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Electrochemical Synthesis of Ultrathin Film Composite Membranes

by

Chao Liu, Mark W. Espenscheid, Wen-Janq Chen
and Charles R. Martin*

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Department of Chemistry
Texas A&M University
College Station, TX 77843

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The development of ultrathin film composite membranes was an important breakthrough in the membranes-separation area. Ultrathin film composite membranes consist of a porous support layer, and a dense, ultrathin active layer. The porous support layer provides mechanical strength yet is highly permeable. The separation process occurs primarily in the ultrathin active layer; because this layer is thin, the overall flux of permeate through the membrane is high. Thus, ultrathin film composite membranes can provide good mechanical strength, high selectivity, and high permeability. This combination of attributes usually cannot be obtained with homogeneous membranes. We have developed a new method for preparing ultrathin film composite membranes. This method involves electrochemically-initiated polymerization at a microporous support-membrane surface and yields an ultrathin polymer film on one face of the support-membrane. Composite membranes with separating layers as thin as 50 nm have been prepared using this new electrosynthetic method. (Continued on next page)					
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Electrochemical Synthesis of Ultrathin Film Composite Membranes

Chao Liu, Mark W. Espenscheid, Wen-Janq Chen
and Charles R. Martin*

Department of Chemistry
Texas A&M University
College Station, TX 77843

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Membrane-based separations are often less energy intensive and more resource conservative than alternative separations methods (1). Synthetic membranes have, therefore, been the focus of considerable recent research effort (1). The development of ultrathin film composite membranes was one of the most important breakthroughs in the synthetic membranes area (1b,2); these membranes consist of a porous support layer, and a dense, ultrathin (2) active layer. The porous support layer provides mechanical strength yet is highly permeable. The separation process occurs primarily in the ultrathin active layer; because this layer is thin, the overall flux of permeate through the membrane is high. Thus, composite membranes can provide good mechanical strength, high selectivity, and high permeability. This combination of attributes usually cannot be obtained with homogeneous membranes (1b,3).

We have developed a new method for preparing ultrathin film composite membranes. This method involves electrochemically-initiated polymerization at a microporous support-membrane surface and yields an ultrathin (2) polymer film on one face of the support-membrane. We describe the synthesis, and preliminary results of electrochemical characterizations, of such membranes in this correspondence.

Figure 1 shows a schematic of the procedure used to prepare the ultrathin film composites. Anopore (Alltech) Al_2O_3 filters were used as the support membranes (4); Anopore is 65 % porous, and contains linear, cylindrical, 200 nm-diameter pores. The

Anopore surface is first coated with a ca. 50 nm layer of gold (5); this layer is too thin to block the pores (Figure 1B). A copper wire is attached and the resulting electrode (Figure 1C) is immersed into a solution containing the electropolymerizable monomers. Electropolymerization causes a thin polymer skin to "grow" over the Anopore surface (Figure 1D).

Our work to date has focused on copolymers of divinylbenzene (DVB) and ethylvinylbenzene (EVB). These monomers can be reduced electrochemically to anions which polymerize via a conventional anionic mechanism (6). Technical grade DVB (55 % DVB and 45 % EVB, Polysciences) was extracted with 10 % NaOH to remove polymerization inhibitors. The extract was washed 3 times with purified water. The DVB/EVB was then passed through a column of activated alumina; the effluent was stored (in the dark) over calcium hydride at -5°C . Polymerization solutions were prepared by mixing measured volumes of the purified DVB/EVB with N,N'-dimethylformamide (DMF) (7); solutions were also 0.2 M in Bu_4NClO_4 , which served as the supporting electrolyte (7).

The electropolymerization cell contained the Au/Anopore working electrode, an Ag wire quasi-reference, and a Pt foil counter electrode. The polymerization solution was vigorously degassed with purified Ar. Polymerization was initiated by scanning the working electrode potential (200 mV sec^{-1}) once from 0 to -2.75 V and back (8). The voltammetric wave consisted of a single cathodic peak, with no anodic return wave. The poly(DVB-EVB) film which had formed across the membrane surface was rinsed

with copious quantities of acetone and air dried.

