Metal Nanotubule Membranes with Electrochemically Switchable Ion-Transport Selectivity

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Membranes containing cylindrical metal nanotubules that span the complete thickness of the membrane are described. The inside radius of the nanotubules can be varied at will; nanotubule radii as small as 0.8 nanometer are reported. These membranes show selective ion transport analogous to that observed in ion-exchange polymers. Ion permselectivity occurs because excess charge density can be present on the inner walls of the metal tubules. The membranes reject ions with the same sign as the excess charge and transport ions of the opposite sign. Because the sign of the excess charge on the tubule can be changed potentiostatically, a metal nanotubule membrane can be either cation selective or anion selective, depending on the potential applied to the membrane.

A variety of materials that contain pores of molecular dimensions are known, including the porin proteins (*1*, *2*), zeolites (*3*), and fullerene tubules (*4*). Synthetic membranes with monodisperse pores that approach molecular dimensions might be useful as mimics for biological systems and would be useful in membrane science and technology. Here we introduce a class of membranes that contain cylindrical nanoscopic metal tubules that run the complete width of the membrane. These metal nanotubule membranes show selective ion transport analogous to that observed in ion-exchange polymers (*5*). Ion permselectivity (*6*) occurs because excess charge density can be present on the inner walls of the tubules. The tubes reject ions of the same sign, and transport ions of the opposite sign, as this excess charge. This is only possible when the inside radius of the tubule is small relative to the thickness of the electrical double layer (*7*) within the tubule. These membranes can be either cation-selective or anion-selective, depending on the potential applied to the membrane; hence, these metal nanotubule membranes can be viewed as universal ion exchange membranes.

The pores in a commercially available polycarbonate filtration membrane (Poretics) were used as templates (*8*) to form the metal (Au) nanotubules. These membranes contain cylindrical nanopores of uniform radius (25 nm, 6×10^8 pores per square centimeter) that run through the complete thickness (6 μm) of the membrane. Gold was electrolessly plated (*9*) onto the walls of these pores to yield a Au nanotubule within each pore (Fig. 1). Gold films were also deposited on both faces of the membrane. These Au surface layers allow us to make electrical contact with the nanotubules within the pores. The thickness of the Au layers deposited on the pore walls can be controlled by varying the plating time. As a result, the inside radius of the Au nanotubules can be varied at will [as determined from measurements of gas (He) flux (*10*) across the tubule-containing membrane].

We describe the results of three sets of experiments that demonstrate that these metal nanotubule membranes can show selective ion transport. All of these experiments involve a U-tube cell in which the membrane to be studied separates two aqueous solutions. The simplest experiment entails using a "feed" solution of a colored anionic or cationic species on one side of the membrane and a "receiver" solution that is initially devoid of the colored species on the other side of the membrane. A membrane that contained Au nanotubules with radii of ~2.5 nm (*10*) was used for these experiments.

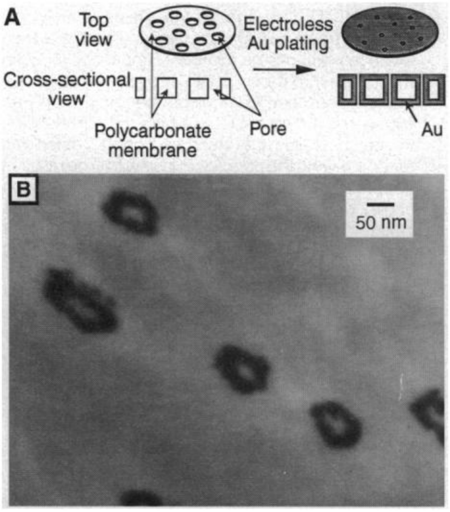

Fig. 1. (**A**) Schematic diagram of the electroless Au plating procedure. (**B**) Transmission electron micrograph showing a cross section of a Au-nanotubule membrane. The Au tubules are the black rings. The elliptical appearance is caused by the microtoming process. Plating time, 10 min.

When the feed solution is 1 mM KCl and 0.5 mM methylene blue (a cationic dye) and the receiver solution is 1 mM KCl, the initially colorless receiver solution turns blue as a result of transport of the cationic dye across the membrane (Fig. 2). In contrast, when the feed solution is 1 mM KCl and 5 mM $KMnO_4$ (MnO_4^- is purple) and the receiver solution is 1 mM KCl, the receiver solution remains colorless (Fig. 2). These experiments provide simple visual evidence that this membrane transports a large cation but does not transport a much smaller anion. We have used potentiometric measurements to explore the nature of this cation permselectivity.

