

OXYGEN ELECTRODES FOR RECHARGEABLE ALKALINE FUEL CELLS

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Summary

The primary objective of this program is the investigation and development of electrocatalysts and supports for the positive electrode of moderate temperature, single-unit, rechargeable, alkaline fuel cells.

Introduction

We define the electrocatalyst as the material with a higher activity for the oxygen electrode reaction than the support. Viable candidate materials must meet the following requirements:

- (i) good electrical conductivity (typically a more demanding requirement for supports than for electrocatalysts);
- (ii) high resistance to chemical corrosion and electrochemical oxidation and/or reduction;
- (iii) electrocatalysts, in addition, must exhibit high bifunctional electrocatalytic activity (O_2 evolution and reduction).

Advanced development will require that the materials be prepared in high-surface-area forms, and may also entail integration of various candidate materials, *e.g.*, one or two electrocatalysts distributed on a less active support material.

At this point in the program, eight candidate support materials and seven electrocatalysts have been investigated. Of the eight supports, three materials meet the preliminary requirements in terms of electrical conductivity and stability. Emphasis has now shifted to preparation in high-surface-area form, and testing under more severe corrosion stress conditions. Of the seven electrocatalysts prepared and evaluated, at least five materials remain as potential candidates. The major emphasis remains on preparation, physical characterization and electrochemical performance testing.

For supports, an acceptable conductivity should exceed about $1 \Omega \text{ cm}^{-1}$. This is a difficult initial screening criterion since these materials are being drawn from metal oxides, carbides, nitrides, etc. For catalysts we anticipate that the conductivity can be more than an order of magnitude lower on a high conductivity support. In preliminary corrosion testing, the

material is held at 1.4 V *versus* RHE in 30% KOH at 80 °C for 15 - 20 h. An acceptable anodic current is of the order of a few microamps/mg of material. For more stringent corrosion testing, and for further evaluation of electrocatalysts (which generally show significant O₂ evolution at 1.4 V), samples will be held at 1.6 V or 0.6 V for about 100 h. The materials and solutions will then be physically and chemically analyzed for signs of degradation.

Determining electrochemical activity for the oxygen electrode reaction requires considerable exploratory electrode preparation and testing, since the measured polarization is highly dependent on surface area and the hydrophobic/hydrophilic balance or "flooded agglomerate" configuration achieved [1]. For the experimental materials being studied, a customized electrode fabrication procedure has to be developed for each material. For preliminary testing, catalysts of interest should show <500 mV polarization (from 1.2 V) in either mode at 200 mA cm⁻². In advanced development we would expect to reduce the polarization to 300 - 350 mV.

Materials investigated

Supports

LaNiO₃
 LaCrO₃
 Ba₅Nb₄O_{15-x}
 TiC
 B₄C
 NbN
 Material A[†]
 Material B[†]

Electrocatalysts

PbPdO₂
 CdPd₃O₄
 Bi₂PdO₄
 Pb₂(Ir_{2-x}Pb_x)O_{7-y}
 Pb₂(Ru_{2-x}Pb_x)O_{7-y}
 Na_xPt₃O₄
 CoTMPP (Cobalt tetramethoxyphenylporphyrin)

Reference materials

O₂ reduction
 10% Pt/Au (Johnson-Matthey, 11 m² g⁻¹)
 10% Pt/Vulcan XC-72 Carbon (Johnson-Matthey, 120 - 140 m² g⁻¹)
 O₂ evolution
 Ni₂Co₂O₄ (Basic Volume, Ltd.)

[†]Patent applications under consideration for these materials.

Material sources

Materials have been acquired both by purchase, where commercially available, and/or by preparation. Initial preparations have tended to follow procedures documented in the literature where available, and vary greatly according to reaction requirements, *e.g.*, thermal decomposition of mixed salts (LaNiO_3 , LaCrO_3), high temperature firing of mixed reactant powders or pellets ($\text{Ba}_5\text{Nb}_4\text{O}_{15-x}$, LaCrO_3 , $\text{Na}_x\text{Pt}_3\text{O}_4$, PbPdO_2), co-precipitation and heat treatment (PbPdO_2 , CdPd_3O_4 , Bi_2PdO_4 , $\text{Pb}_2\text{Ir}_2\text{O}_{7-x}$), adsorption/thermal decomposition (CoTMPP on carbon), and gas phase reactions (TiC). The emphasis has been on obtaining materials of verifiable composition and, secondarily, with desirable electrochemical properties such as high surface area and small particle size. Materials are typically characterized by X-ray diffraction, and occasionally in conjunction with thermal gravimetric analysis*.

Experimental

Electrical conductivity

The electrical conductivity of materials is estimated by compressing a small quantity of the powder at about 12 000 p.s.i. between metal pistons within an insulating cylinder; the resistance of the powder is measured directly with an ohmmeter. If the resistivity thus measured is in the range of a few ohm cm, the resistance is determined more accurately by measuring the voltage drop across the powder under the flow of sufficient current to generate easily measured current and voltage signals. When appropriate, a more accurate value can be obtained by a four-point method in which the voltage drop is measured across contacts separate from the current carrying metal pistons.

