

CATALYSTS FOR ULTRAHIGH CURRENT DENSITY OXYGEN CATHODES  
FOR SPACE FUEL CELL APPLICATIONS

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## I. SUMMARY

The objective of this research was to identify promising electrocatalyst/support systems for the oxygen cathode in alkaline fuel cells operating at relatively high temperatures,  $O_2$  pressures and current densities. A number of materials were prepared, including Pb-Ru and Pb-Ir pyrochlores,  $RuO_2$  and Pt-doped  $RuO_2$ , and lithiated NiO. Several of these were prepared using techniques that had not been previously used to prepare them. Particularly interesting is the use of the alkaline solution technique to prepare the Pt-doped Pb-Ru pyrochlore in high area form.

Well-crystallized  $Pb_2Ru_2O_{7-y}$  was used to fabricate high performance  $O_2$  cathodes with relatively good stability in room temperature KOH. This material was also found to be stable over a useful potential range at  $-140^\circ C$  in concentrated KOH. Other pyrochlores were found to be either unstable (amorphous samples) or the fabrication of the gas-fed electrodes could not be fully optimized during this project period. Future work may be directed at this problem. High area platinum supported on conductive metal oxide supports produced mixed results: small improvements in  $O_2$  reduction performance for  $Pb_2Ru_2O_{7-y}$  but a large improvement for Li-doped NiO at room temperature. Nearly reversible behavior was observed for the  $O_2/OH^-$  couple for Li-doped NiO at  $-200^\circ C$ .

## II. INTRODUCTION AND OBJECTIVES

Improvements in the performance of the oxygen cathode in alkaline fuel cells can lead to major improvements in the overall operation of such cells. The areas in which improvements can be made include both the electrocatalysis and the electrode structure. The achievement of ultrahigh current densities will rely on both aspects, with optimization of mass transport and electronic conductivity. The stability of the catalyst and electrode structure is also of utmost importance.

The objective of this research is to identify promising electrocatalyst/support systems for the oxygen cathode in alkaline fuel cells operating at relatively high temperatures,  $O_2$  pressures and current densities. The research has focused on the preparation and characterization of candidate catalyst/support systems offering high catalytic activity, electronic conductivity and physical/chemical stability.

Significant progress has been made during the past year in the preparation and evaluation of transition metal oxide materials both as catalyst supports and catalysts in their own right. Methods have been developed to fabricate some of these oxides into PTFE-bonded gas-fed electrodes with high performance. Electrodes have also been examined at relatively high temperatures ( $-140^\circ C$ ) in concentrated KOH, and the stability of the lead ruthenate pyrochlore  $Pb_2Ru_2O_{6.5}$  was found to be quite encouraging.

A number of new compounds were synthesized, including platinum-doped lead ruthenate pyrochlore and platinum-doped  $RuO_2$ . The preparation of highly dispersed platinum on conductive metal oxide supports was initiated with encouraging results.

The choice of candidate support materials was guided first by considerations of 1) stability in concentrated alkaline solution over the

range of potentials expected to be operative for the high performance fuel cell and 2) high electronic conductivity, preferably at least  $10^2$  ( $\Omega$  cm)<sup>-1</sup>. The materials receiving the most attention were lead ruthenate and iridate pyrochlores, RuO<sub>2</sub> and Ir-substituted RuO<sub>2</sub>, and lithiated NiO. Efforts were also made to prepare layered perovskite-type materials in high area form. The latter materials are related structurally to the oxide superconductors.

### III. EXPERIMENTAL METHODS

#### A. Preparation of Metal Oxide Catalysts and Supports

##### 1. Pyrochlores and ruthenium oxides

Lead-ruthenium and lead-iridium pyrochlores were prepared using a modified version of the alkaline solution precipitation method developed by Horowitz et al. (1-5). This method utilizes an alkaline solution both as a means of reacting the metal ions by precipitation to form an amorphous pyrochlore precursor and subsequently as a reaction medium for the crystallization of the precipitate.

The first step in this preparation technique is to mix solutions of the cations in the proper stoichiometric ratio. In our work, stock solutions were made with the following compositions: 0.025 M Ru (chloride), 0.025 M Ir (chloride), and 0.025 M Pb (acetate). These molarities are based on the concentrations of the cations. The cation solutions are stirred and heated to 60 - 70°C. The oxygen gas is sparged into the solutions, and KOH is slowly added. These procedures involve some modification of the aqueous hydroxide precipitation method of Horowitz et al. that may provide some additional control over the process.

After filtering and washing, the precipitates were dried and in some cases not heat-treated further. In other cases the samples were heat-treated at temperatures up to 400°C in air for times up to 24 h.

A type of preparative method that had not been initially considered for this project involves the use of molten salts. Methods that make use of alkali metal chloride melts have been employed to prepare LiAlO<sub>2</sub> (6), SrTiO<sub>3</sub> (7) and a number of electronically conductive oxides for use as cathodes in molten carbonate fuel cells (8). Nitrate melts have been used to prepare RuO<sub>2</sub>-IrO<sub>2</sub> solid solutions in high area form, from 40 to 90 m<sup>2</sup> g<sup>-1</sup> (9). These methods involve the reaction of the precursor metal salts as dissolved species in the molten salt to form a dissolved product (6). This product is then at a very high state of dispersion and uniformity of composition. It is recovered by dissolving out the water-soluble alkali metal chloride or nitrate.

The method for preparing the RuO<sub>2</sub>-IrO<sub>2</sub> solid solutions consisted of mixing appropriate quantities of iridium chloride and/or ruthenium chloride with NaNO<sub>3</sub> in a 1:5 weight ratio of the chloride to the NaNO<sub>3</sub> (9). This mixture was then fused at 500°C for 3 hours. When the sample had cooled, the nitrate was dissolved in distilled water, and the oxide was filtered out. After the filtered powder was dried, it was then heat-treated at 550°C for one hour.

This procedure was used to make pure RuO<sub>2</sub>. It was also modified to produce Pb<sub>2</sub>Ru<sub>2</sub>O<sub>6.5</sub> by adding the appropriate amount of lead acetate to the

ruthenium chloride and adjusting the amount of  $\text{NaNO}_3$  so that the weight ratio of combined ruthenium and lead salts to  $\text{NaNO}_3$  remained 1:5.

## 2. Platinum-substituted oxides

Methods were developed to dope  $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$  and  $\text{RuO}_2$  with platinum as an integral part of the oxide structure. This is one approach to achieving supported Pt at an extremely high state of dispersion. The Pt would substitute for Ru in the structure possibly in a random manner and would subsequently be partially electrochemically reduced, forming either small Pt metal clusters or isolated Pt metal atoms. The following compositions were prepared:  $\text{Pb}_2\text{Ru}_{1.98}\text{Pt}_{0.02}\text{O}_{7-y}$ ,  $\text{Pb}_2\text{Ru}_{1.905}\text{Pt}_{0.095}\text{O}_{7-y}$ ,  $\text{RuO}_2$  and  $\text{Ru}_{0.98}\text{Pt}_{0.02}\text{O}_2$ . These were prepared via the hydroxide precipitation technique, where the pH for the pyrochlore compositions was adjusted to 12-12.5 and that for the  $\text{RuO}_2$  composition to  $10.5 \pm 0.1$ . The solutions used for these preparations were as follows: 0.025M ruthenium chloride, 0.025 M lead acetate and 0.025 M chloroplatinic acid. The appropriate volume ratios of these solutions were mixed to yield the desired oxide compositions.

The mixed aqueous solutions for the pyrochlores were heated for 3 h at  $65^\circ\text{C}$  with  $\text{O}_2$  gas bubbling through them. This is very similar to the processing procedure that was done on prior batches of crystalline  $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ . The solutions for the  $\text{RuO}_2$  compositions were heated at  $45^\circ\text{C}$  for 2 h with no gas bubbling. All powders were filtered, washed with water, dried at  $90^\circ\text{C}$  for 3 h and heated in air at  $205\text{-}210^\circ\text{C}$  for 16-18 h. The above procedure produced  $\text{Pb}_2\text{Ru}_2\text{O}_{7-y}$  with the pyrochlore crystal structure and a BET area of  $56.1 \text{ m}^2\text{g}^{-1}$ .

The oxides  $\text{RuO}_2$ ,  $\text{Ru}_{0.9}\text{Pt}_{0.1}\text{O}_2$  and  $\text{Ru}_{0.5}\text{Ir}_{0.5}\text{O}_2$  were prepared via the citric acid decomposition method (discussed in III.A.3.). This was done by adding one mole of citric acid and urea for every mole of the cations in the solution. Then these solutions were stirred and dried in a drying oven. The char residue was then heated in a furnace at  $-600^\circ\text{C}$  for 4 h.

## 3. Lithiated nickel oxide

Lithiated nickel oxide samples with Li contents of 0 to 10 at.% were prepared using the citric acid-urea decomposition method. This is a modification of the citric acid-ethylene diamine process used by Chen and Anderson (10) to prepare Y-Ba-Cu perovskites.

The preparative method involves the formation of an organic gel based on citric acid and urea together with the Ni(II) acetate and Li carbonate. The citric acid and urea were present in a mole ratio in excess of unity with respect to the combined total of Ni and Li. This method is partly based on the work of Sale and coworkers on the "amorphous citrate" process for preparing perovskites and other oxides (11). In the present work, a series of compounds including undoped NiO and two Li-doped samples ( $\text{Ni}_{0.96}\text{Li}_{0.04}\text{O}$  and  $\text{Ni}_{0.9}\text{Li}_{0.1}\text{O}$ ) was prepared.

### B. Preparation of Highly Dispersed Platinum on Metal Oxide Supports

In addition to the materials above in III.A.2, which have platinum incorporated into the bulk structure, platinum was also deposited on oxide supports using the Prototech method, which involves the decomposition of the sulfite complex of platinum with hydrogen peroxide in the presence of an

aqueous suspension of the support material (12). This precipitates a platinum hydroxide colloid. After filtering and washing the samples, they were dried in air at  $-150^{\circ}\text{C}$ . No reduction step was employed.

### C. Physical Characterization

X-ray diffraction was carried out on most of the samples, using the Philips diffractometer in the Materials Science Department at CWRU. BET surface area measurements were made using the Leeds and Northrup automatic BET analyzer at NASA-Lewis. Scanning electron microscopy was done on some samples using the JEOL SEM instrument at the Macromolecular Science Department at CWRU.

For doing the conductivity measurements, a conductivity cell for powder samples was fabricated. The design (Fig. 1) is similar to designs that have been described in the literature (13, 14) and consists of a non-conductive die body, in this case, Macor machinable ceramic (Corning), and stainless steel pistons. A constant current was applied across the pistons, and the voltage drop was measured across two silver voltage probes that were inserted into the die body. The latter were at a fixed distance of 0.44 cm from each other. The cross-sectional area of the cavity was  $0.248\text{ cm}^2$ .

### D. Fabrication of Porous Electrodes

The procedure for the fabrication of porous Teflon-bonded gas-fed electrodes based on metal oxides for  $\text{O}_2$  reduction measurements is briefly as follows.