The extent of ion permselectivity displayed by a membrane can be expressed quantitatively by the transference numbers (*11*) for cations (t_+) and anions (t_-) within the membrane. Transference numbers can be determined potentiometrically with a concentration cell (*11*), in which the membrane to be evaluated separates two electrolyte solutions that contain the same salt at different concentrations. For a 1:1 salt, the membrane potential (E_m) is given approximately by

$$E_m = (2.303RT/nF)(t_+ - t_-)\log(a_h/a_l) \quad (1)$$

where R is the universal gas constant, T is the temperature of the solution, n is the charge of the ions, F is Faraday's constant, and a_h and a_l are the activities of the salt in the solution of high and low salt concentration, respectively (*6*). Equation 1 indicates that for an ideal cation-permselective membrane ($t_+ = 1.0$ and $t_- = 0.0$), a plot of E_m versus $\log(a_h/a_l)$ would be linear with an intercept of 0 and a slope of 59 mV (dashed line, Fig. 3).

A concentration cell was assembled in which a Au-nanotubule membrane separat-

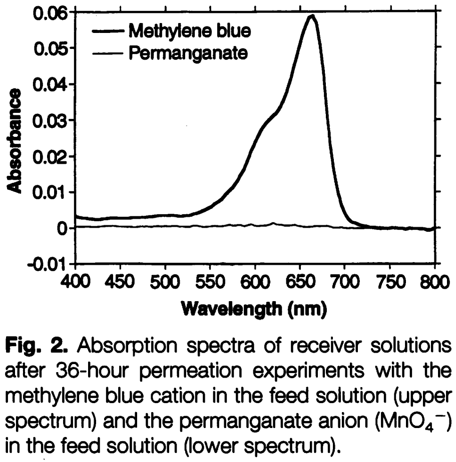

Fig. 2. Absorption spectra of receiver solutions after 36-hour permeation experiments with the methylene blue cation in the feed solution (upper spectrum) and the permanganate anion (MnO_4^-) in the feed solution (lower spectrum).

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ed two KCl solutions. The potential of the membrane was not controlled with a potentiostat. However, Cl^- adsorbs strongly to Au (*12*), and the Au films on the membrane faces and the inside walls of the Au tubules had excess negative (Cl^-) charge on their surfaces. This excess negative charge was balanced by a layer of excess positive charge (K^+) in the solution immediately adjacent to the Au surfaces (the electrical double layer) (*7*).

Data obtained from this concentration cell for membranes prepared with various plating times (Fig. 3) show that these membranes can display ideal cation-permselective behavior and that the region over which ideal behavior is observed is extended to higher salt concentrations (on the high-concentration side of the membrane) as plating time increases. These observations can be explained as follows: Over the range of plating times used in Fig. 3, the average inside radii of the Au tubules varied from ~9.4 nm (plating time, 60 min) to ~0.8 nm (plating time, 180 min) (*10*). Gouy-Chapman theory (*7*) predicts that over the salt concentration range used here, the thickness of the electrical double layer within the tubules (as approximated by the Debye length) varies from ~30 nm (lowest concentration) to ~0.3 nm (highest concentration). Figure 3 indicates that the Au-nanotubule membranes show ideal cation permselectivity if the radius of the tubule is small relative to the thickness of the electrical double layer within the tubule.

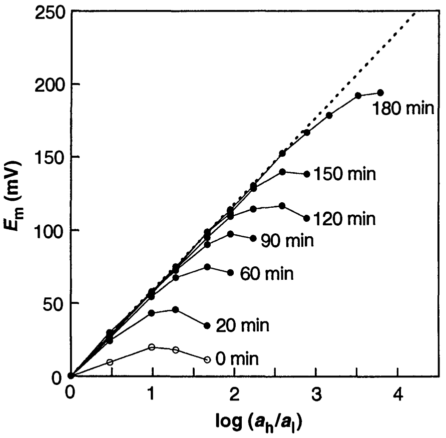

Fig. 3. Values of E_m obtained for membranes prepared for the indicated plating times. The solution on the low-concentration side of the membrane was 0.1 mM KCl. The solution on the high-concentration side of the membrane was varied from 0.1 mM to 1 M KCl. The E_m values were measured by two Ag/AgCl (KCl saturated) electrodes placed in each half-cell through agar salt bridges. Mean activities were calculated from Debye-Hückel theory (*22*) (<0.1 M) and from reported activity coefficients (*23*) (≥0.1 M). The dashed line is for ideal cation-permselective behavior (Eq. 1, with $t_+ = 1$ and $t_- = 0$).

