments. A membrane separated the diffusion cell into two compartments (reservoir and sink). The reservoir contained an aqueous solution (35 mL) of the permeant, and the sink contained an aqueous solution (35 mL), initially without the permeant. The effective area of the membrane was 1.77 cm^2. Vigorous stirring (400 rpm) was applied in both compartments in all diffusion experiments by using two magnetic stirrers and a Corning stirring plate. Fluxes of permeants through the membrane were measured by UV–visible spectroscopy in a manner as described before.[14] The flux of the permeant across the membrane was obtained from the slope when the measured permeant concentration in the sink was plotted versus the diffusion time.

In the applied potential experiments, we used the same diffusion cell as described above. The reference electrode was Ag/AgCl/3 M NaCl. Platinum wire was used as the counter electrode, and the gold-coated membrane was the working electrode. Figure 1 shows the diffusion apparatus with an applied potential to the membrane. Before the diffusion experiments with applied potentials to the membrane were carried out, the stable potential region without oxidation and reduction of the solutions was found. Using cyclic voltammetry, it was observed that the stable potential region was -0.4 to $+0.4$ V. The diffusion experiments were conducted within this potential region.

Table 1. Combination of All Species in Each Compartment According to Ionic Strengths

ionic strength (mM)	reservoir	sink	variation of *x*
1.5	1 mM BS *x* mM HCl (NaOH) (0.5 − *x*) mM NaCl	0 mM BS *x* mM HCl (NaOH) (1.5 − *x*) mM NaCl	$0 < x < 0.5$
2	1 mM BS *x* mM HCl (NaOH) (1 − *x*) mM NaCl	0 mM BS *x* mM HCl (NaOH) (2 − *x*) mM NaCl	$0 < x < 1$
3	1 mM BS *x* mM HCl (NaOH) (2 − *x*) mM NaCl	0 mM BS *x* mM HCl (NaOH) (3 − *x*) mM NaCl	$0 < x < 2$
4	1 mM BS *x* mM HCl (NaOH) (3 − *x*) mM NaCl	0 mM BS *x* mM HCl (NaOH) (4 − *x*) mM NaCl	$0 < x < 3$

Results and Discussion

We first investigated the effect of external pH and ionic strength on the ion flux through the membranes. The hydraulic pore radius (R) of the template PCTE membranes was 28 nm, and that of the final membranes with the gold and the self-assembled monolayers was 4.0–5.9 nm. We used benzene sulfonate (BS) anion as the permeant, and the pH of the solution in both the reservoir and the sink was controlled in a range from 2.5 to 9.5. Before diffusion experiments were started, the reservoir contained an aqueous solution of 1 mM sodium benzene sulfonate (SBS) plus other ionic species as shown in Table 1. The sink solution did not contain SBS but did contain other salts, so that the ionic strength and pH were identical to that in the reservoir. As indicated in Table 1, the HCl or NaOH solutions were used to adjust the external pH of the solutions to be equal in both compartments. The actual pH values were measured with an Orion Research pH meter (model 601A). We used NaCl as a balance component to maintain the ionic strengths of the solutions in both compartments to be the same and constant (ionic strengths: 1.5, 2, 3, and 4 mM) at various pH values.

The concentration of benzene sulfonate in the sink (C_s) with time (t) as a function of external pH values and different ionic strengths is shown in Figure 2 for a PCTE/Au/$HS(CH_2)_{10}COOH$ membrane. The hydraulic pore radius of this membrane is 5.5 nm. The initial concentration of SBS in the reservoir ($C_{R,0}$) was 1 mM in all cases. As shown in Figure 2, the concentration of benzene sulfonate drops dramatically as the external pH increases, consistent with our previous results.[14] At low pH, the carboxylic acid terminal groups of the thiol give a low surface charge due to the acidic condition of the solutions. Thus, the increase of the benzene sulfonate concentration is relatively large with time for low pH in comparison to high pH values. At high pH, the carboxylic acid terminal groups of the thiols are negatively charged. The negatively charged surface of the pore wall rejects the benzene sulfonate anions from the pore. The change of benzene sulfonate concentration with time is relatively low at high pH values compared to low pH values. Electrostatic repulsion between the charge on the pore walls and the benzene sulfonate in the solution is significant and leads to a decrease in the benzene sulfonate flux. From the above results, it is obvious that the pH-dependent flux of benzene sulfonate across the PCTE/Au/$HS(CH_2)_{10}COOH$ membrane is influenced by the ionization of the carboxylic acid groups lining the pore walls.