A sample of 100-200 mg of the oxide was mixed ultrasonically for five minutes in  $30\text{ cm}^3$  of deionized water. Magnesium sulfate (200 mg) was added to increase ionic strength and to aid in the coagulation of the Teflon emulsion (subsequently added). A measured volume of pre-diluted Teflon suspension (2-3 % w/v) was further diluted by a factor of  $\sim 10$  and was added to obtain 25 wt% Teflon solids based on the total weight of oxide plus Teflon. The PTFE suspension was diluted from a commercially available emulsion, DuPont Teflon T30B. The mixture was then ultrasonically blended for 15 minutes. After removing from the ultrasonic bath, the material was filtered and washed thoroughly five times to remove the magnesium sulfate. The resulting paste was then manually worked with a spatula on an FEP sheet to fibrillate the dispersed PTFE. The mass was then spread on a 1.75 cm diameter disk of approximately 0.5 mm thick conductive hydrophobic backing material (Electromedia Corp., Englewood, N.J.) by pressing at about  $250\text{ kg cm}^{-2}$ . The electrodes were heat-treated at  $330^{\circ}\text{C}$  in flowing helium for 2 h in order to deactivate the Triton X-100 surfactant in the Teflon dispersion.

In order to obtain a reasonably porous electrode, it was found necessary to add ammonium bicarbonate as a pore-former. The initial method involved working the ammonium bicarbonate powder into the moist pyrochlore-Teflon paste. From 20 to  $30\text{ mg cm}^{-2}$  was typically used (based on the electrode area).

A second method was instituted to avoid some of uncertainty as to the amount of pore-former that goes into solution in the moist paste. A slurry was prepared and mixed using a Waring-type blender with isopropanol, in which the ammonium bicarbonate is only slightly soluble. The slurry was then

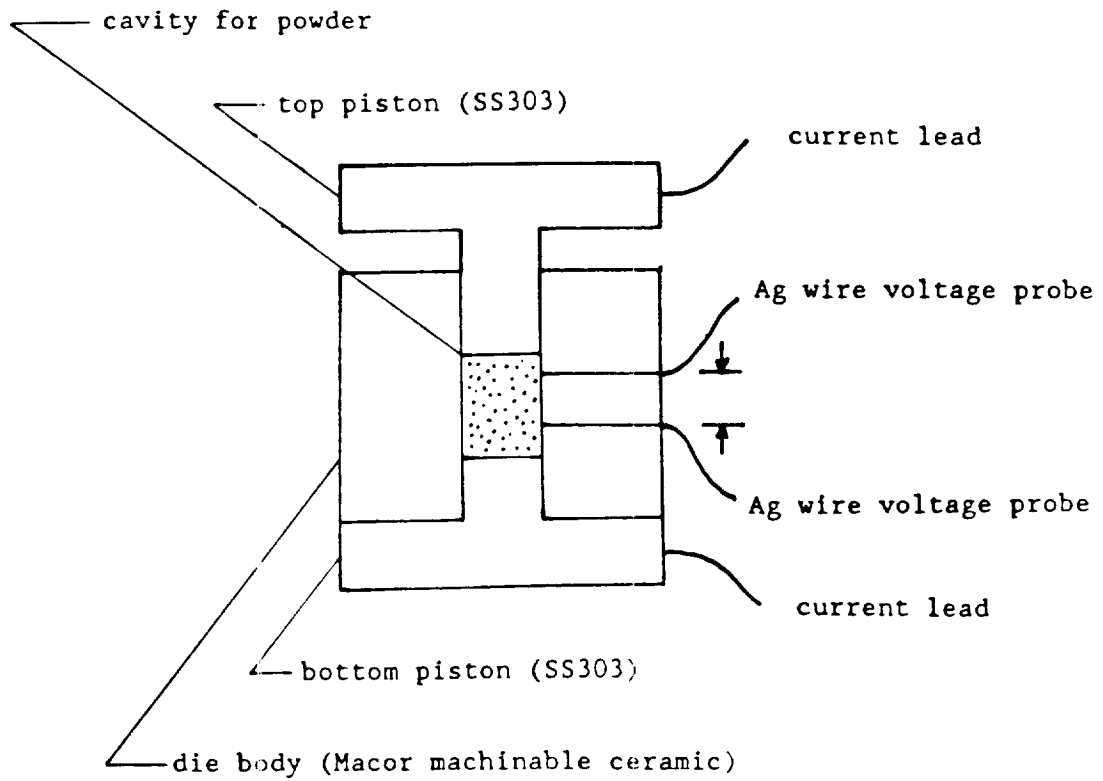


Fig. 1. Conductivity cell for powder samples under pressure loads, based on Beyerlein et al. (13) and Espinola et al. (14).

filtered, and then the resulting paste was worked, shaped and finally pressed, just as in the usual procedure.

#### E. Electrochemical Measurements

The gas-fed electrode measurements were carried out galvanostatically using a BCl200 Potentiostat (Stonehart Associates). Each current was applied for a time sufficient to achieve steady state, usually 1-5 min. The IR drop was corrected using the current interruptor method, which corrects only for the solution resistance external to the porous electrode.

A diagrammatic sketch of the electrochemical cell used for high temperature experiments is shown in Fig. 2. An outer cylindrical shell of aluminum was heated with resistance heater elements, which were controlled with an Omega CN9000 microprocessor controller. The cell itself was made from Teflon, and a Viton O-ring sealed the cap to the main body. The cap assembly was bolted onto the bottom part of the aluminum shell. The working electrode shown in the diagram is of the flooded type for voltammetry and stability studies. For O<sub>2</sub> reduction measurements, a gas-fed electrode holder can be inserted. Alternatively, a floating electrode arrangement can be used. A Hg/HgO reference electrode was maintained at room temperature for measurements involving electrolyte concentrations up to 45 wt% KOH. For higher concentrations, a dynamic hydrogen electrode was used.

### IV. RESULTS AND DISCUSSION

#### A. Preparation and physical characterization of support materials catalysts

A total of about 26 different catalyst samples were prepared as part of this project (see Table I). These included mainly pyrochlores but also included RuO<sub>2</sub>, both undoped and doped with platinum. They were prepared mostly with the alkaline solution precipitation method (1-5) except for two that were prepared using the molten salt (fusion) technique (6-9). The latter has never been used, to our knowledge, to prepare pyrochlores. The XRD showed that this process successfully produced the pyrochlore. The BET surface area was not as high as expected (3.8 m<sup>2</sup> g<sup>-1</sup>), but it should be possible to improve this with better control of the processing variables.

The catalysts were characterized with X-ray diffraction (XRD) and BET surface area measurements, with some of the latter reaching quite high values (>100 m<sup>2</sup> g<sup>-1</sup>).

It should be noted that the Pb-Ir pyrochlore was found to be difficult to prepare in high area form, as was also found by Horowitz and coworkers (1). The product obtained using the alkaline solution method is typically amorphous and must be heat-treated to develop the crystallinity.

The conductivity for Pb<sub>2</sub>Ru<sub>2</sub>O<sub>6.5</sub> in the form of the high area powder was quite good [ $\sim 170$  ( $\Omega$  cm)<sup>-1</sup>] when the powder was pressed to a density of 38% theoretical, which is in the range that might be used in the Teflon-bonded electrodes.

A series of Pt-doped lead ruthenate pyrochlores was prepared, and the X-ray diffraction (XRD) indicated that these materials retained the pyrochlore structure with no apparent additional phases. The use of the alkaline



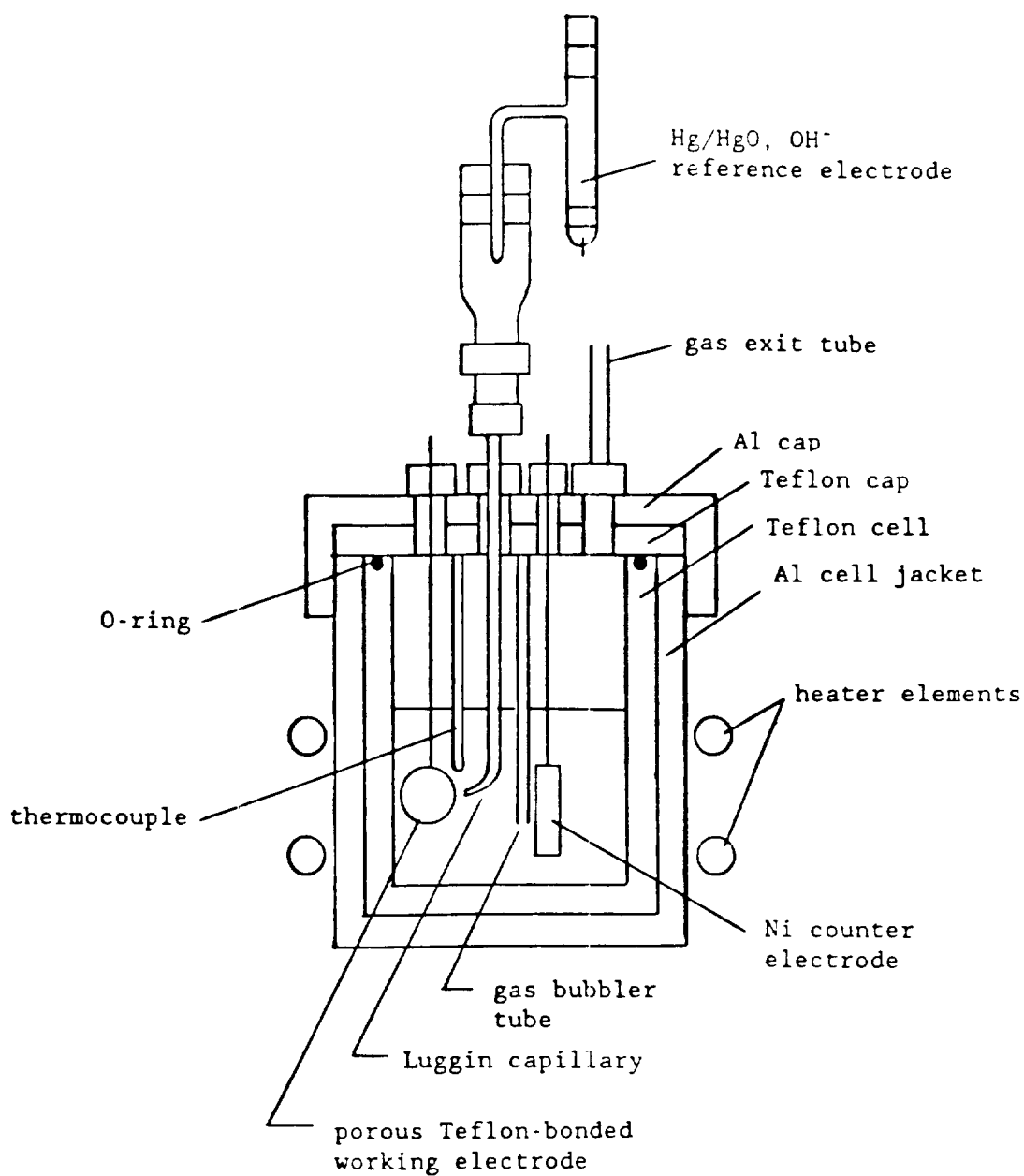


Fig. 2. Diagrammatic sketch of the electrochemical cell used for voltammetry and O<sub>2</sub> reduction polarization measurements at elevated temperatures ( $\leq 220^{\circ}\text{C}$ ) in alkaline electrolyte.

