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TOPICAL REPORT FUEL CELL MEMBRANE ELECTRODE CONFIGURATION

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### ABSTRACT

A new method of fabricating fuel cell membrane electrodes has been developed which yields polytetrafluoroethylene-containing, platinumblack catalyzed electrodes which are highly active as hydrogen, hydrazine, methanol and propane anodes and as oxygen cathodes. The electrochemical activity of these membranes together with the activity of carbon-black polytetrafluoroethylene membranes of similar structure has been measured in half-cell and full-cell experiments. The membranes containing carbon black appear to be promising as support structures for metal chelate catalysts. The electrode fabrication technique is simple and appears to be applicable to many other combinations of fuel cell catalyst or catalyst support powders and hydrophobic binder materials.

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### I. INTRODUCTION

One objective of the current chelate fuel cell catalyst program is the development of standard electrode substrates that yield optimum electrochemical activity when used as supports for the metal chelate catalysts. In the course of the development of these standard substrates, electrodes have been fabricated that show exceptional electrochemical activity with noble metal catalysts. Although complete characterization as to performance and life of these electrodes has not been made, results to date appear to be of sufficient interest to warrant a full disclosure at this time.

The author would like to acknowledge the contributions to this work of Dr. John O. Smith of Monsanto Research Corporation as well as the technical guidance and encouragement of Mr. Raymond H. Comyn and Dr. Gwendaline B. Wood of the Harry Diamond Laboratories, United States Army Materiel Command.

### II. BACKGROUND

In attempting to fabricate a standard fuel cell electrode support for evaluation of chelate catalysts, the following desirable characteristics of a substrate have been considered:

- (1) Contribution of maximum degree of three-phase (gas, electrolyte, and catalyzed electrode surface) contact, preferably without requiring precision control of pressures and temperatures in the fuel cell.
- (2) Capability for adsorbing and holding the chelate catalysts in regions of the three-phase contact.
- (3) Possession of high electrical conductivity, conducting electrons between the external circuit and the catalytically reacting chelate.
- (4) Impermeability to the electrolyte (i.e., hydrophobic in the case of aqueous electrolytes).
- (5) Favorable mechanical strength and reasonable flexibility to facilitate fuel cell assembly.
- (6) Thermal stability.
- (7) Amenability to fabrication in large area sheets with relatively uniform properties.
- (8) Utilization of relatively inexpensive materials.

The problem of fabricating an electrode support membrane has been approached by first preparing and attempting to optimize the structure of electrodes containing known electrochemically active catalysts and then attempting to duplicate the configuration of these electrodes using potential support materials for the chelate compounds. Platinum black has been used as one of the known catalysts, with the expectation that an electrically conducting carbon black could be substituted in the fabrication of chelate support membranes. Polytetrafluoroethylene has been used as a binder and hydrophobic agent in these electrodes.

### III. ELECTRODE FABRICATION

Continuous films containing platinum black and polytetrafluoroethylene in a 1-to-1 volume ratio have been fabricated using polytetrafluoroethylene in a water dispersion\*. This form of polytetrafluoroethylene appears to have binding qualities for the platinum particles superior to those of dry Teflon-type polytetrafluoroethylene powder. Mixtures of platinum black, polytetrafluoroethylene and water, in proportions approximating those listed in Table 1, yield elastic, high viscosity agglomerates at room temperature that can be rolled into continuous membranes with thicknesses from 0.001 inch up. These membranes, after drying and suitable heat treatment up to about 300°C, yield electrodes with about 90 per cent porosity (formed by the displaced water) and with a surface area of exposed platinum of about 1.8  $m^2/in.^2$  for a sample film about 0.003 in. thick, containing about 60 mg of Pt/in.<sup>2</sup> These membranes have a fair amount of mechanical strength and are highly flexible without fracture or loss of material. For incorporation into a fuel cell or test electrode, the wet membranes are pressed into a wire screen current collector before drying and heat treatment.

Electrode membranes containing a 1-to-1 volume ratio of carbon black and Teflon-type polytetrafluoroethylene have also been fabricated by a procedure identical with that used to make the platinum polytetrafluoroethylene electrodes. The physical properties of a typical carbon polytetrafluoroethylene membrane are also summarized in Table 1.