Figure 2 shows electron micrographs of cross sections of typical ultrathin film composite membranes. The poly(DVB-EVB) films are uniformly coated across the Anopore support-membrane surfaces, and have uniform film thicknesses (9). Film thickness was approximated from such micrographs. Films with thicknesses ranging from 3.0 μm to 50 nm have been prepared via this method (10). The chemical identity of the poly(DVB/EVB) films was established using Fourier transform infrared spectroscopy (11).

We have used gas-transport (1b,c), voltammetric, and potentiometric (12) experiments to prove that the composite membranes are defect-free. Only the potentiometric measurements will be discussed here. Potentiometric data were obtained from sulfonated (13) versions of the poly(DVB/EVB) based-composites. The following cell was employed:

$\text{Ag/AgCl/ (NaCl, 2 mM) /Composite/ (NaCl, 2 mM to 5 M) /Ag/AgCl}$
The potential of this cell is given by (12)

$$E_{\text{cell}} = 2t_{\text{Na}}RT/F \ln[(a_{\text{r}}/a_{\text{l}})] \quad (1)$$

where t_{Na} is the transference number for Na^+ in the membrane, and the a terms are the Na^+ activities. If the poly(DVB/EVB- SO_3^-) films are defect-free (and cation permselective), the composite membranes will show cation transference numbers of unity.

Figure 3 shows potentiometric data, plotted as per Equation 1; the dashed curve was calculated assuming $t_{\text{Na}} = 1.0$. The experimental data are for an 1100 equivalent weight Nafion^R (14) and an ultrathin film composite membrane. Nafion is one of the

most cation-permselective materials known to man (14). This is reflected in the enormous concentration range over which the Nafion data fall on the $t^+ = 1.0$ line. Remarkably, the ultrathin film composite membrane data are essentially identical to the Nafion data (Figure 3). These data indicate that the composite membranes are permselective and defect-free.

In closing, it is worth noting that the method described here should be applicable to any of the vast number of materials which can be synthesized electrochemically (15). Other microporous support membranes could also be employed.

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Figure Captions

Figure 1. Schematic of ultrathin film composite membrane fabrication procedure.

Figure 2. Electron micrographs of cross-sections of ultrathin film composite membranes. A. Film thickness is ca. 80 nm. B. Film thickness is ca. 800 nm.

Figure 3. Plot of cell potential (see Equation 1) vs. log of ratio of the activities of Na^+ on either side of the membrane. Concentration of NaCl on the left side was 2 mM; concentration on the right side was varied between 2 mM and 5 M. ● = Nafion membrane. ○ = Ultrathin film composite membrane; film thickness was ca. 1.5 μm .