TABLE I

## Transition Metal Oxides Prepared for this Project

Compound	BET surface area, m <sup>2</sup> g <sup>-1</sup>	Structural characteristics based on XRD
<u>Pb-Ir compounds</u>		
Pb <sub>2</sub> Ir <sub>2</sub> O <sub>7-y</sub>	1.6	crystalline
Pb <sub>2</sub> Ir <sub>2</sub> O <sub>7-y</sub>	4.3	crystalline
Pb-Ir oxide (16 h, 195°C)	47.8	amorphous
Pb-Ir oxide (4 h, 90°C)	66.0	amorphous
<u>Pb-Ru compounds</u>		
Pb <sub>2</sub> Ru <sub>2</sub> O <sub>7-y</sub>	21.4	crystalline, some RuO <sub>2</sub>
Pb <sub>2</sub> Ru <sub>2</sub> O <sub>7-y</sub>	43.4	crystalline, some RuO <sub>2</sub>
Pb <sub>2</sub> Ru <sub>2</sub> O <sub>7-y</sub>	49.8	crystalline
Pb <sub>2</sub> Ru <sub>2</sub> O <sub>7-y</sub>	54.8	-
Pb <sub>2</sub> Ru <sub>2</sub> O <sub>7-y</sub> (16 h, 195°C)	56.1	crystalline
Pb <sub>2</sub> Ru <sub>2</sub> O <sub>7-y</sub>	66.1	-
Pb <sub>2</sub> Ru <sub>2</sub> O <sub>7-y</sub> (4 h, 90°C)	104.6	crystalline (broad peaks)
Pb <sub>2</sub> Ru <sub>2</sub> O <sub>7-y</sub> (4 h, 600°C)	3.5	crystalline
<u>Pb-Ru-Pt compounds</u>		
Pb <sub>2</sub> Ru <sub>1.98</sub> Pt <sub>0.02</sub> O <sub>7-y</sub>	51.5	crystalline
Pb <sub>2</sub> Ru <sub>1.98</sub> Pt <sub>0.02</sub> O <sub>7-y</sub>	64.4	amorphous
Pb <sub>2</sub> Ru <sub>1.905</sub> Pt <sub>0.095</sub> O <sub>7-y</sub>	72.1	amorphous
Pb <sub>2</sub> Ru <sub>1.9</sub> Pt <sub>0.1</sub> O <sub>7-y</sub>	47.6	crystalline
Pb <sub>2</sub> Ru <sub>1.8</sub> Pt <sub>0.2</sub> O <sub>7-y</sub>	67.7	crystalline
Pb <sub>2</sub> Ru <sub>1.98</sub> Pt <sub>0.02</sub> O <sub>7-y</sub> (4 h, 600°C)	2.6	crystalline
Pb <sub>2</sub> Ru <sub>1.94</sub> Pt <sub>0.06</sub> O <sub>7-y</sub> (4 h, 600°C)	3.8	crystalline
Pb <sub>2</sub> Ru <sub>1.9</sub> Pt <sub>0.1</sub> O <sub>7-y</sub> (4 h, 600°C)	3.1	crystalline
<u>RuO<sub>2</sub>-based compounds</u>		
RuO <sub>2</sub>	8.0	crystalline
RuO <sub>2</sub>	66.4	amorphous
Ru <sub>0.98</sub> Pt <sub>0.02</sub> O <sub>2</sub>	68.1	amorphous
Ru <sub>0.9</sub> Pt <sub>0.1</sub> O <sub>2</sub>	-	-
Ru <sub>0.5</sub> Ir <sub>0.5</sub> O <sub>2</sub>	-	-
<u>Lithiated nickel oxide</u>		
Ni <sub>0.9</sub> Li <sub>0.1</sub> O	0.86	crystalline

solution technique to prepare such compounds is new and was introduced as part of this project. These compounds were prepared with the idea of achieving atomic-level dispersion of the platinum in the pyrochlore, which could result in very high levels of catalytic activity if the Pt clusters are spaced far enough apart that the diffusion fields around each cluster do not overlap. This so-called microelectrode effect has recently been described by Watanabe, Sei and Stonehart (see Ref. 15 and discussion below). With the pyrochlores that exhibit high activity for O<sub>2</sub> reduction, this effect will perhaps not be as pronounced as with supports that are not highly catalytic for O<sub>2</sub> reduction, such as RuO<sub>2</sub>. It is interesting to compare the catalytic activity of these materials with that of Pt/pyrochlore samples prepared using more conventional methods, such as the Prototech method (12). One sample of the latter type was prepared.

The very high current density requirement means that the active catalyst layer should be kept as thin as possible to minimize the ohmic losses in the solution within the porous layer. The catalyst surface area must be as high<sup>+</sup> as possible, however, to minimize the activation polarization. To achieve both of these optimizations, the catalyst should be highly dispersed so as to obtain very high surface areas and at the same time be at high loadings to keep the active layer thin. This requires the use of high surface area supports. Modelling studies are required to establish what is the optimum support area and configuration, but areas of at least 50 m<sup>2</sup> g<sup>-1</sup> probably are necessary for oxides consisting of predominantly the first transition row elements.

Conductivity measurements were carried out for a Pt-doped pyrochlore Pb<sub>2</sub>Ru<sub>1.8</sub>Pt<sub>0.2</sub>O<sub>7-y</sub> as a function of theoretical density (Fig. 4). This compound showed lower conductivity than the undoped pyrochlore by ~25% at the highest density used. The conductivity of the undoped compound at this density (38% theoretical) is roughly a factor of 5 lower than that obtainable for powders pressed at higher pressures (13). Part of the difference may also be associated with the amorphous nature of this particular sample, which is known to lead to lower conductivity for this compound (13). The presence of platinum replacing part of the Ru in pyrochlores has been shown to lead to decreased conductivity in the Pb-Bi-Ru-Pt-O system (22). This is consistent with the fact that Pb<sub>2</sub>Pt<sub>2</sub>O<sub>7</sub> has relatively low conductivity (17), which is due to the filling of the t<sub>2g</sub> conduction band (18). Lowered conductivity must be kept in mind as a possible problem with these types of catalysts.

In related work at CWRU, the temperature dependence of O<sub>2</sub> reduction on lithiated nickel oxide was examined. As a first step, powder samples were

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<sup>+</sup> The catalytic activity per unit area appears to decrease with increasing area with highly dispersed platinum (16). This may occur because the higher index surfaces which become predominant with very small particles have smaller catalytic activity. Electronic factors may also be involved with small platinum clusters. Similar effects may occur with the gold-platinum and other bimetal clusters. Recently Watanabe et al. (15) have proposed that the apparent decrease in catalytic activity with highly dispersed platinum is not due to a crystallite effect but rather to interaction of the hemispherical O<sub>2</sub> concentration gradient around the nearest neighbor platinum particles on the substrate (Fig. 3). This effect depends on the distance between neighboring catalyst particles. The use of high area substrates should decrease the effect and lead to higher apparent catalytic activity.

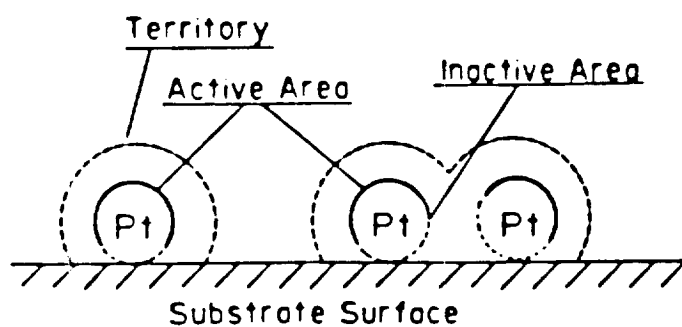


Fig. 3. Diagrammatic sketch of the interaction of the diffusion fields for an electroactive species such as  $O_2$  around electrocatalyst particles on an inert (but electronically conductive) substrate (taken from Watanabe et al., Ref. 15).

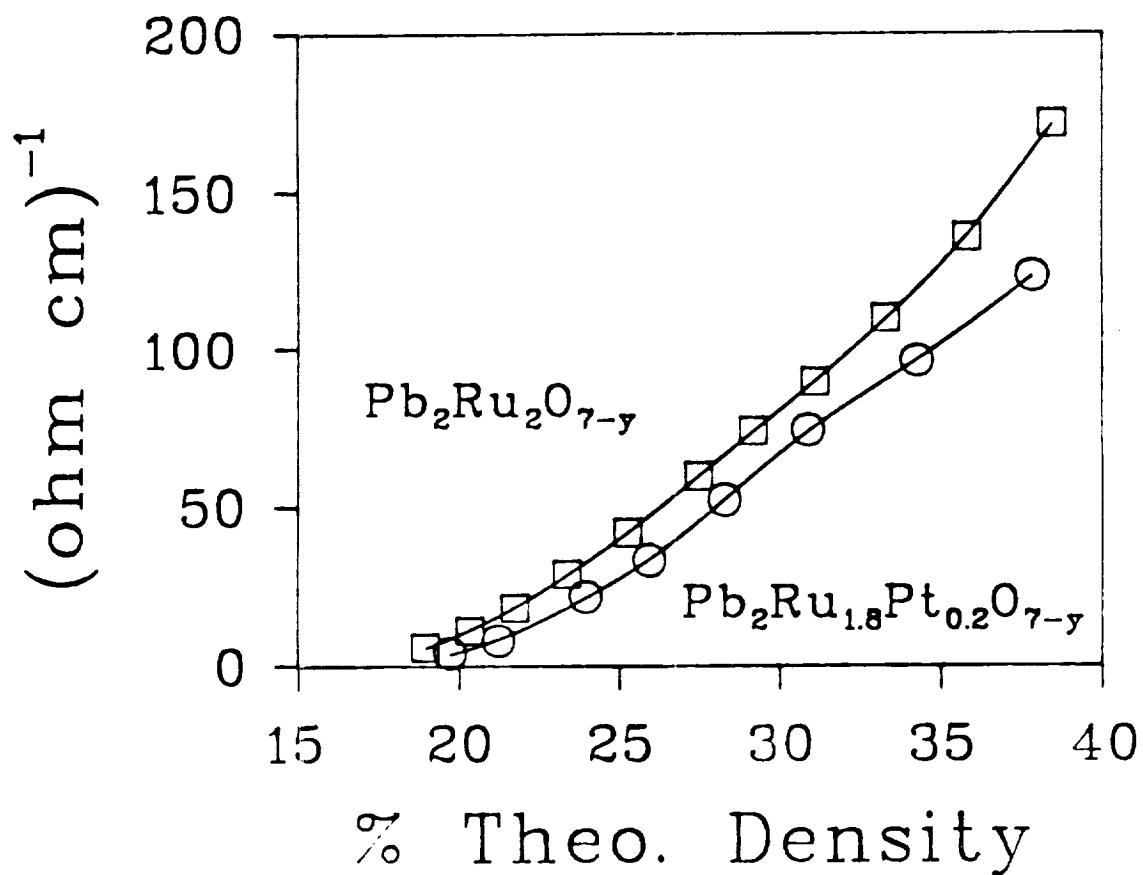


Fig. 4. Effect of Pt substitution in  $\text{Pb}_2\text{Ru}_2\text{O}_{7-y}$  pyrochlore on the conductivity at densities up to 38% theoretical using powder samples under pressure loads in the cell shown in Fig. 1.

prepared, from which both porous as well as relatively-non-porous electrodes were made. These powders were also used in the NASA project as candidate support materials for noble metal catalysts. As mentioned earlier,  $\text{Ni}_{0.9}\text{Li}_{0.10}$  and  $\text{Ni}_{0.96}\text{Li}_{0.040}$  powders were prepared using a method involving the formation of an organic glass based on citric acid and urea. The powders were heat-treated in air at  $650^{\circ}\text{C}$  as well as higher temperatures and characterized using X-ray diffraction. The lattice parameters for the Li-NiO system are known to decrease with increasing amounts of Li doping (19, 20). Data from these two references are shown in Fig. 5 together with that for the compounds prepared at CWRU. The agreement with the literature data is rather good, but it should be pointed out that the Li content for the CWRU samples has not yet been determined. These samples will be analyzed for Li content in the future using atomic emission spectroscopy. It was found that with higher heat treatment temperatures, e.g.,  $900$  and  $1200^{\circ}\text{C}$ , substantial amounts of Li were lost from the sample. Evidence for this was an increase in the lattice parameter.