The basic manufacturing process, then, consists in mixing the catalyst and/or conducting filler with the Teflon dispersion and water, limited mulling to form a mass of rubberlike consistency, rolling to desired membrane thickness, application to screen or other current collector material, and final drying and heat treatment.

Heat treatment will vary depending on the type of filler employed and the proportions of binder and filler. Electrodes described in this report were treated as follows:

<sup>\*</sup> Teflon type polytetrafluoroethylene dispersion in water, Dupont No. 852-201.

### Table 1

### COMPOSITION AND PHYSICAL PROPERTIES OF ELECTRODE MEMBRANES

		Platinur	m Membrane	
	% by Solids	Wt Mix	<u>% by V</u> Solids	Vol Mix
Platinum	90	45.5	50	4
Polytetrafluoroethylene	10	4.6	50	4
H <sub>2</sub> 0	-	50.0	-	92

Typical Platinum-Polytetrafluoroethylene membrane Thickness  $\approx 0.003$  in. Platinum content  $\approx 60$  mg Pt/in.<sup>2</sup> (20-30 m<sup>2</sup>/g Pt) Surface area  $\approx 1.8$  m<sup>2</sup>/in.<sup>2</sup> of membrane

		Carbon	Membrane	
		Wt		<u>′01</u>
	Solids	<u>Mix</u>	Solids	Mix
Carbon black	50	16.6	50	8.3
Polytetrafluoroethylene	50	16.6	50	8.3
H20	-	66.8	-	83.4

Typical Carbon-Polytetrafluoroethylene membrane Thickness  $\approx 0.005$  in. Contains  $\approx 50$  mg carbon/in.<sup>2</sup> ( $\approx 75 \text{ m}^2/\text{g C}$ ) Surface area  $\approx 4.0 \text{ m}^2/\text{in.}^2$  of membrane

- (1) Room temperature drying for 3-12 hours.
- (2) One hour heat treatments at 100, 200, and 300°C.

No complete characterization of electrode materials or intermediate processing stage physical properties have been made; and therefore it is not yet possible to more precisely describe the manufacturing process.

### IV. ELECTRODE TEST PROCEDURE

Two types of tests were conducted on the electrode membranes. They were tested in half-cell units for activity as anodes for the oxidation of hydrogen, propane, hydrazine, and methanol and as cathodes for the reduction of both pure and atmospheric oxygen. Both potassium hydroxide and phosphoric acid were used as electrolytes in the half-cell work. Two electrodes were also tested in a hydrogenoxygen full cell.

For the half-cell tests, electrode membranes were prepared and pressed into electrode brackets as shown in Figure 1. Tantalum brackets were used for tests conducted with acid electrolytes and nickel brackets for those conducted with caustic electrolytes. Although the electrode brackets provide about  $6.45 \text{ cm}^2$  of exposed electrode surface, all but  $1 \text{ cm}^2$  of the surface of each electrode was masked off with treated Teflon washers in each test\*.

The half-cell test unit is shown in Figure 2 and the accompanying circuitry in Figure 3. In the test cell the tip of a Luggin capillary was spaced about 1.5 mm from the electrode face in the electrolyte. In general, the tests were conducted without fuel gas breakthrough through the electrode, although a few of the membranes tested leaked electrolyte, necessitating breakthrough operation. In those tests conducted without breakthrough, a continuous flush of fuel gas or oxygen was maintained across the electrode surface.

Two sets of voltage readings were taken in each half-cell test. These were the actual potential between the electrode and the reference electrode, including the IR losses, and a Kordesch-Marko bridge potential reading free of IR losses\*\*. The bridge generally used was limited to currents of about 500 ma so that this was the maximum current tested on most electrodes. A few tests in the highly conductive electrolytes were extended as far as 900 ma with other equipment.

The full-cell design is shown in Figure 4. The area of the electrodes tested in this cell was about 37 cm<sup>2</sup>. Only the voltage produced by the cell, including IR losses, was measured. Moisture balance was obtained by manual control of fuel and oxidant flow rates.

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<sup>\*</sup> Except Electrode No. 60456-I as noted in Table 2.

<sup>\*\*</sup> Kordesch, K., and Marko, <u>J. Electrochem. Soc.</u>, <u>107:6</u>, 486 (1960).