Corrosion resistance

For an initial assessment of the stability of candidate support materials and catalysts, the steady-state anodic current is measured in the range 1.0 - 1.4 V *versus* RHE in N_2 -sparged 30% KOH at 80 °C. The powder to be tested is blended with PTFE (DuPont type 30 Teflon suspension) at about 10% by weight and heated to 275 °C, to try to achieve a suitable compromise between physical integrity and good electrolyte penetration. A pure gold mesh is used as the current collector and the electrode is suspended vertically in solution to prevent gas bubble occlusion of the surface. If the anodic

*See footnote p. 407.

current observed, after initiation of potentiostatic control, drops to the microamp range, the system is allowed to equilibrate overnight; the steady-state anodic current is then recorded. In a second stage of testing, candidate materials are subjected to higher potentials (1.6 V) representative of oxygen evolution conditions, and lower potentials (0.6 V) representative of oxygen reduction conditions. The latter is intended to place stress on the materials used in the oxide form.

The value of residual anodic current measured by these methods is not an unequivocal indicator of electrochemical stability. A low value of anodic current (*e.g.*, a few microamps/mg) is necessary, but not sufficient to demonstrate corrosion resistance, since the powder may passivate or delaminate from the current collector and exhibit a deceptive value. At the other extreme, a high current may represent the onset of oxygen evolution rather than corrosion, especially in the case of catalytic materials. Finally, the gold current collector always exhibits a base level of anodic current. Consequently, the anodic current values measured must be combined with other observations such as weight loss or gain, color changes, and microscopic examination.

Measurement of oxygen reduction/evolution performance

For determination of oxygen reduction/evolution performance, materials are tested in a floating electrode cell [2] in 30% KOH at 80 °C. An appropriate electrode is fabricated by blending the powder with PTFE (typically DuPont type 30 TFE suspension, in the range 15 - 60% by weight) and heating at temperatures from 300 - 360 °C. A gold-plated nickel mesh is used as the current collector. Generally, several iterations of electrode fabrication are necessary to achieve a Teflon-agglomerate structure with a suitable hydrophobic/hydrophilic balance. At this stage, a single structure is not always suitable for both modes of operation.

The polarization characteristics of such electrodes are established by measuring the steady-state current density (compensated for iR loss) at controlled potential steps, using the Dynamic Hydrogen Electrode (DHE [3]), as a reference (typically 2 - 4 mV negative of Reversible Hydrogen at 1 mA cm⁻²). The oxygen evolution measurements can be severely compromised by gas bubble occlusion of the horizontal electrode surface, however. Thus, efforts are currently underway to develop an integral electrolyte membrane suitable for these tests and more representative of a fuel cell operating configuration.

Results and discussion

Supports

Of the eight candidate supports evaluated, LaNiO₃, Material A and Material B remain as potentially suitable materials. B₄C, LaCrO₃, and Ba₅Nb₄O_{15-x} did not exhibit sufficient electrical conductivity to serve as

catalyst supports. Boron carbide in stoichiometric form is an insulator. A boron-deficient form was reported to be conductive and was used by General Electric investigators as a support for platinum [4]. Such material could not be obtained, but if it derived its conductivity from free carbon it would not be a suitable candidate in any event. Oxygen deficient barium niobate was also anticipated to be conductive. Most materials prepared, however, exhibited resistivities in the range of megohm cm, or, when significantly lower, showed evidence of residual carbon (used in the preparation). One preparation of LaCrO_3 , obtained by solid state reaction of La_2O_3 and black Cr_2O_3 (from thermally decomposed chromium oxalate), was considerably more conductive, but still unacceptable at about 1400 ohm cm.

The remaining candidate support materials all show high conductivity. The conductivities, in increasing order, are (ohm cm^{-1}): LaNiO_3 (5), TiC (50 - 200), Material B (125), NbN (300), Material A (390). In chemical testing of TiC, NbN, and Material A, after about 5 h in 45% KOH at 100 °C, none of the materials showed any signs of reaction, such as gassing or color change, and all retained high conductivity. In electrochemical testing, however, TiC and NbN gave evidence of reactions. A TiC electrode, for example, exhibited a high anodic current even at 1.0 V *versus* RHE, *e.g.*, about 12 $\mu\text{A mg}^{-1}$ after 22 h in 30% KOH at 80 °C. Post-test examination by scanning electron microscopy showed signs of changes in morphology also. NbN showed a very low anodic current at 1.4 V (0.1 $\mu\text{A mg}^{-1}$) but higher currents at 1.2 V *versus* RHE, suggesting passivation (*e.g.*, NbO_2 formation).