Discussions with Dr. Joseph Singer of NASA-Lewis have brought out the fact that the apparent lattice parameter for Li-NiO is somewhat dependent upon the preparation method. Tseung et al. (20) mention that the lattice parameter is highly sensitive to the presence of impurities. It could also be dependent upon heat treatment conditions such as the  $\text{O}_2$  partial pressure, the time and the cooling rate. All of these factors can affect the concentration of cation vacancies, which could run as high as 1 at.%, which in turn affects the observed lattice parameter.

## B. Electrochemical Characterization

After initial difficulties, the CWRU group had a good measure of success in the fabrication of pyrochlore-based gas-fed electrodes. Much of the experience in the fabrication of such electrodes at CWRU has involved structures based on high-area carbons. The fabrication methods must be modified significantly for structures not involving carbon, and the preferred method developed during the past year made use of a pore-former material, ammonium bicarbonate. This was introduced into the pyrochlore-PTFE paste in a specific manner, which yields a pore structure with pores in the range of  $1\text{-}2\ \mu\text{m}$ , as seen by SEM (Fig. 6). The  $\text{O}_2$  reduction polarization curves obtained for  $\text{Pb}_2\text{Ru}_2\text{O}_6$ -based electrodes in  $5.5\ \text{M}\ \text{KOH}$  at room temperature (Fig. 7) are among the best obtained in this laboratory for any catalyst, including the best transition metal macrocycles and platinum.

The incorporation of the pore-former into the "green" catalyst layer (before heat treatment at  $320^{\circ}\text{C}$ ) was difficult to control in a reproducible fashion (Fig. 8). In some cases, the performance was as poor as that of electrodes fabricated without the benefit of a pore-former (Fig 9). For this reason, the alcohol suspension method was initiated. Although more reproducible, it led to generally poorer performance (Fig. 10), due to the fact that very little porosity actually resulted at the  $1\ \mu\text{m}$  level, according to the SEM (Fig. 11b). A number of larger pores ( $10\text{-}20\ \mu\text{m}$ ) were observed (Fig. 11a). After the failure of this method, the methodology for reproducing the superior results of the wet paste method was optimized. This method can be optimized further in future work in order to achieve better longer-term stability.

Preliminary examination of lead ruthenate was also carried out at higher temperatures ( $\sim 140^{\circ}\text{C}$ ) in concentrated  $\text{KOH}$  in order to establish the stability

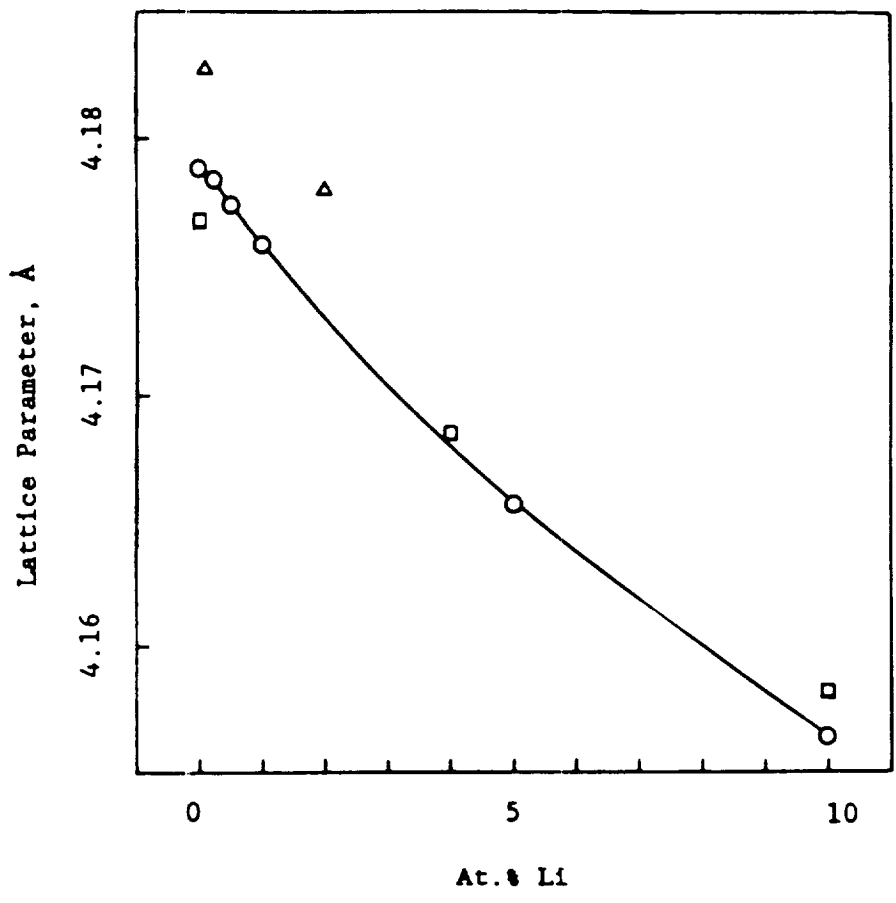
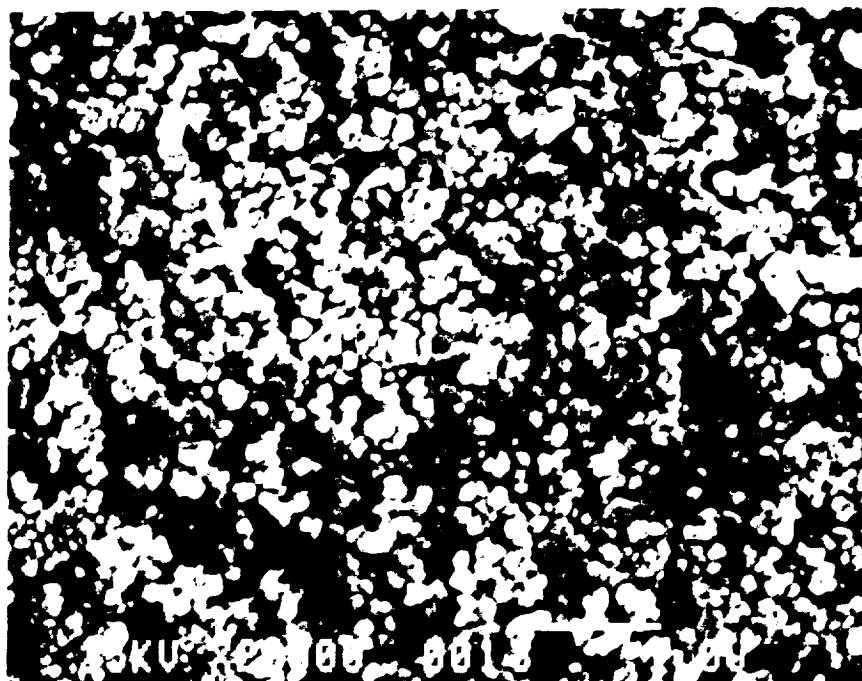


Fig. 5. Lattice parameters for lithium-doped nickel oxide: (o) data of Tseung et al. (20); (Δ) data of Verwey et al. (19); (□) present work, assuming that negligible lithium was lost when the samples were fired at 650°C for 24 h.

A



B

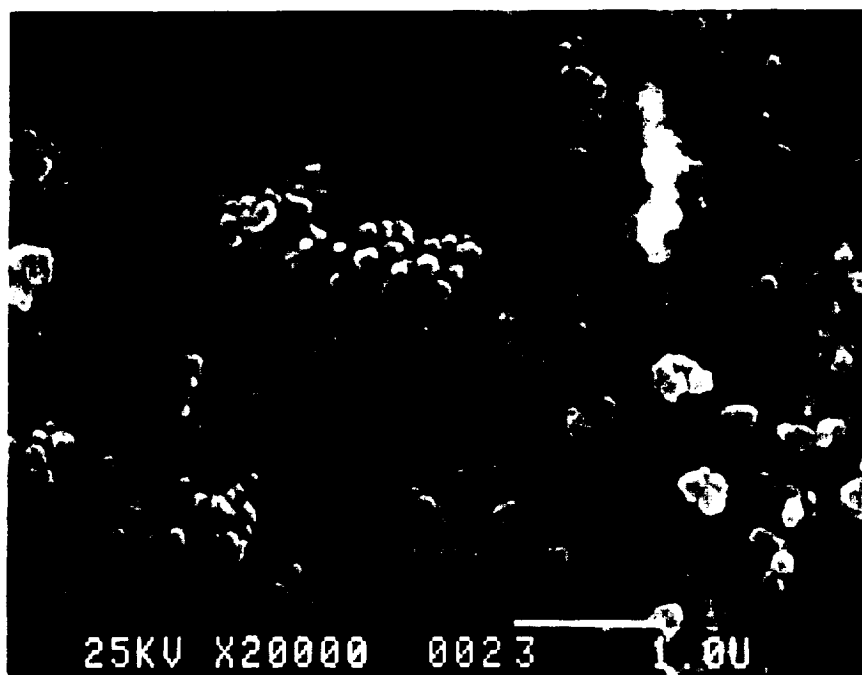


Fig. 6. Scanning electron micrographs of Teflon-bonded  $\text{Pb}_2\text{Ru}_2\text{O}_{7-y}$  active layers fabricated A) without pore-former and B) with  $9.6 \text{ mg cm}^{-2}$   $\text{NH}_4\text{HCO}_3$  worked into the pyrochlore-Teflon paste while still moist. The electrodes contained  $41.7 \text{ mg cm}^{-2}$  pyrochlore and  $13.9 \text{ mg cm}^{-2}$  Teflon T30B. The electrodes had been subjected to polarization measurements on 10-6-89 (A) and 11-6-89 (B) respectively.