The flux of benzene sulfonate passing through the membrane was determined from the slope of the C_s-t plot.[8] It is noted here that the fluxes reported in Figure 2 are repeatable to within ±4%. The fluxes of benzene

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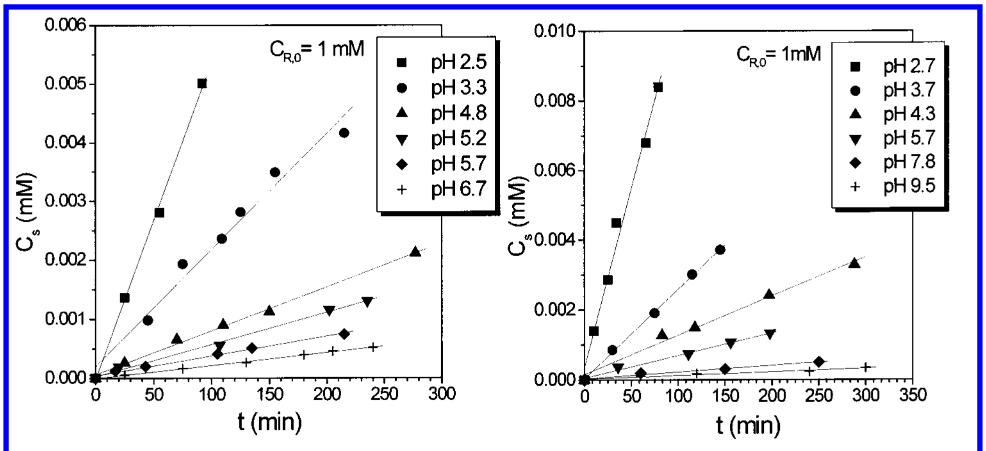
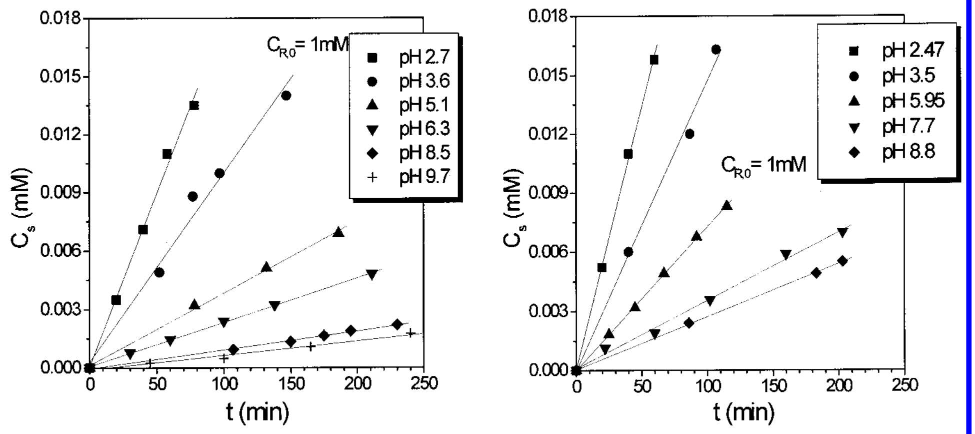


(Ionic strength = 1.5mM, λ_D= 8.2 nm) (Ionic strength = 2mM, λ_D= 7 nm)



(Ionic strength = 3mM, λ_D= 5.8 nm) (Ionic strength = 4mM, λ_D= 5 nm)

Figure 2. Diffusion of benzene sulfonate anions across a PCTE/Au/HS$(CH_2)_{10}$ COOH membrane: effect of external pH and ionic strength (R = 5.5 nm; SBS concentration, $C_{R,0}$ = 1 mM).

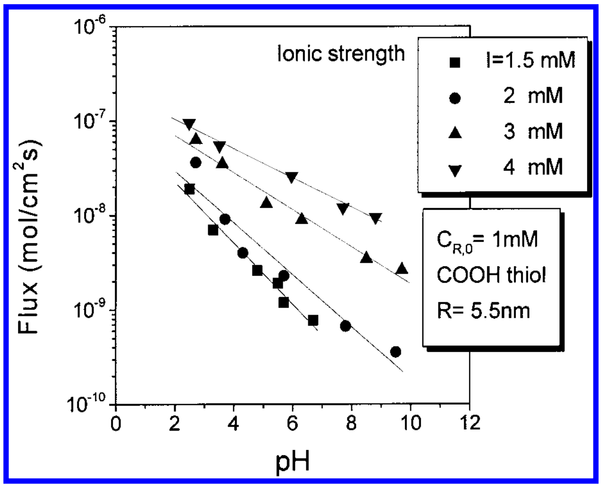


Figure 3. Flux of benzene sulfonate as a function of external pH and ionic strength obtained with a PCTE/Au/HS$(CH_2)_{10}$-COOH membrane.