Figure 1. Exploded View of Half-Cell Test Electrodes







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### A. HYDROGEN ANODE HALF-CELL TESTS

Several tests were made on the activity of the platinum-polytetrafluoroethylene membranes as hydrogen anodes. The results of these tests are shown in Table 2 and in Figures 5 and 6.

Tests were conducted in both 85% H<sub>3</sub>PO<sub>4</sub> and 40% KOH at 25°C and 90°C. The open-circuit potentials were near the reversible hydrogen potential in each case. In 85% H<sub>3</sub>PO<sub>4</sub> at 90°C the IR-free polarization from open-circuit potential was generally less than 0.05 volt at 500 ma/cm<sup>2</sup>. In 40% KOH at 90°C the IR-free polarization was about 0.04 volt from open-circuit at 900 ma/cm<sup>2</sup>. IR losses were generally high (0.3 to 0.5 volt at 500 ma/cm<sup>2</sup>) in the poorly conducting 85%  $H_3PO_4$  but were much lower ( $\approx 0.09$  volt at 500 ma/cm<sup>2</sup>) in 40% KOH. The 25°C test results demonstrated much higher IR losses in 85% H3PO4, but generally only slightly more polarization than the corresponding 90°C tests in 40% KOH. One electrode operated in 85% H<sub>3</sub>PO<sub>4</sub> was subjected to a 65-hour test at 246 ma/cm<sup>2</sup> at 25°C as noted in Table 2. Polarization data taken on this electrode before and after this constant current test show little degradation of its activity. Another electrode operated in 40% KOH at 90°C was subjected to a 24-hour test at 500 ma/cm<sup>2</sup>. The IR-free polarization from open circuit at the beginning and end of this test was 0.08 and 0.15 volt respectively. The carbon-polytetrafluoroethylene membranes demonstrated no activity as a hydrogen oxidation electrode and were therefore not tested with the other fuels.

### B. PROPANE ANODE HALF-CELL TESTS

The activity of the platinum-polytetrafluoroethylene membranes as propane anodes in 85% H<sub>3</sub>PO<sub>4</sub> at 150°C is shown by the data in Table 3 and by the polarization curve in Figure 5. The open-circuit poten-) tial is about 0.13 volt more positive than the reversible hydrogen potential at 150°C. The polarization from open-circuit potential at a current density of 50 ma/cm<sup>2</sup> was generally about 0.3 volt. The potential rose sharply in a positive direction at current densities ranging from 50 to 200 ma/cm<sup>2</sup> on the 7 electrodes listed in Table 3. In constant current tests at 50 ma/cm<sup>2</sup> the electrodes maintained a potential of about 0.28 volt above the OCP for about one hour, at which time the voltage rose sharply. When the electrode was allowed to rest for a few minutes, the potential returned to the original OCP. In a subsequent constant current test at 50 ma/cm<sup>2</sup> the electrode maintained a potential 0.28 volt above the OCP for a much shorter time than in the original test, increasing with the length of time the electrode was allowed to rest at the OCP.

### C. HYDRAZINE HALF-CELL TESTS

The activity of the platinum-polytetrafluoroethylene electrodes for hydrazine oxidation was demonstrated in a test conducted using a 95% H<sub>3</sub>PO<sub>4</sub> electrolyte at  $90^{\circ}$ C and 100% hydrazine hydrate in the fuel side of the half cell. Data are shown in Table 4 and in Figure 5.

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NTOROGEN INLI-CELL TEST DATA ON PLATICIA-POLITICATIVATIONOCTINIZATI ELECTRODES

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Electrode Area = 1 cm<sup>2</sup>

## 856 HaPOs Electrolyte

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				÷										

Baturated entered stream to an room temporature for all readings.
IR -- Potential with half-cell IR loss included.
IR -- In-three potential obtained with Eordesent Marko Bridge.
Buttre scittre electrode area arposed to the electrolyte. I.e., no electrode meating.
After 65 hours of operation at 26 M/cm<sup>2</sup> at 25°C.
After 65 hours at 500 msi. IR -- 0.95 v; Eff -- -1.04 v.