To illustrate this point, consider the membrane plated for 60 min. The tubules in this membrane have an average inside radius of ~9.4 nm. At low concentrations of salt, the electrical double layer should be thicker than this tubule radius. Anions are excluded from the tubes, and ideal cation permselectivity is observed. At high salt concentrations, the electrical double layer is thin relative to the tubule radius. Anions can now enter the tubules and ideal cation permselectivity is lost (Fig. 3). Finally, the membrane plated for 180 min shows cation permselectivity almost identical to that of the ionomer Nafion (*13*), which is a highly cation-permselective polymer used in industrial electrolytic processes also (*5*).

The permselectivity can also be controlled by potentiostatically injecting excess charge into the Au nanotubules. For these studies, it is essential to use an anion that does not adsorb to Au because we do not want the excess charge to be determined by adsorption. Because F^- does not adsorb to Au (*14*), KF was chosen as the electrolyte. A concentration cell was assembled in which a Au-nanotubule membrane separated 1 mM and 10 mM KF solutions. This membrane was connected (through the Au surface layers) to the working electrode lead of a potentiostat, and the potential applied to the membrane was varied from −0.5 to +0.5 V versus Ag/AgCl. The E_m values were measured at each applied potential (Fig. 4).

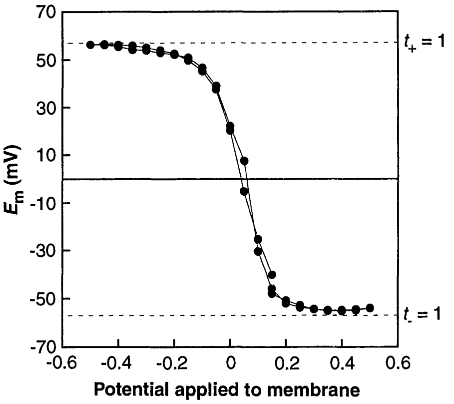

Fig. 4. Variation of E_m with potential applied to the Au-nanotubule membrane (1 mM KF on the low side and 10 mM KF on the high side of the membrane; tubule radius, ~1.1 nm). The dashed lines at the top and bottom are the E_m values that would be achieved if the nanotubule membrane showed ideal cation and ideal anion permselectivity, respectively (Eq. 1). Electrical contact was made to the membrane by sandwiching it between two copper foils that have a conductive adhesive. The Cu was masked with plastic adhesive tape and epoxy. Immediately before measurement, we cathodically cleaned the membranes (stripped of adsorbed ions) by holding the potential at −0.5 V versus Ag/AgCl for 10 min in 50 mM KF solution. The potential of the membrane was controlled with a potentiostat versus a Ag/AgCl reference electrode immersed in the high-concentration solution. E_m was measured with the membrane under potential control.

At negative applied potentials, the nanotubule membrane shows ideal cation permselectivity, whereas at positive applied potentials, the membrane shows ideal anion permselectivity. This selectivity occurs because at negative applied potentials, excess electrons are present on the walls of the tubes, and excess positive charge (K^+) accumulates within the tubes. As a result, anions (F^-) are excluded and cations (K^+) are transported by the membrane. At positive applied potentials, the opposite situation occurs: Cations are excluded and anions are transported.

For any combination of metal and electrolyte, there is a potential called the potential of zero charge (pzc), where there is no excess charge on the metal. At this potential, the nanotubule membranes should show neither cation nor anion permselectivity, and E_m should approach (*15*) 0 mV. For the tubule-containing membrane, E_m does indeed go from the ideal cation permselective value, through zero, to the ideal anion permselective value (Fig. 4). Furthermore, the potential at which E_m approaches (*15*) zero is close to the reported pzc [−4 mV for Au in 1 mM NaF (*16*)].

The Au-nanotubule membranes can therefore function as electronically switchable ion exchange membranes (Fig. 4). However, it would seem that this would only be possible if the electrolyte

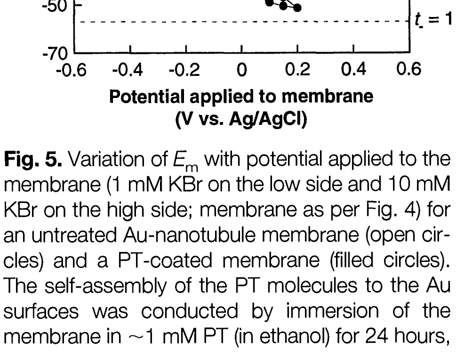

Fig. 5. Variation of E_m with potential applied to the membrane (1 mM KBr on the low side and 10 mM KBr on the high side; membrane as per Fig. 4) for an untreated Au-nanotubule membrane (open circles) and a PT-coated membrane (filled circles). The self-assembly of the PT molecules to the Au surfaces was conducted by immersion of the membrane in ~1 mM PT (in ethanol) for 24 hours, followed by careful rinsing with pure ethanol and water.