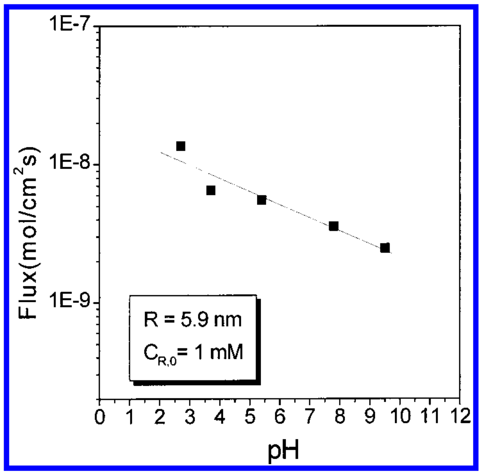


Figure 4. Flux of benzene sulfonate as a function of external pH obtained with a PCTE/Au/SO_3H thiol membrane (R = 5.9 nm; ionic strength = 2 mM; SBS concentration, $C_{R,0}$ = 1 mM).

sulfonate across a PCTE/Au/HS$(CH_2)_{10}$COOH membrane are given in Figure 3 as a function of the ionic strength. As expected, the benzene sulfonate flux decreases as the ionic strength decreases. The reduction of the benzene sulfonate flux is directly related to the change of the Debye length (λ_D) with the ionic strength. The Debye length is a rough measure of the thickness of the diffuse double layer on the inside of the pore wall where anion repulsion is dominant. The Debye lengths associated with the various ionic strengths of 1.5, 2, 3, and 4 mM are 8.2, 7.0, 5.8, and 5.0 nm, respectively. Thus, as the ionic strength increases, the Debye length decreases and the benzene sulfonate can diffuse more easily through the charged porous membrane because of the reduced screening effect along the periphery of the pore wall.

The fluxes of benzene sulfonate with a PCTE/Au/HS-$(CH_2)_3SO_3H$ membrane, measured at different external pH values, are shown in Figure 4. The hydraulic pore radius of this membrane was 5.9 nm. The initial concentration of SBS in the reservoir ($C_{R,0}$) was 1 mM, and the

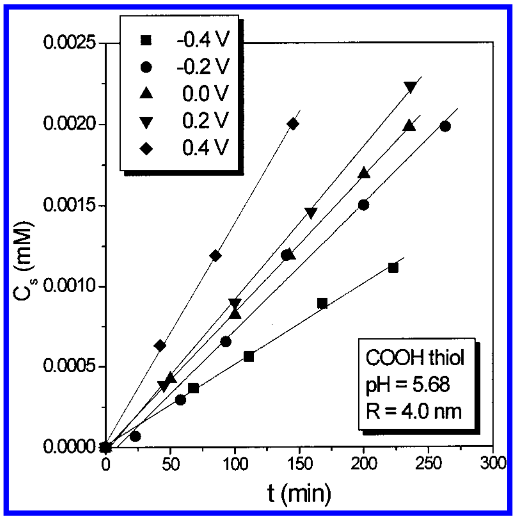


Figure 5. Diffusion of benzene sulfonate across a PCTE/Au/HS(CH$_2$)$_{10}$COOH membrane as a function of the potential applied to the membrane (SBS concentration, $C_{R,0}$ = 1 mM).

ionic strength of the solution in the two compartments was 2 mM. The flux of benzene sulfonate is less sensitive with external pH compared to the results obtained with the membrane prepared with a SAM of the weak acid thiol. The negative charge of the sulfonic acid group in the SAM is less sensitive to the external pH of the electrolyte solution, compared to carboxylic acid, because sulfonic acid is a strong acid while carboxylic acid is a weak acid. Even at low pH, the sulfonic acid groups of the SAM still have significant negative surface charge. The change of the benzene sulfonate flux in Figure 4 is about a factor of 6 from low to high pH. For the carboxylic acid membrane, the change of flux with pH is a factor of 100.

The sink concentration of benzene sulfonate with time, measured for different applied potentials to a carboxylic thiol membrane, is shown in Figure 5. The applied potential experiments were conducted in the range of −0.4 to 0.4 V in order to eliminate oxidation and/or reduction in the solutions. The linearity of the data points is as good as that found in the experiments without applied potential. The hydraulic pore radius of this membrane was 4.0 nm. The initial concentration of SBS in the reservoir ($C_{R,0}$) was 1 mM, the ionic strength of the solutions in the two compartments was 2 mM, and the external pH was fixed at 5.68. Clearly, the rate of the concentration change of benzene sulfonate drops as the potential decreases. At this pH, the application of a negative potential to the membrane causes the negative surface charge to become more negative and consequently the electrostatic force repelling the benzene sulfonate from the charged pore is increased. From the results in Figure 5, the fluxes of benzene sulfonate can be obtained and are given in Figure 6 as a function of the applied potential to the membrane. The repeatability of the fluxes was ±5%. The change in the flux with applied potential is approximately a factor of 3 from −0.4 to +0.4 V. From these experiments, it is difficult to determine what the surface charge and the potential are at the pore wall. The SAMs of HS(CH$_2$)$_{10}$-COOH coating the pores should cause a significant voltage drop of the applied potential across the thiol.[18] In fact, a SAM with a shorter hydrocarbon length could be more beneficial in that it would offer a lower resistance and therefore may give rise to a higher surface potential and charge on the pore wall.[18] Self-assembled monolayers of thiols with three carbons are disorganized and are less effective in charge blockage as measured by cyclic voltammetry.[18]