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Table 3

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# PROPAGE NALE-CELL TEST DATA ON PLATHAM POLYTERANDUMOETRYLENE ELECTRORES

## Electrode Area = 1 cm<sup>2</sup>

Electrode	Test			80	856 HaPos El	Potent1e ectrolyt	1 VB BCE + (volta),	Potential ve SCE 4 . Electrolyte (volta), 7 = 150°C			Constant Current	Frent Tests
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60431 IV	23090	ñğ	88 88	0.28 0.28	0.37 0.28	0.52 11.0	fell off fell off	• •			Borne	
60431	53092	۲ğ	0.0		8 25	0. <i>3</i> 5 0. <i>2</i> 7	0.45 45	0.55	fell off fell off			•
12 14	16065	٤ğ	0.07	0.22 0.19	0.26	0.33 12.0	0.41 0.29	• •	0.5 X	fell off fell off		
778 78	62303	٢đ	0.04	0.00 0.10	0.2	¥	fell off fell off	••		·	88	ዾዾ
60129 60129	62305	٢đ	<b>6</b> .0	0.19	0.27	5.0	0.44 0.32	fell off			ខ្មន	11
803 111 111	62316	5ğ	80	0.18 0.18	8.0 8.0	0. <u>3</u> 5	4.0 7	fell off fell off			52	8
60110 17a	63701	fi ğ	0 - 0	0.17 0.17	0.27 0.25	0.35 0.32	0.40 (75 m) 0.36	fell off fell off				
			-									

· Saturated Calonel Electrode is at room temperature for all readings.

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£.? 40 OS 85. 00 5.0 bethanol Potential ve BCR 30 mm 100 mm 200 mm CE (volte) 200 me 200 me **H** 80 8.0 8.0 0.23 \$?; ; P# 2% 0.52 0.53 22 00 0.13 0. 28. 28. transfer Potential ve 5.9 2.8 88 8... 8... 84 0.0 100 86 0.0 8 9 58 99 2% 2% 97 97 К, ,, 9 6.0 10 9.9 2.9 8.9 5.0 8 **X** 1 . **특**호 ۶ğ 취준 ñğ ٢ğ 14 MOS and 14 Nells in 42.55 NaFOs IN NaHe in 42.96 Haros 100% CK.OH Puel Risture Puel Neture 1000 NaN. -NaO SOF CHON and A2. 36 NaPo. Test Reference Test Meference 53904 60139 Electrode Maber Bleetrode Merer IE NOS 109 111

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HIDAAZINE AND NETHANOL HALF-CELL TEST DATA ON PLATINGH-POLITETRAPLOROETRYLENE ELECTRODES

Temperature = 90°C 896 NaPO. Electrolyte Electrode Area = 1 cm<sup>2</sup>

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### Table 4

· Seturated calomel electrode is at room temperature for all readings.

85% Na No. Electrolyte, 90°C Except Propane and Air at 150°C

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Figure 5. Maif-Cell Electrode Performance of Platimum- Polytetrafluoroethylene Mar

Figure 6. Half-Call Electrode Performance of Electrode Membranes



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The OCP was about 0.12 volt more negative than the hydrogen potential in this electrolyte. The polarization from open circuit at 500 ma/cm<sup>2</sup> was about 0.12 volt. Other tests were conducted using  $1M N_2H_4$  in 42.5% H<sub>3</sub>PO<sub>4</sub> and in 42.5% H<sub>3</sub>PO<sub>4</sub> containing  $1M HNO_3$ . These tests showed higher polarizations from open circuit than the test conducted on 100%  $N_2H_4 \cdot H_2O$ . Nitric acid contamination increased the potentials obtained with the  $1M N_2H_4$  at low current densities (below 200 ma/cm<sup>2</sup>) but did not affect the half-cell potentials at 300 to 500 ma/cm<sup>2</sup>.

### D. METHANOL HALF-CELL TESTS

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The activity of the platinum-polytetrafluoroethylene membranes as electrodes for methanol oxidation using a 95% H<sub>3</sub>PO<sub>4</sub> electrolyte at 90°C is shown in Table 4 and in Figure 5. The OCP with 100% MeOH fuel was about 0.16 volt more positive than the reversible hydrogen potential. After an initial polarization from open circuit of 0.38 volt at 100 ma/cm<sup>2</sup>, the potential increased only an additional 0.04 volt up to 740 ma/cm<sup>2</sup>. Using 50% MeOH fuel dissolved in 42.5% H<sub>3</sub>PO<sub>4</sub> electrolyte improved the OCP by 0.05 volt and also decreased the polarization from open circuit. This resulted in potentials 0.10 to 0.05 volt more negative than those obtained with the 100% MeOH fuel at current densities from 100 to 740 ma/cm<sup>2</sup>.