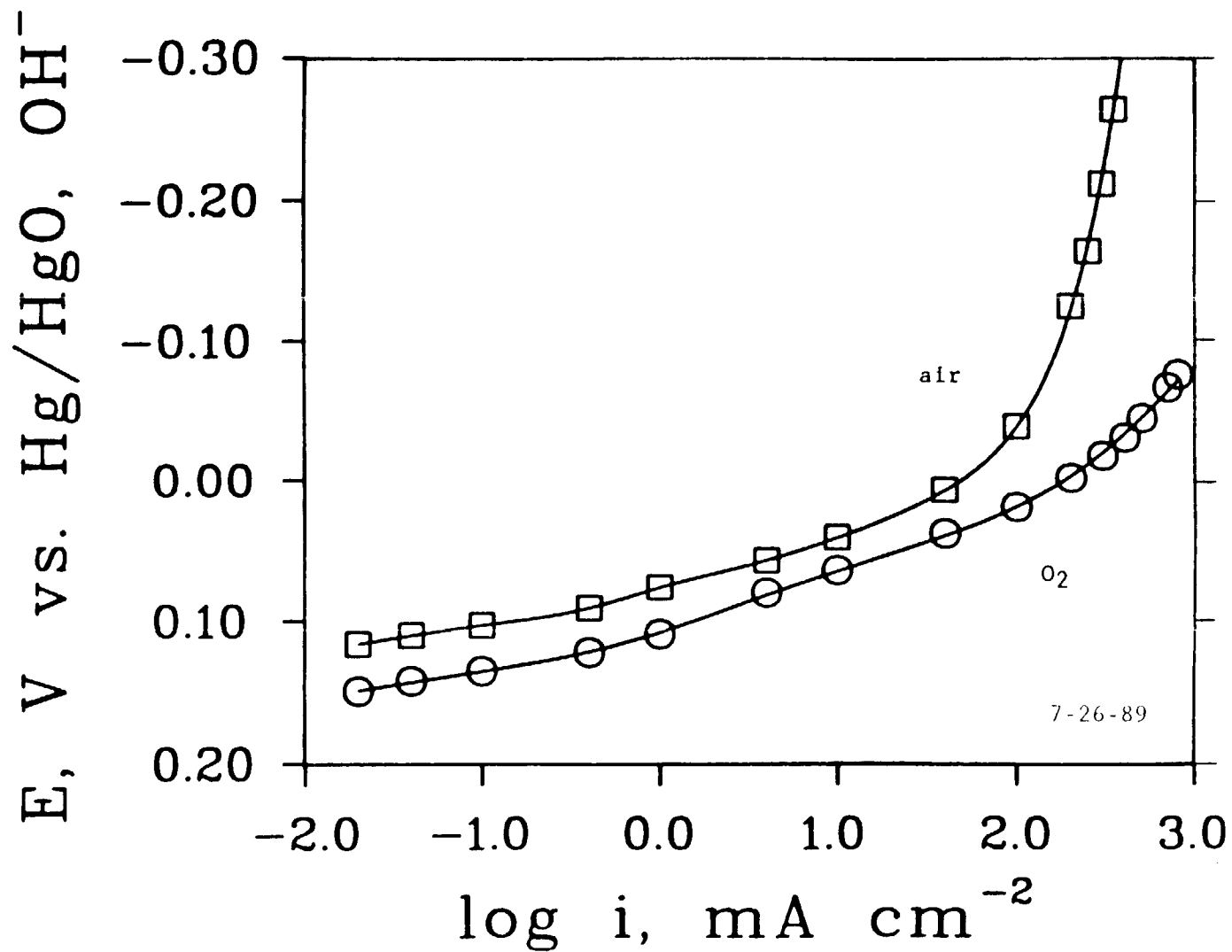


Fig. 7. Polarization curves for O<sub>2</sub> reduction with porous gas-fed (1 atm) electrodes in 5.5 M KOH at 25°C. The electrode contained 83.3 mg cm<sup>-2</sup> pyrochlore and 27.8 mg cm<sup>-2</sup> Teflon T30B and was heat-treated at 330°C for 2 h in flowing He. Ammonium bicarbonate (18.8 mg cm<sup>-2</sup>) was added as a pore-former before the heat treatment.

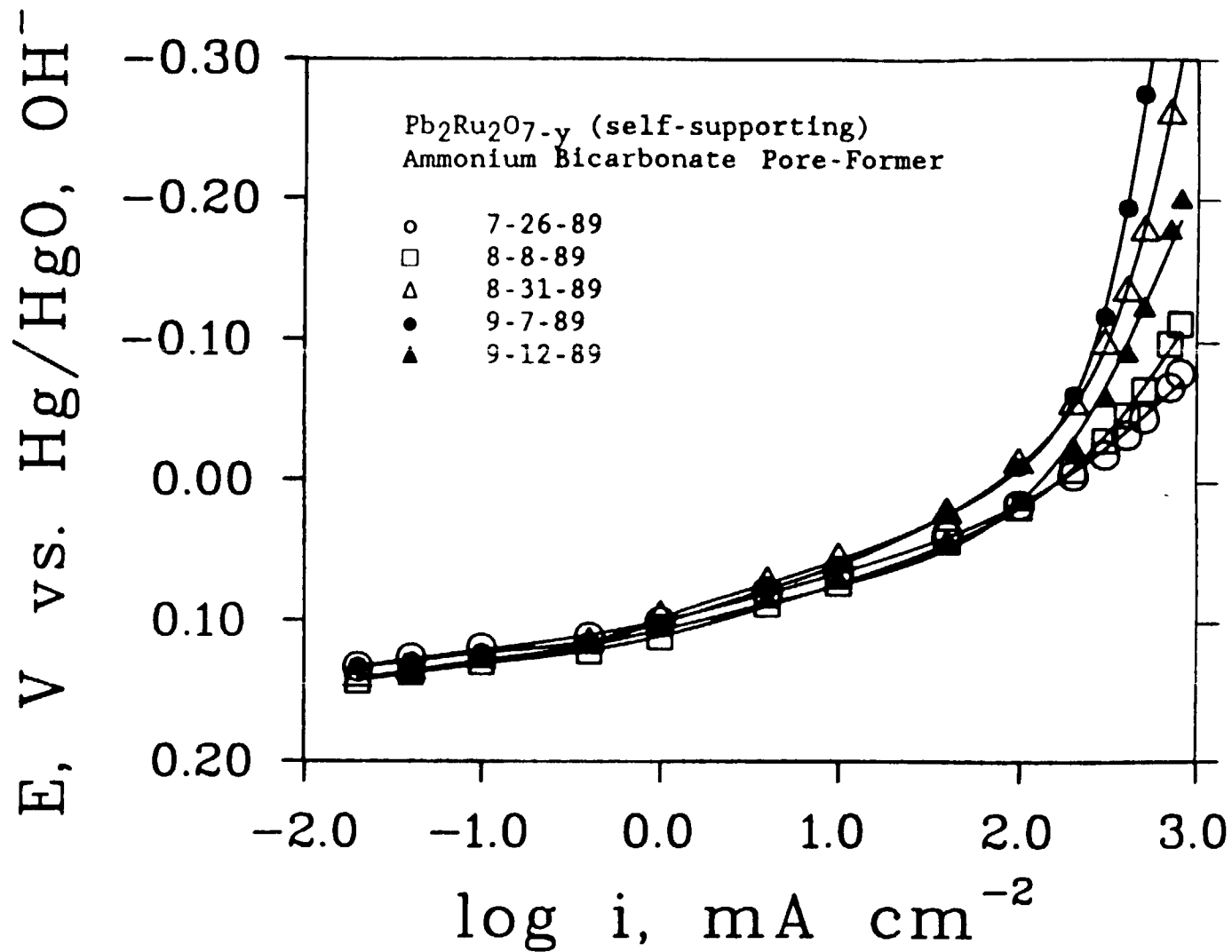


Fig. 8. Polarization curves for  $\text{O}_2$  reduction with gas-fed electrodes using  $\text{O}_2$  (1 atm) in 5.5 M KOH at 25°C. The electrodes contained  $83.3 \text{ mg cm}^{-2}$  pyrochlore and  $27.8 \text{ mg cm}^{-2}$  Teflon T30B. Ammonium bicarbonate ( $18.8 \text{ mg cm}^{-2}$  for 7-26-89,  $16.7 \text{ mg cm}^{-2}$  for others) was worked into the moist pyrochlore-Teflon paste. The electrodes were heat-treated at 330°C for 2 h in flowing He. All of the curves were from the second polarization run and were recorded with decreasing current density.

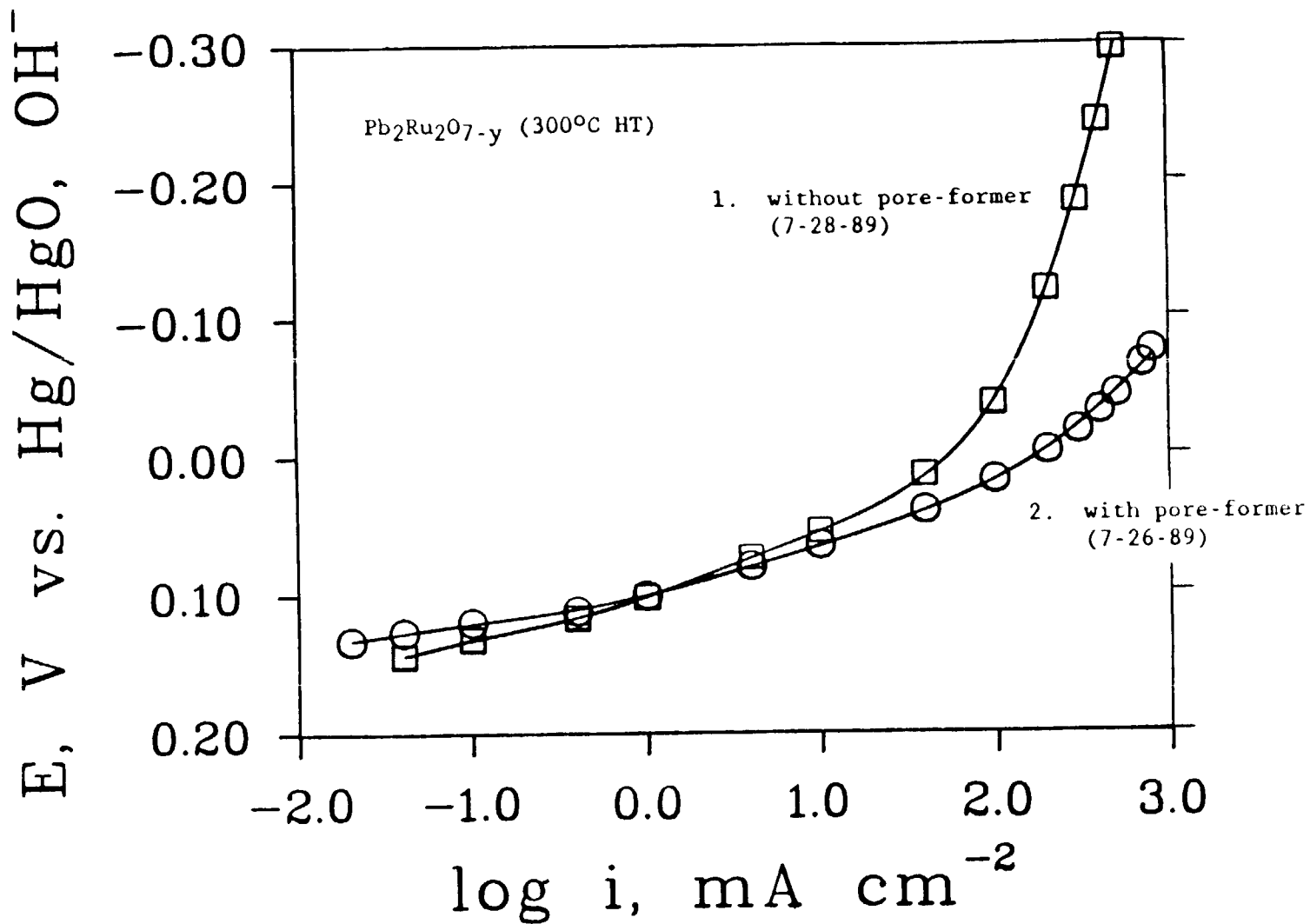


Fig. 9. Polarization curves for  $\text{O}_2$  reduction with gas-fed electrodes using  $\text{O}_2$  (1 atm) in 5.5 M KOH at 25°C. The electrodes contained 83.3 mg cm<sup>-2</sup> pyrochlore and 27.8 mg cm<sup>-2</sup> Teflon T30B. Ammonium bicarbonate (18.8 mg cm<sup>-2</sup>) was used as a pore-former and was worked into the moist paste for the electrode in curve 2. The electrodes were heat-treated at 330°C for 2 h in flowing He.