contained only nonadsorbing anions such as F$^-$. If an adsorbing anion (such as Cl$^-$ or Br$^-$) (*12, 17*) were present, it would adsorb at positive applied potentials, yielding a cation permselective membrane. Although the anion would not adsorb at sufficiently negative applied potentials, the metal would have excess electron density at such potentials, and again, cation permselectivity would be observed. Hence, in the presence of an adsorbing anion, cation permselectivity will be observed at all applied potentials (Fig. 5, open circles).

Anion adsorption can be prevented by adsorbing a monolayer of a strongly adherent thiol molecule to the Au surfaces (*18, 19*). We used 1-propanethiol (PT) because the Au nanotubules can still be wetted with water after adsorption of the PT monolayer (*19*). The E_m versus applied potential curves for an untreated and PT-treated Au-nanotubule membrane, with KBr solutions present on either side of the membrane, are shown in Fig. 5. The untreated membrane shows only cation permselectivity, but the permselectivity of the PT-treated membrane can be switched, exactly as was the case with the nonadsorbing electrolyte (Fig. 4).

We have demonstrated that these metal nanotubule membranes can be cation permselective, anion permselective, or nonselective, depending on the potential applied to the membrane (*20*). These membranes can be as permselective as the commercially relevant Nafion polymer and should have applications in both fundamental and applied electrochemistry. In addition, because the Au tubules have radii that approach molecular dimensions, these membranes might have applications in chemical separations, for example, industrial gas separations (*21*).

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24. This work was supported by the Office of Naval research. M.N. acknowledges support from a research fellowship of the Japan Society for the Promotion of Science. We also acknowledge H. S. White for valuable discussions.

5 December 1994; accepted 2 March 1995

Prebiotic Synthesis of 5-Substituted Uracils: A Bridge Between the RNA World and the DNA-Protein World

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Under prebiotic conditions, formaldehyde adds to uracil at the C-5 position to produce 5-hydroxymethyluracil with favorable rates and equilibria. Hydroxymethyluracil adds a variety of nucleophiles, such as ammonia, glycine, guanidine, hydrogen sulfide, hydrogen cyanide, imidazole, indole, and phenol, to give 5-substituted uracils with the side chains of most of the 20 amino acids in proteins. These reactions are sufficiently robust that, if uracil had been present on the primitive Earth, then these substituted uracils would also have been present. The ribozymes of the RNA world would have included many of the functional groups found in proteins today, and their catalytic activities may have been considerably greater than presently assumed.

The discovery of catalytic RNA (*1*) gave credibility to prior suggestions that the first living organisms were RNA molecules with catalytic activity (*2*), a situation that is called the RNA world (*3*). However, the catalytic activities of RNA known so far are mostly limited to phosphodiester reactions. This limitation may be due to the small number of functional groups available in RNA—hydroxyls, phosphates, and the amino and imidazole parts of the bases. It has also been proposed that metal ions are the catalytic agents rather than the RNA functional groups and that the role of the RNA is to hold the metal ions in the correct position (*4*).

It is usually assumed that proteins largely replaced ribozymes because the additional functional groups available gave proteins greater versatility. There are many modified nucleosides in transfer RNA (tRNA), some of which have functional groups of potential catalytic importance (*5*). These nucleosides may be molecular fossils from the RNA world. We show here that, under potentially prebiotic conditions, RNA, particularly the 5-substituted uracils in RNA, would have had many of the functional groups that are available in proteins, and that, as a result, the catalytic activities of the ribozymes of the RNA world may have been considerably greater than presently assumed.

Cytosine and uracil can be efficiently synthesized prebiotically from cyanoacetaldehyde and urea, and a similar reaction with thiourea gives 2-thiocytosine and 2-thiouracil (*6*). Formaldehyde (HCHO) is generally believed to have been present on the early Earth because it is synthesized in good yield under reducing conditions with ultraviolet light and electric discharges (*7*). Both uracil and cytosine and their nucleosides are subject to electrophilic addition of formaldehyde at the C-5 position. We have concentrated on uracil because cytosine, 2-thiouracil, and uridine all react at 1/27 of the rate at which uracil acts, and cytidine reacts at 1/140 of uracil's rate. The pH rate

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