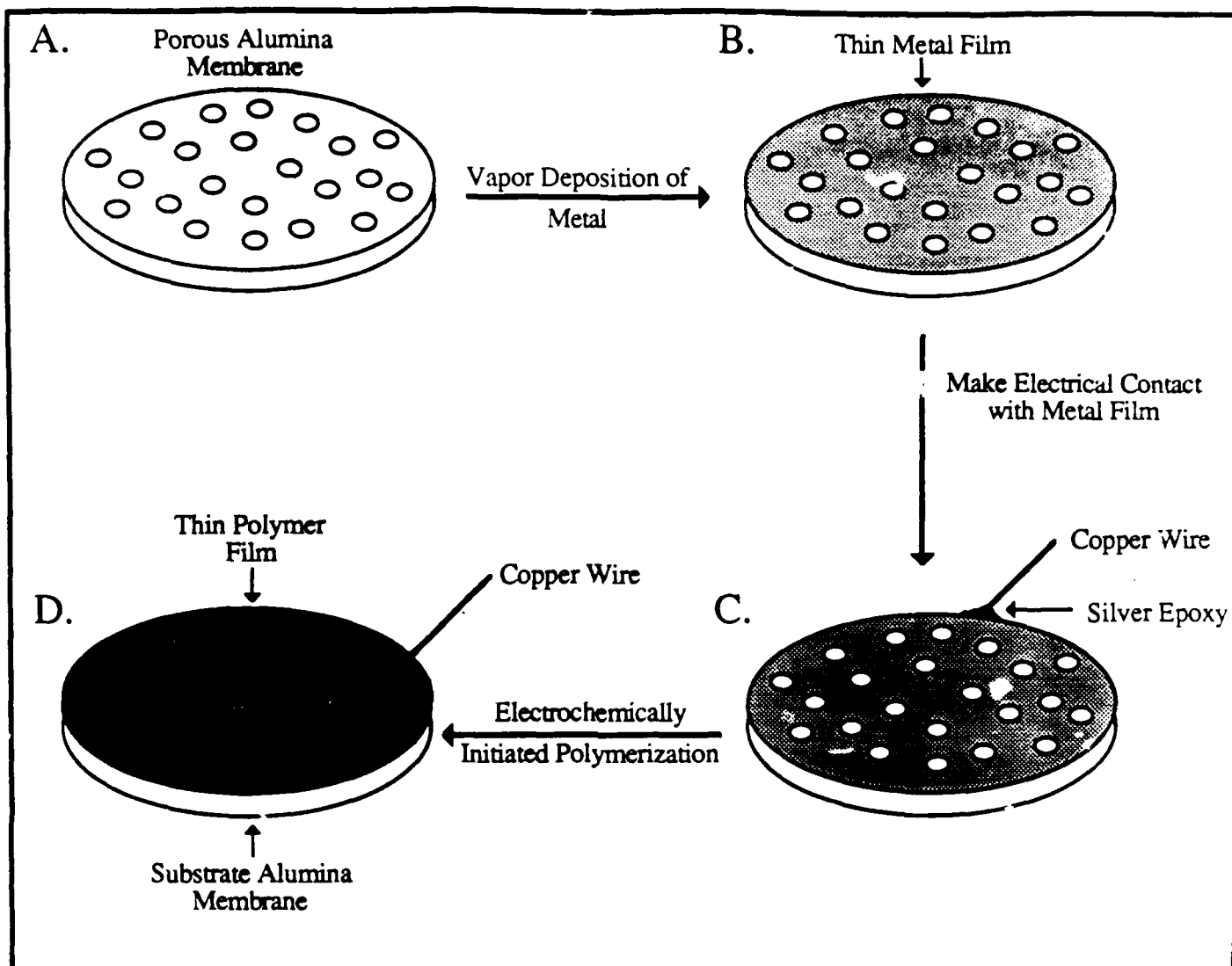


Figure 1

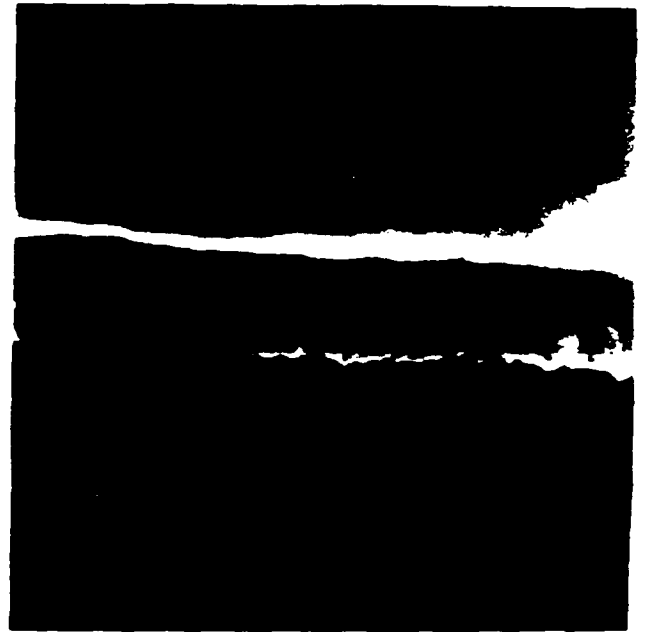
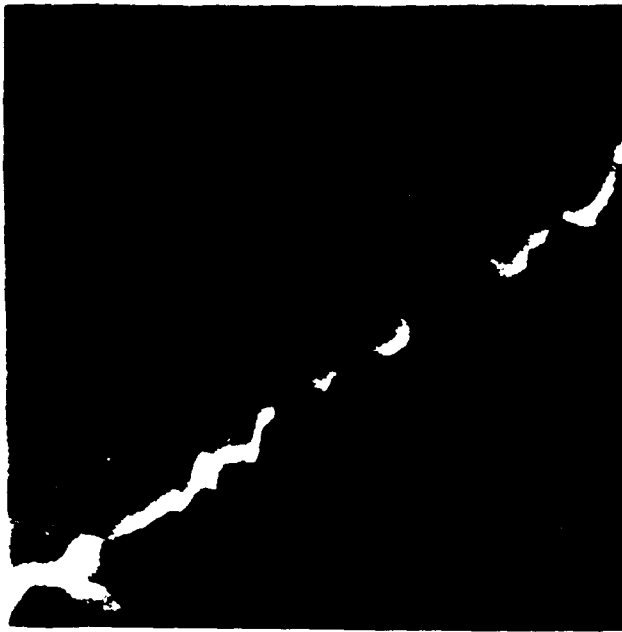