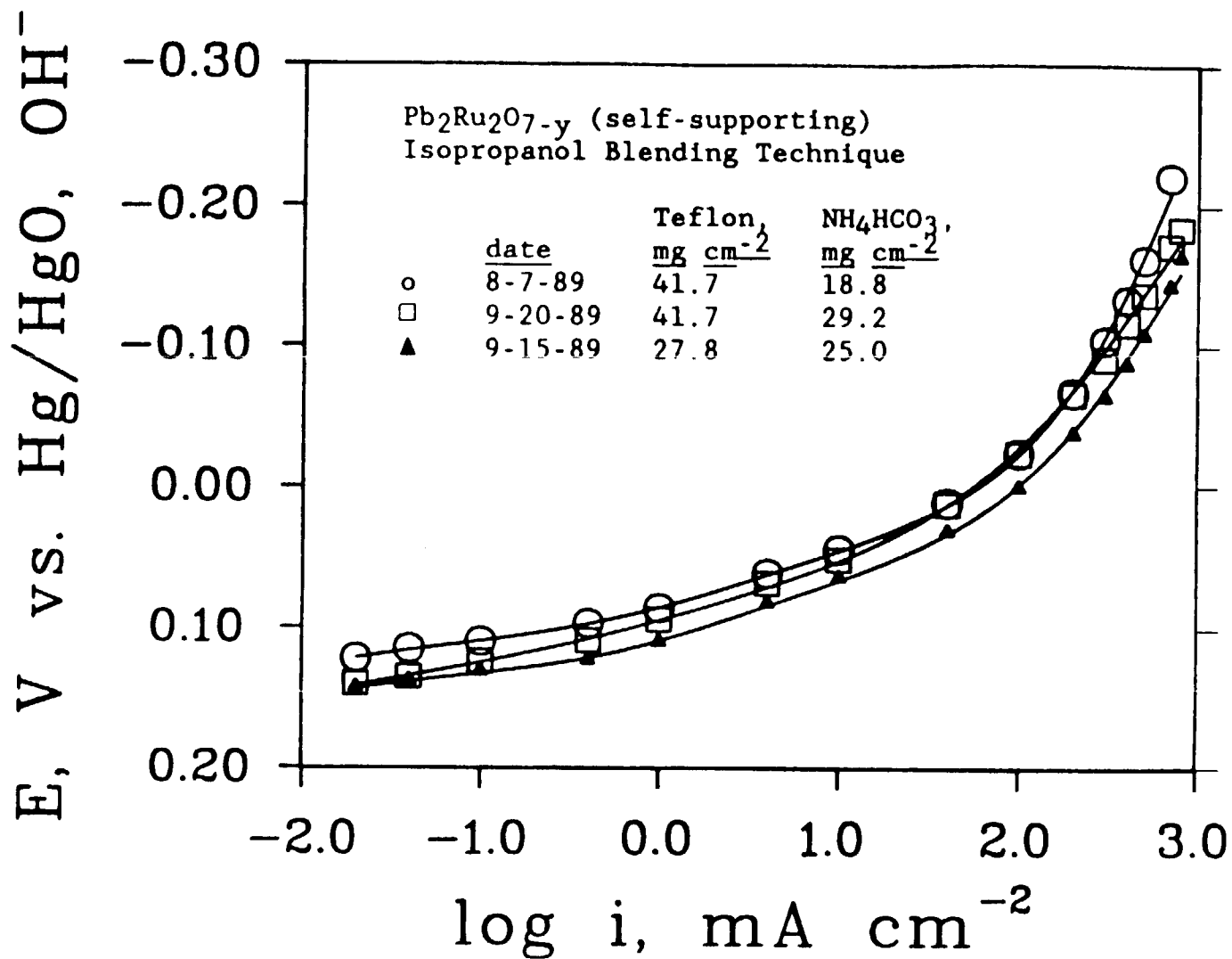
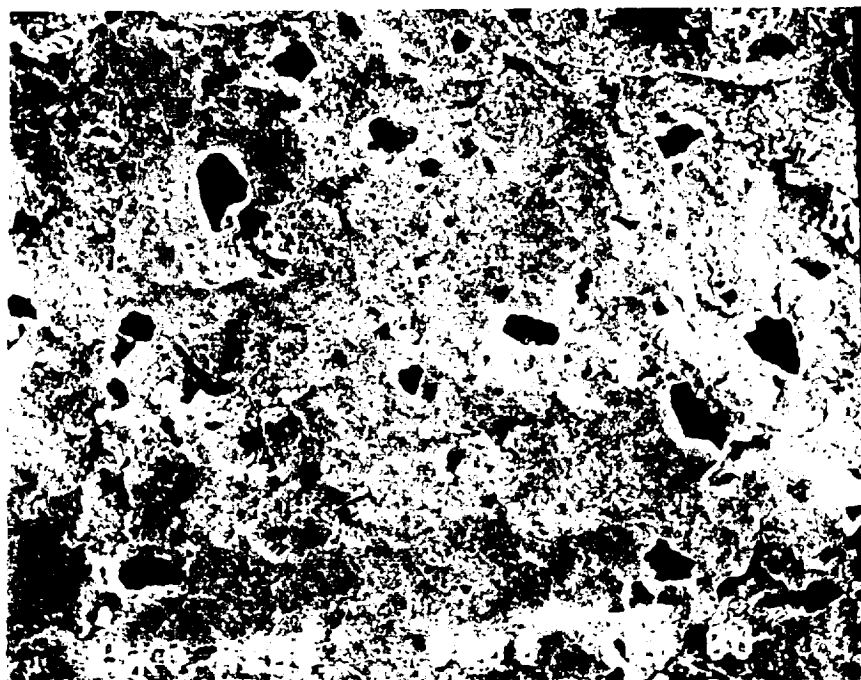


Fig. 10. Polarization curves for  $O_2$  reduction with gas-fed electrodes using  $O_2$  (1 atm) in 5.5 M KOH at 25°C. The electrodes contained 83.3  $\text{mg cm}^{-2}$  pyrochlore and designated amounts of Teflon T30B. Ammonium bicarbonate was used as a pore-former and was blended at high speed in a slurry in 2-propanol with the pyrochlore and Teflon. The electrodes were heat-treated at 330°C for 2 h in flowing He. All of the curves were from the first polarization run and were recorded with decreasing current density.

A



B

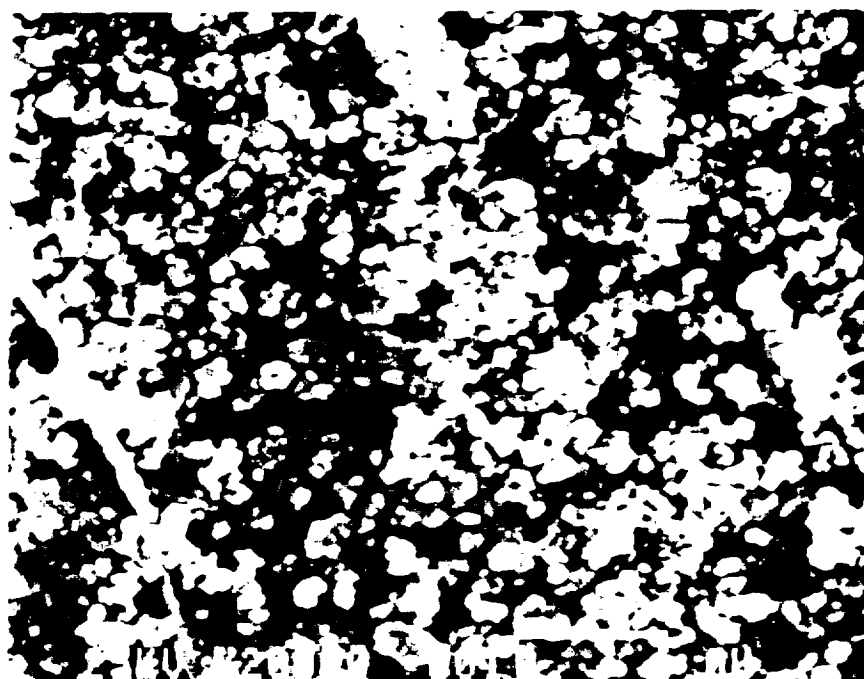


Fig. 11. Scanning electron micrographs of a Teflon-bonded  $\text{Pb}_2\text{Ru}_2\text{O}_{7-y}$  active layer fabricated with  $29.2 \text{ mg cm}^{-2}$   $\text{NH}_4\text{CO}_3$  mixed with the pyrochlore ( $41.7 \text{ mg cm}^{-2}$ ) and Teflon ( $13.9 \text{ mg cm}^{-2}$ ) in an isopropanol slurry in a high-speed blender. The electrode had been subjected to polarization measurements on 9-20-89.

under these conditions. Porous PTFE-bonded electrodes were fabricated on nickel screens and dipped in the electrolyte so that they became flooded. A nitrogen atmosphere was used. The voltammetry curves were obtained at a slow potential sweep rate so that the highly distributed impedance of the porous electrodes would be able to keep pace with the potential change (Fig. 12). These curves show that the electrodes are relatively stable over a period of at least several hours, and there was no sign of degradation at the end of the experiment. The three indicators of this stability were as follows:

- 1) The apparent capacitance, which is estimated from the vertical separation of the anodic and cathodic currents at the minimum point, did not change noticeably; this indicates that there was no loss of electrochemically active material. While this is not an extremely sensitive indicator, it would easily show a change of 5%.
- 2) There were only very slight changes in the shape of the voltammetry curves at potentials where there was apparently flow of Faradaic current, associated with either redox processes intrinsic to the oxide or O<sub>2</sub> generation, which would be expected at the more positive potentials. This indicated that there were no irreversible changes in the oxide over this potential region, which encompasses potentials which would commonly be experienced by an O<sub>2</sub> fuel cell cathode. Outside this region, irreversible changes are expected to occur based on present knowledge of the lead ruthenate.
- 3) When the potential sweep was reversed at intermediate points, there was a very reproducible steep rise or fall in the current. This indicates that there was good electronic conductivity within the electrode phase and that it did not degrade noticeably. The shapes of voltammetry curves at such reversal points have been mathematically modeled (21), and it is possible to estimate quantitatively the conductivity from the curves. Experience with other porous electrodes in this laboratory indicates that the behavior is similar to that of ones made from highly conductive carbon blacks.

The O<sub>2</sub> reduction behavior of such electrodes at elevated temperatures (~140°C) was also examined using the floating gas-fed electrode configuration (Fig. 13). The curve was similar to those obtained at room temperature (Fig. 10) for similar electrodes that were fabricated using the isopropanol blending technique. The polarization behavior was quite stable until the higher current densities were reached, where the performance began to degrade. Reasons for this degradation will be examined in future work.

Another indicator of the stability is the build-up of dissolved species in the electrolyte. This is a sensitive indicator in the case of ruthenium-containing compounds, because the orange HRuO<sub>4</sub><sup>-</sup> (ruthenate) ion is highly colored. In all of the experiments just described, there was a build-up of ruthenate, judging from the coloring of the electrolyte. Future work will indicate whether this arises from dissolution of the pyrochlore or from traces of RuO<sub>2</sub>, which are known to be present in some samples.