### E. OXYGEN HALF-CELL TESTS

Both the platinum-polytetrafluoroethylene and the carbon-tetrafluoroethylene membranes were tested for their activity as oxygen electrodes in KOH and  $H_3PO_4$  electrolytes. The results of these tests are indicated by the data in Table 5 and the oxygen curves in Figures 5 and 6.

A platinum-polytetrafluoroethylene membrane operating as an oxygen cathode in 40% KOH at 90°C gave an OCP 1.04 volts above the reversible hydrogen potential. The polarization from open circuit was 0.11 volt at a current density of 500 ma/cm<sup>2</sup>. Using air as the oxidant under similar conditions gave an OCP 0.96 volts above the reversible hydrogen potential and a polarization from open circuit of 0.22 volt at 300 ma/cm<sup>2</sup>. With 85% H<sub>3</sub>PO<sub>4</sub> electrolyte at 90°C oxygen gave an OCP 1.03 volts above the reversible hydrogen potential. In this case the polarization from the OCP was 0.27 volt at 500 ma/cm<sup>2</sup>. Utilizing air as the source of oxygen with 85% H<sub>3</sub>PO<sub>4</sub> electrolyte at 145°C an OCP about 0.85 volt above reversible hydrogen was obtained with a decline to 0.47 volt at 300 ma/cm<sup>2</sup>.

The carbon-polytetrafluoroethylene membranes operating on oxygen gave an OCP about 0.87 volt above the reversible hydrogen potential in 5M KOH at 90°C. The polarization from open circuit was about 0.15 volt at 500 ma/cm<sup>2</sup>. At room temperature the OCP was slightly higher, but the voltages obtained with current flow are about the same as those obtained at 90°C. These electrodes appeared nearly inactive using an 85% H<sub>3</sub>PO<sub>4</sub> electrolyte at 90°C, the OCP being 0.71 volt above Table 5

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## OXYODI AND AIR HALF-CELL TEST DATA ON ELECTRODE NEGRANES

## Electrode Area - 1 cm<sup>2</sup>

<b>1</b> 0 00		89 99	79 78	0.14 0.63			<b>PR</b> 99	87 99	<b>2%</b> 99	69 99	<b>XX</b> 99
11 N N N N N N N N N N N N N N N N N N	•				-0.12 0.12						
<b>3CE (</b> vo)(		8.9 9.7	<b>- 18</b> 99	°.3 °.3	5%			88 99	<b>57</b> 99	<b>89</b> 99	99 20
Potential v 803 (volta) 23 26 100 26 200 26 400 26		9.9 9.13	<b>78</b>		19		5.9 7 7	яћ 99	85) 99	<b>7</b> %	6. 199
	되	4.9 9.9	<b>%</b> %	0.72	0.61 0.62	2	<u>к</u> ;; 99	г. 99	99 28	к;; 99	99 88
8	a Rentance	<b>8</b>	-0.16	8.' '	0-75	The Marthurs	-0.14	8.' %	0.18	8.0	95.0
Temperature C	Pirtimus-Tetrafivorostiziene Nembrane	90, 0 <mark>2</mark>	90, AIF	90, 0 <mark>8</mark>	145, ALF	Carbon-Tetrafluorostigulens Hashrense	25, 0 <b>.</b>	90, 0 <mark>e</mark>	25, 0 <b>.</b>	90, 0 <mark>8</mark>	90, 0 <mark>8</mark>
Rectrolyte	Pletimm-Tet:	HOSE SON	HON SON	By Hapoa	By Haroa	Carbon-Te	Non NC		HON NS		Byk Karoa
		٢ğ	ñð	ĩğ	۶ğ		<b>1</b> 2	äğ	취출	5 <u>5</u>	äğ
Test Noference		11629	62314	63711	62316		63706		63707		63713
Electrode Number		-		~	×109		T I		HI03		Ling HI

· Saturated Calemai Electrode is at ross temperature for all readings.

the reversible hydrogen potential and the polarization from open circuit being 0.53 volt at 25 ma/cm<sup>2</sup>. The carbon-polytetrafluoroethylene electrodes have not been tested with air as the oxidant.