Figure 2

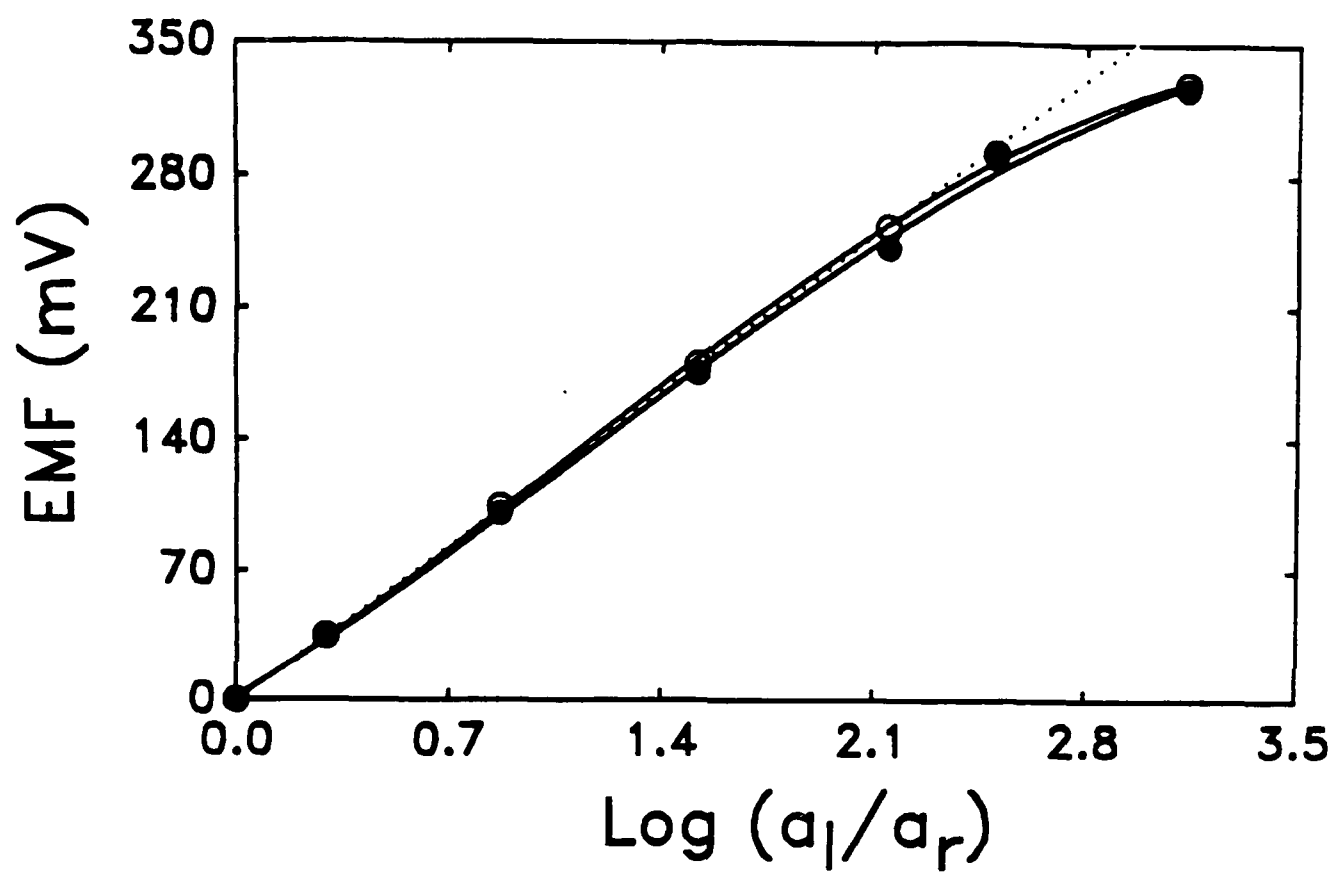


Figure 3