It should be noted that the O<sub>2</sub> reduction results for the Pb<sub>2</sub>Ru<sub>2</sub>O<sub>6.5</sub> materials were obtained for samples with relatively low area (11 - 12 m<sup>2</sup> g<sup>-1</sup>) and good crystallinity prepared by Jai Prakash, a graduate student in Prof.

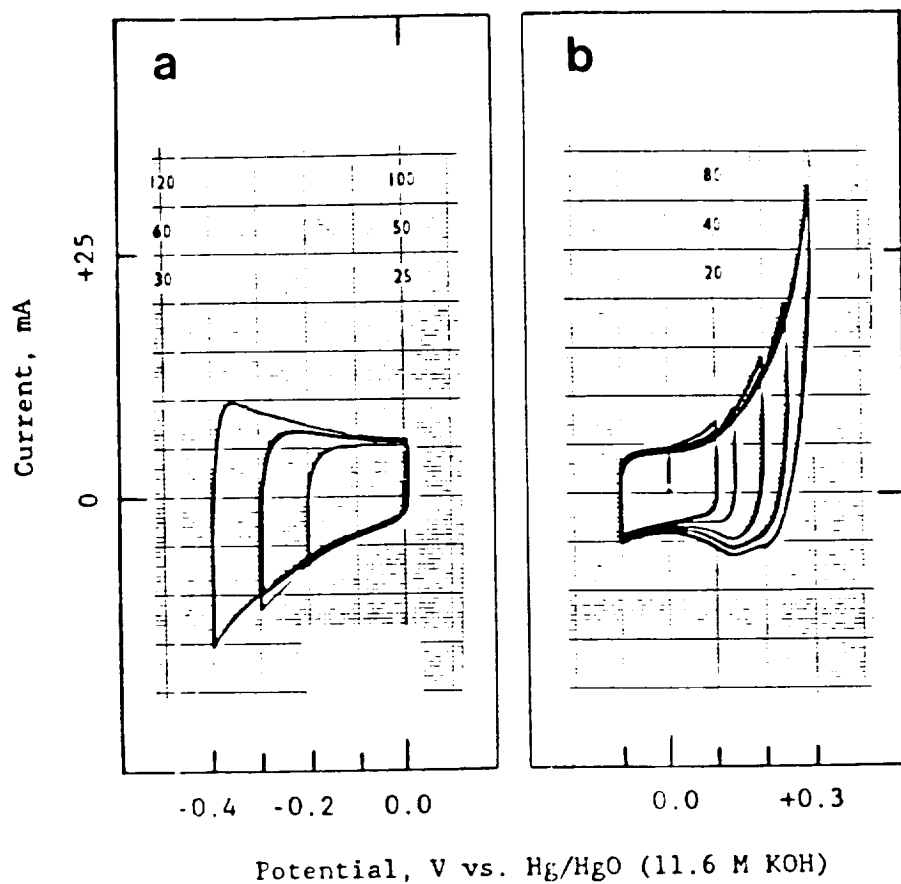


Fig. 12. Cyclic voltammety curves in  $N_2$ -saturated 11.6 M KOH at  $154 \pm 2^\circ C$  for a PTFE-bonded porous electrode fabricated from  $Pb_2Ru_2O_{7.7}$  (no heat treatment,  $11.6 \text{ m}^2 \text{ g}^{-1}$  BET surface area;  $41.7 \text{ mg cm}^{-2}$  loading) and Teflon T30 ( $13.9 \text{ mg cm}^{-2}$ ): a) more negative potential range; b) more positive potential range. The electrode was heat-treated at  $280^\circ C$  for 3 h in flowing He.

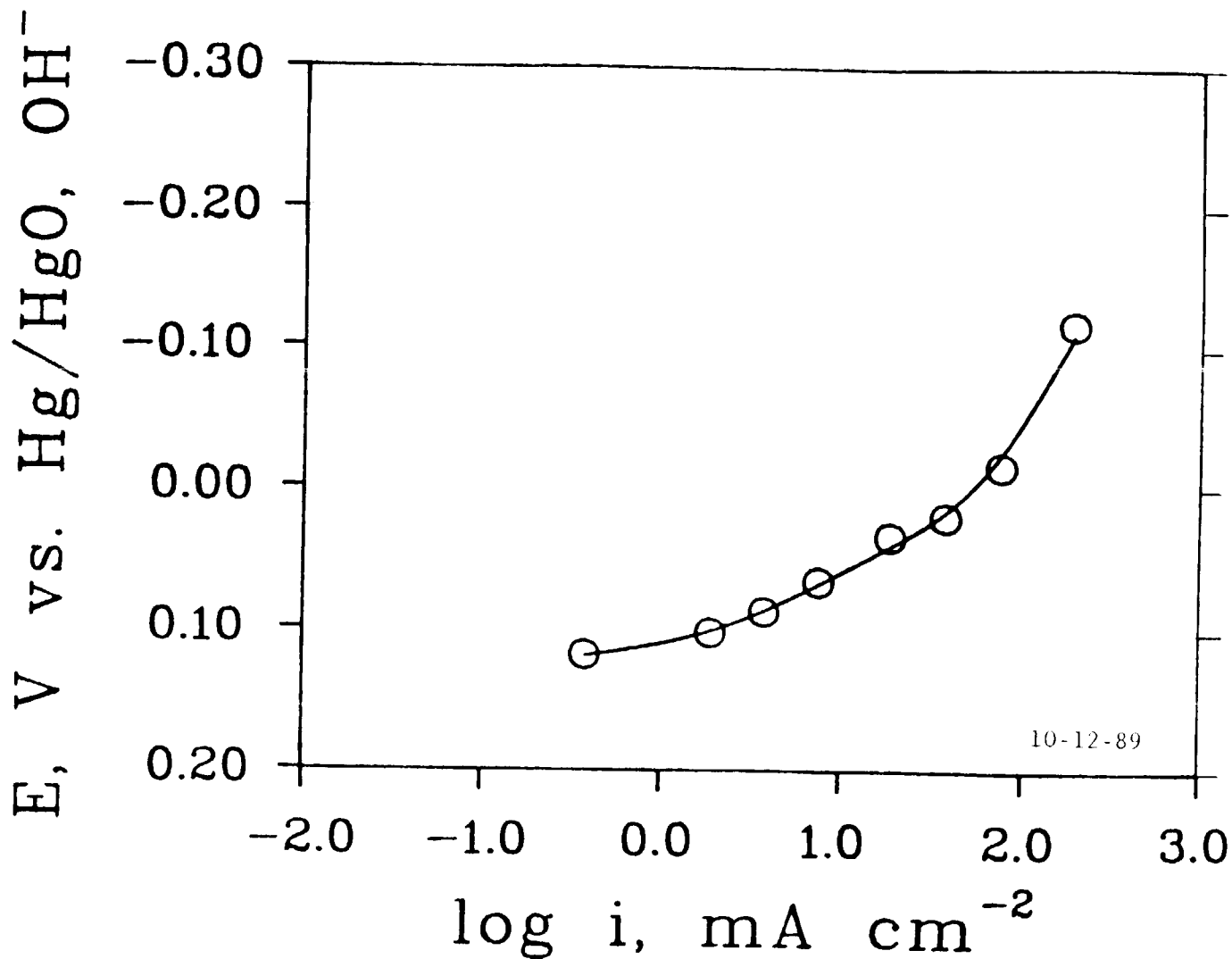


Fig. 13. Polarization curve for  $\text{O}_2$  reduction for a gas-fed electrode using  $\text{O}_2$  (1 atm) in 11.6 M KOH at  $147.5^\circ\text{C}$ . The PTFE-bonded electrode was fabricated with  $\text{Pb}_2\text{Ru}_2\text{O}_7\text{-y}$  (heat-treated at  $300^\circ\text{C}$  in air for 24 h,  $11.4 \text{ m}^2 \text{ g}^{-1}$  EEF surface area,  $41.7 \text{ mg cm}^{-2}$  loading) and Teflon T30B ( $13.9 \text{ mg cm}^{-2}$ ). Ammonium bicarbonate ( $29.2 \text{ mg cm}^{-2}$ ) was used as a pore-former and was blended at high speed in 2-propanol with the pyrochlore and Teflon. The electrode was heat-treated at  $330^\circ\text{C}$  for 2 h in flowing He. Data were recorded point-by-point in the cathodic direction.



Yeager's group. This is partly due to the fact that a large sample was prepared (~30 g), and this afforded the opportunity for a good deal of trial-and-error optimization of electrode structure. Many of the other materials were not available in large quantities. It was also surprising that the various samples behaved so differently in the electrode fabrication. For example, some of the higher area materials produced poor-quality electrodes when fabricated using the previously optimized method. This experience points out the need for optimization of each individual type of sample as long as the preparation conditions are different.

Preliminary experiments were also carried out at higher temperatures using gas-fed electrodes fabricated from lithiated nickel oxide ( $\text{Ni}_{0.9}\text{Li}_{0.1}\text{O}$ ). At temperatures approaching  $200^\circ\text{C}$ , the oxygen electrode reaction became essentially reversible, with negligible polarization at low current densities. At lower temperatures, e.g.,  $150^\circ\text{C}$ , the electrocatalytic activity was much poorer. There is much interest in this result because of the insight it may provide into the kinetics and their dependence upon the surface electronic properties. The result is also important because it implies that there may be large gains in catalytic activity at higher temperatures for other materials.

Some  $\text{O}_2$  reduction polarization results were obtained for platinum-containing catalysts. The Pt-doped lead ruthenate containing 4.75 at. % Pt showed only a slight improvement in  $\text{O}_2$  reduction performance at the higher current densities as compared with the undoped material although surprisingly the potentials reached at low current density were as high as +0.208 V vs.  $\text{Hg}/\text{HgO}$ ,  $\text{OH}^-$  (Fig. 14). The similarity at high cd may be due to several factors:

- 1) the electronic conductivity of Pt-rich phases may be poor, as discussed earlier;
- 2) the catalytic activity of the Pt may be only slightly higher than that of the pyrochlore itself;
- 3) the Pt may have remained in the oxide form instead of undergoing reduction on the surface as hoped;
- 4) the Pt may not have become fully incorporated into the structure, i.e., it may be agglomerated; or
- 5) the Pt may not be present in the same level it was added, i.e., there may have been some loss.

These possibilities will be examined in future work.

Aside from this problem, it was definitely shown that samples of  $\text{Pb}_2\text{Ru}_2\text{O}_7-y$  that were amorphous had very poor stability. This may be understandable in the light of the electrochemical behavior of the pyrochlore vs. that of other ruthenium oxides. It is known that hydrated  $\text{RuO}_2$  can be oxidized to the +6 oxidation state, which can readily yield the soluble ruthenate ion at potentials in the +0.4 V vs.  $\text{Hg}/\text{HgO}$  range (23), whereas it appears that the pyrochlore does not go to  $\text{Ru}^{6+}$  until the potential is positive of +0.5 V vs.  $\text{Hg}/\text{HgO}$  (24, 25), thus stabilizing it considerably when crystallized. The amorphous  $\text{Pb}_2\text{Ir}_2\text{O}_7-y$  was also found to be unstable at the more positive potentials.