### F. FULL-CELL TEST

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Two platinum-polytetrafluoroethylene electrodes with an area of  $37 \text{ cm}^2$   $(0.04 \text{ ft}^2)$  each were utilized as the anode and cathode in a hydrogenoxygen cell. The cell was operated at 100°C with an electrolyte of 40% KOH contained in an 0.030-in. asbestos mat. The oxygen and hydrogen were supplied at atmospheric pressure.

The results of two current-potential tests conducted on this cell are shown in Figure 7. In the first test only the individual anode and cathode potentials (including IR losses) are indicated. There was some difficulty in operating the cell with an effective water balance during this test. Most of the decrease in cell voltage with increasing current resulted from a decrease in the cathode potential. The nearly linear nature of the cathode current-potential curve indicates that a great deal of IR loss may be included in the cathode potential values because of the geometry of the capillary to the reference electrode. The essential lack of anode polarization supports the half-cell data obtained earlier.

During a second test run on this cell a more effective water balance was maintained for a few hours, with a commensurate improvement in operation. The current full-cell potential curve (with IR losses) for this second run is shown in Figure 7. The cell delivered an OCP of 1.07 volts and from 175 to 200 watts/ft<sup>2</sup> of electrode area at current densities varying from 250 to 400 amp/ft<sup>2</sup> and potentials from 0.68 to 0.50 volt. This cell was operated for about 8 hours at a current output of 125 amp/ft<sup>2</sup> at a voltage of 0.80 volt.

### VI. CONCLUSIONS AND RECOMMENDATIONS

The platinum-polytetrafluoroethylene membranes demonstrate excellent potential as hydrogen and hydrazine anodes and some potential as propane and methanol anodes. They also show some promise as oxygen electrodes. This potential has been demonstrated both in half-cell and full-cell data.

The carbon-black polytetrafluoroethylene membranes have some activity as oxygen electrodes. They appear highly promising as supports for anodically active chelate catalysts. This is indicated by their completely hydrophobic nature, their high surface area of carbon per unit area of membrane, and their activity as oxygen electrodes. This activity indicates that these membranes have the three-phase contact properties desired of an electrode support. These flexible membranes are simple to fabricate and are relatively inexpensive.

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Potential (Volts) vs SCE Anode and Cathode Half Cells

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The electrode membrane fabrication technique developed in this work appears to have promise in many other electrode systems. Other high surface area solids can be incorporated in similar high surface area membranes by this technique, individually or in combination, both mixed and in laminar membrane structures. The surface areas of the carbon black and platinum black in the membranes discussed above are nearly identical with those of the pure powders, indicating that little of the surface of these powders has been covered by the polytetrafluoroethylene. This is true despite the fact that the powders are strongly bonded in the membrane structure and that no polytetrafluoroethylene is visible, even with an infrared detection device, on the membrane surface.

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The electrode fabrication technique developed here should be applicable using hydrophobic binder materials other than polytetrafluoroethylene. It would appear that the organic materials and surfactants that stabilize the Teflon-water dispersion lead to the formation of elastic, rubberlike mixtures of water, polytetrafluoroethylene, and the catalyst or catalyst support powder at room temperature. It is the ease of fabrication of these elastic mixtures into thin continuous membranes by simple rolling or pressing operations and the highly porous structure remaining after removal of the volatile diluent (e.g., water) that make this electrode fabrication technique especially promising. Other combinations of high surface area hydrophobic powders, surface active agents, and other additives that give elastic mixtures with powdered solids may also yield stable, porous, electrode membranes.

In comparing the electrochemical performance of the electrodes described with performance of other electrodes described in the literature, the reader is cautioned to consider that no particular electrode optimizing effort has been undertaken in this work. It is quite likely that a concentrated development program on optimization of performance of this electrode type, particularly those catalyzed with noble metals, would result in improved operation.

No further work on noble-metal-catalyzed membrane electrodes is anticipated for this contract. Application of this electrode type to the testing of potential metal chelate electrocatalysts will be undertaken on the present contract and progress will be reported in the regular monthly and quarterly reports.

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