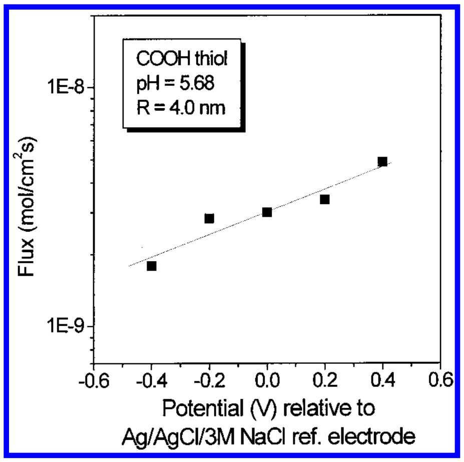


Figure 6. Flux of benzene sulfonate across a PCTE/Au/HS-(CH$_2$)$_{10}$COOH membrane as a function of the applied potential to the membrane (SBS concentration, $C_{R,0}$ = 1 mM).

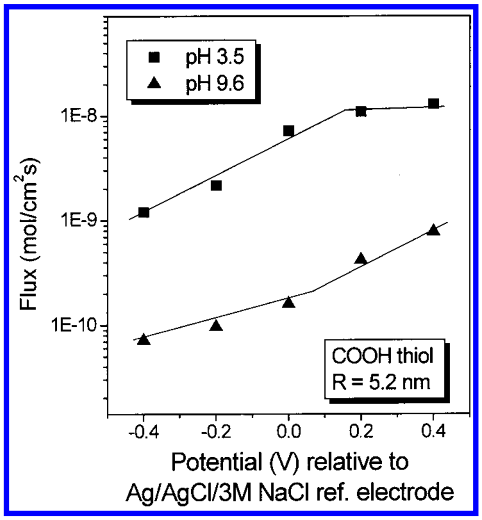


Figure 7. Flux of benzene sulfonate across a PCTE/Au/HS-(CH$_2$)$_{10}$COOH membrane as a function of the applied potential to the membrane at different external pH conditions (SBS concentration, $C_{R,0}$ = 1 mM).

The pH is also a factor in separations using applied potentials. Figure 7 shows that the benzene sulfonate flux increases with increased applied potential to the membrane and decreased external pH. The change in the flux between the lowest and highest values is about a factor of 170. This is indeed a very large change in the flux and makes the use of external control very attractive in these surface-modified membranes. For the case of high pH (9.6), the effect on the flux of benzene sulfonate is more significant for positive applied voltages. At high pH, the thiols on the pore wall will have maximum negative charge (of the order of 1 negative charge per 4 nm^2 area) and the surface potential of the pores will be large and negative. In the case of large negative surface potential, decreasing the negative surface potential by external means will only have a secondary effect on the negative potential in solution.[19] Consequently, the negative applied potential has a secondary effect on the flux of ions through the pore. On the other hand, the imposition of a positive potential will reduce the negative surface potential to lower values and this will have a more significant effect on the transport of ions through the pores. In the case of low pH, the charge of the thiols will be close to neutral and imposing a negative

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[18] Zhang, L. Q. Ph.D. Thesis, University of California, Davis, CA, 2001.

potential should have a profound effect on ion transport as is shown in Figure 7.

Applying a voltage to the membrane surface and using different pH values can be a promising method for enhancing the permselectivity of porous membranes. The selectivity of one ionic species over another can be tailored with appropriate external control. For example, these porous membranes can be used in the separation of proteins that have similar molecular sizes but different isoelectric points.

Conclusions

We demonstrated that the effect of external pH, ionic strength, and applied potential to the membrane can be used to control the transport of ions through porous PCTE/Au/acid thiol membranes. The transport of the anion benzene sulfonate in porous membranes modified with SAMs of $HSC_{10}H_{20}COOH$ weak acid thiol was highly affected by external pH variation. However, transport of benzene sulfonate in porous membranes modified with SAMs of $HSC_3H_6SO_3H$ strong acid thiol was less sensitive to external pH variation than that for the SAM of the $HSC_{10}H_{20}COOH$ weak acid thiol. As the total ionic strength of the bulk solutions increases, the flux of benzene sulfonate increases due to the decrease of the Debye length. In applied voltage experiments, from −0.4 to 0.4 V, the flux of benzene sulfonate increases as the applied potential to the membrane increases. A combination of pH and applied potential can change the flux by a factor of 170.

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