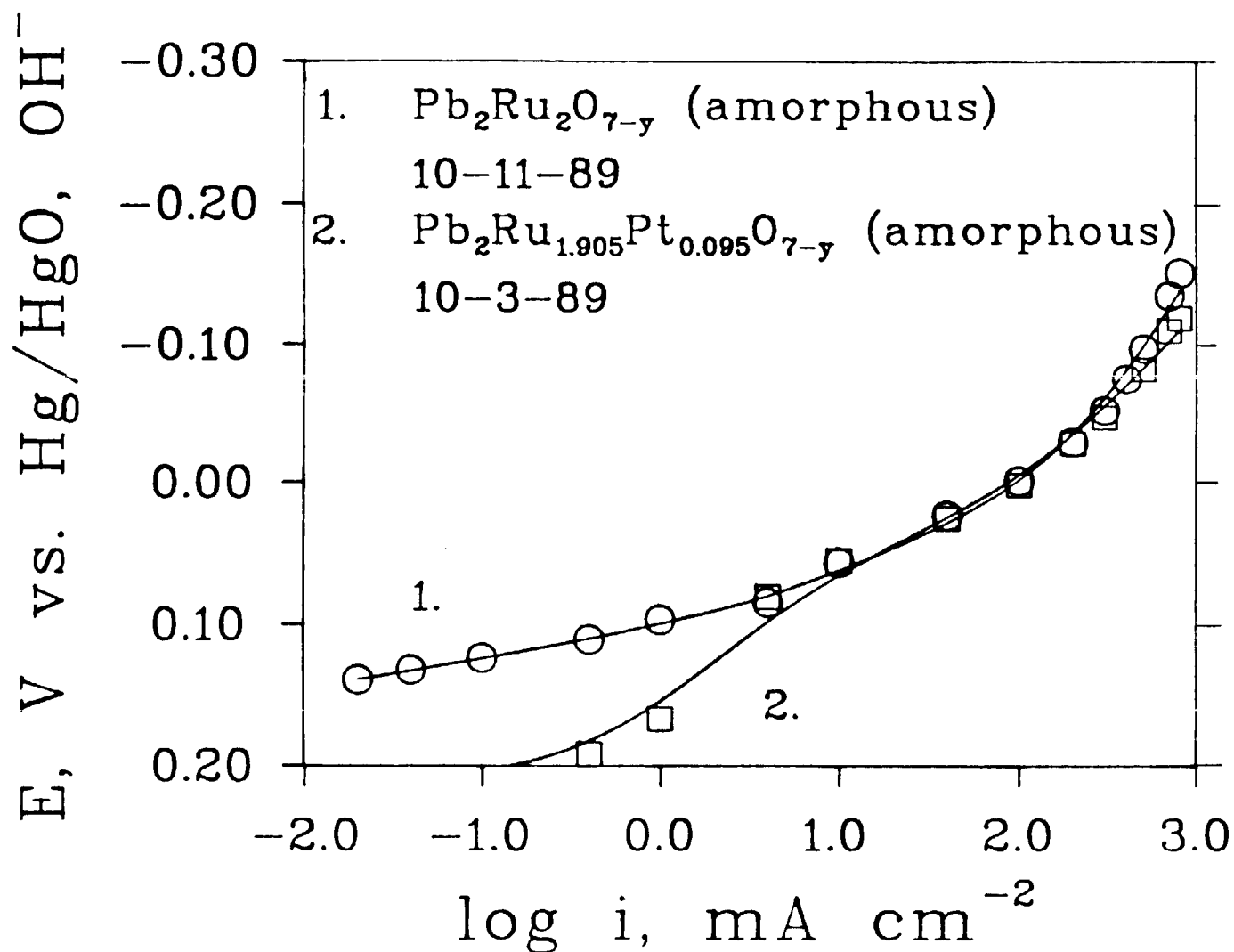


Fig. 14. Polarization curves for  $\text{O}_2$  reduction with gas-fed electrodes using  $\text{O}_2$  (1 atm) in 5.5 M KOH at 25°C. The electrodes contained  $41.7 \text{ mg cm}^{-2}$  oxide and  $13.9 \text{ mg cm}^{-2}$  Teflon T30B. Ammonium bicarbonate ( $18.8 \text{ mg cm}^{-2}$ ) was used as a pore-former and was blended at high speed in a slurry in 2-propanol with the oxides and Teflon. The electrodes were heat-treated at 320°C for 2 h in flowing He.

The  $\text{Ni}_{0.9}\text{Li}_{0.1}\text{O}$  on which Pt was deposited yielded a much enhanced performance for  $\text{O}_2$  reduction, although it was still relatively poor (Fig. 15). This was probably due to the very low area of the material ( $< 1 \text{ m}^2 \text{ g}^{-1}$ ). Thus this approach may be quite encouraging if much higher area lithiated NiO samples can be prepared.

## V. CONCLUSIONS

1. The alkaline solution technique was successful in preparing the stoichiometric  $\text{Pb}_2\text{Ru}_2\text{O}_{7-y}$  in relatively high area form, in one case over  $100 \text{ m}^2 \text{ g}^{-1}$ , confirming the result of Horowitz et al.;
2. The alkaline solution technique was also successful in preparing Pt-doped Pb-Ru pyrochlores with high areas for the first time;
3. The molten salt technique was successful in preparing the Pb-Ru pyrochlore for the first time;
4.  $\text{RuO}_2$  and Pt-doped  $\text{RuO}_2$  were prepared using the citric acid-urea method for the first time;
5. Lithiated nickel oxides were prepared using the citric acid-urea method for the first time, although the areas were low;
6.  $\text{Pb}_2\text{Ru}_2\text{O}_{7-y}$  was fabricated into self-supporting PTFE-bonded  $\text{O}_2$  electrodes with high performance for  $\text{O}_2$  reduction at room temperature;
7.  $\text{Pb}_2\text{Ru}_2\text{O}_{7-y}$  was found to be relatively stable over the potential range relevant for the  $\text{O}_2$  cathode at  $-140^\circ\text{C}$  in concentrated KOH.
8. The  $\text{O}_2$  reduction performance for  $\text{Pb}_2\text{Ru}_2\text{O}_{7-y}$  was encouraging and relatively stable even in a non-optimized electrode at  $-140^\circ\text{C}$ .
9. The electrode fabrication technique could not be optimized for many of the materials given the time and quantity available.
10. More importantly, amorphous materials prepared as  $\text{Pb}_2\text{Ru}_2\text{O}_{7-y}$  and also  $\text{Pb}_2\text{Ir}_2\text{O}_{7-y}$  were relatively unstable in solution at room temperature.
11. The  $\text{Ni}_{0.9}\text{Li}_{0.1}\text{O}$  yielded nearly reversible behavior for the  $\text{O}_2/\text{OH}^-$  redox couple at temperatures approaching  $200^\circ\text{C}$  over a substantial current density range.
12. The Pt-doped  $\text{Pb}_2\text{Ru}_2\text{O}_{7-y}$  produced only a slight improvement in  $\text{O}_2$  reduction performance, for several possible reasons.
13. Pt deposited on  $\text{Ni}_{0.9}\text{Li}_{0.1}$  yielded a very substantial improvement in  $\text{O}_2$  reduction performance even though the support was in low area form.

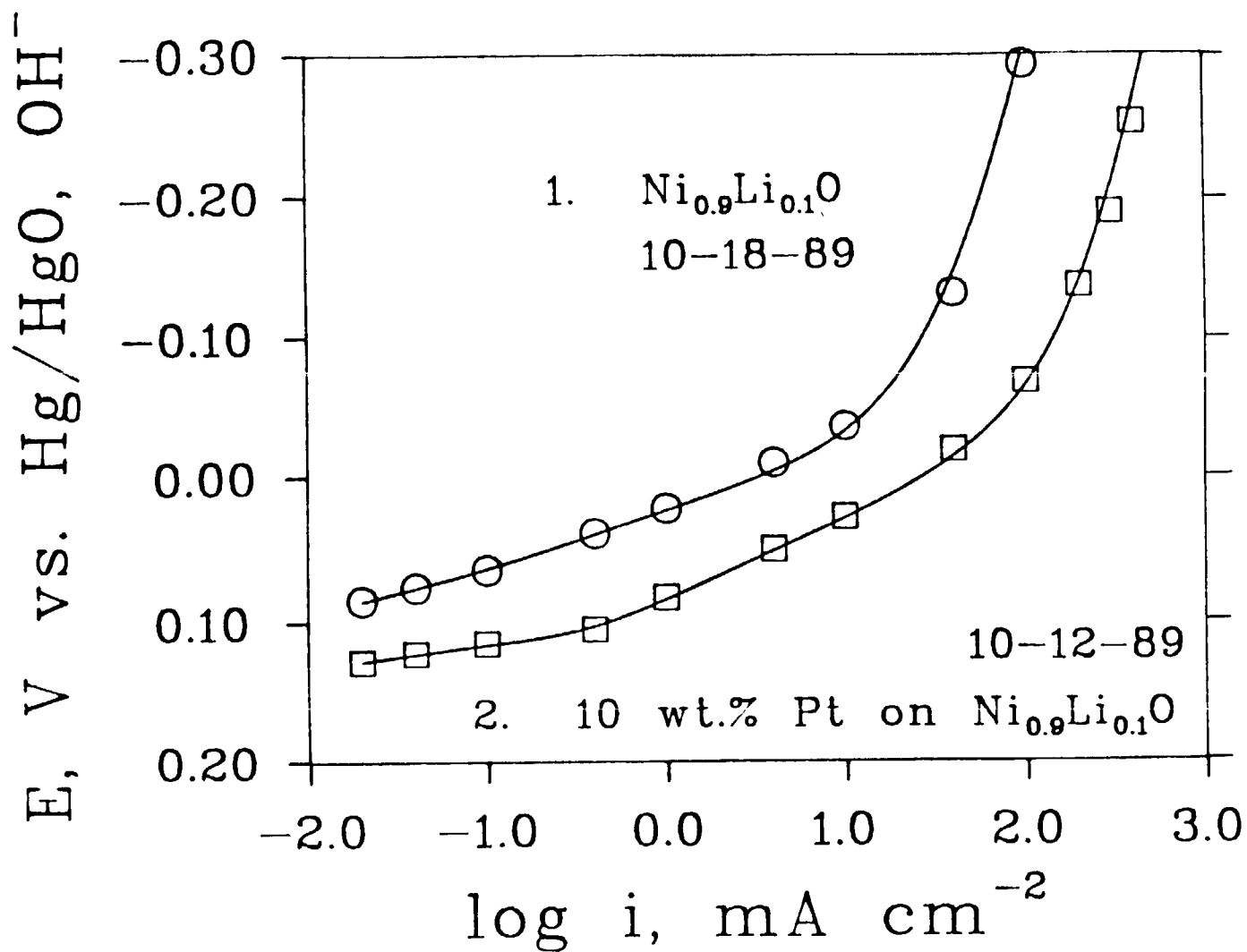


Fig. 15. Polarization curves for  $\text{O}_2$  reduction with gas-fed electrodes using  $\text{O}_2$  (1 atm) in 5.5 M KOH at 25°C. The electrodes contained  $41.7 \text{ mg cm}^{-2}$  oxide and  $8.5 \text{ mg cm}^{-2}$  Teflon T30B. Ammonium bicarbonate ( $12.5 \text{ mg cm}^{-2}$ ) was used as a pore-former and was blended at high speed in a slurry in 2-propanol with the oxides and Teflon. The electrodes were heat-treated at 320°C for 2 h in flowing He.

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