LaNiO_3 , Material A, and Material B appear to be stable at anodic potentials in 30% KOH at 80 °C. LaNiO_3 gave an anodic current of about 0.1 $\mu\text{A mg}^{-1}$ at 1.3 V but showed visible oxygen evolution at 1.4 V, since it is more catalytic than the other materials. At 1.4 V both materials A and B (40 μm powder) show about 0.2 $\mu\text{A mg}^{-1}$; it should be noted that the bare gold mesh current collector exhibits an anodic current of the same order of magnitude at 1.4 V. For a higher surface area preparation of Material A (1 - 3 μm powder) the anodic current measured was about 1 $\mu\text{A mg}^{-1}$ at 1.4 V *versus* RHE. This same electrode was then held at 1.5 V for 28 h. The anodic current was steady at 1.4 mA cm^{-2} (70 $\mu\text{A mg}^{-1}$); the value for 1 cm^2 of bare gold mesh was 1.62 mA. Finally, the electrode was held at 1.6 V for an additional 84 h. The anodic current was about the same as for bare gold mesh, about 90 - 100 mA cm^{-2} . Post-test examination of the electrode showed no weight loss or gain and no visible evidence of change.

Electrocatalysts

Electrical conductivity

Good electrical conductivity will be required for electrocatalysts that serve as both catalyst and electrode structure. For materials that may be

distributed as small particles on a highly conductive support, a much lower conductivity may be tolerated since each catalyst particle will only need to pass a very small current for a short distance. In anticipation of developing such a structure ultimately, some of the materials included in our present investigation are not highly conductive.

The base-metal/palladium oxides studied are examples of materials of lower conductivity; they exhibit a negative temperature coefficient of resistance characteristic of semiconductors. Lazarev and Shaplygin have reported the following resistivities: 3 - 15 ohm cm for PbPdO_2 [5], 300 - 900 ohm cm for Bi_2PdO_4 [6] and 2.1 ohm cm for CdPd_3O_4 [7]. CdPd_3O_4 and PbPdO_2 have been prepared with some success by co-precipitation of the metal salts and heating to about 500 °C. Both show broad line XRD patterns for the compounds with traces of the base metal oxide. Bi_2PdO_4 preparations have not been successful to date. The CdPd_3O_4 powder has a measured resistivity of 0.5 ohm cm, consistent with the range reported for this material. The PbPdO_2 , however, has shown quite high resistivity (megohm cm) in most preparation attempts, the best being about 112 k Ω cm.

The measured resistivity of $\text{Na}_x\text{Pt}_3\text{O}_4$ powders has also been quite variable. Shannon *et al.* [8, 9] have reported metallic conductivity for single crystal $\text{Na}_{1.0}\text{Pt}_3\text{O}_4$, e.g., 9×10^{-5} ohm cm. In our earliest attempts to prepare this material, resistivities of the powders (amorphous) were in the megohm range. In subsequent preparations (at $x = 1$), good conductivities were observed (1.4 - 164 ohm cm^{-1}) but analysis also showed 15 - 25% free Pt*. In the most recent preparations ($x = 0.8$, no free Pt), the conductivity is of the order of 50 ohm cm^{-1} .

Of the two pyrochlores to be studied, only the iridium compound has been prepared. The composition suggested is $\text{Pb}_2(\text{Ir}_{1.33}\text{Pb}_{0.67})\text{O}_{7-y}$ *. The measured conductivity of this powder was about 40 ohm cm^{-1} .

Corrosion testing

Most of the corrosion test data for electrocatalysts are considered preliminary because the electrochemical test data are not so readily interpreted for materials that catalyze oxygen evolution.

$\text{Na}_x\text{Pt}_3\text{O}_4$ showed visible oxygen evolution above 1250 mV *versus* RHE; the anodic current measured after 16 h at 1250 mV was 2.6 $\mu\text{A mg}^{-1}$. CdPd_3O_4 exhibited oxygen evolution above 1275 mV *versus* RHE; the anodic current measured after 15 h at this potential was about 3.5 $\mu\text{A mg}^{-1}$. PbPdO_2 has too low a conductivity for a practical test of the pure material.

The Pb-Ir pyrochlore showed substantial anodic current at 1.0 V *versus* RHE, about 23 $\mu\text{A mg}^{-1}$ after 21 h in 30% KOH at 80 °C. This current level increased slightly at 1200 mV (32 $\mu\text{A mg}^{-1}$) and at 1300 mV (50 $\mu\text{A mg}^{-1}$).

*See footnote p. 407.

At 1400 mV, there was visible oxygen evolution at a current density of about 57 mA cm^{-2} . Subsequently, the electrode was set at 600 mV *versus* RHE and held for 112 h. A low cathodic current was observed during this period ($0.5 \mu\text{A mg}^{-1}$ initially, $1.1 \mu\text{A mg}^{-1}$ finally) which may be attributed to oxygen impurity in the nitrogen. Subsequent measurement of the anodic current at potentials above 1.0 V showed about an order of magnitude decrease at all potentials. Post-test examination of the electrode sample revealed significant morphological changes, *e.g.*, gross cracking of the catalyst layer, shrinkage, and some delamination. These observations may account for the decreased anodic current levels in the final series of measurements.

Oxygen reduction/evolution performance

Reference materials

Three materials were chosen as points of reference for performance: 10% Pt supported on Vulcan XC-72 carbon and 10% Pt/Au for oxygen reduction, and NiCo_2O_4 for oxygen evolution. All of these are commercially prepared catalysts. The 10% Pt/C represents Giner, Inc. electrode technology as an internal baseline. The 10% Pt/Au has been used by United Technologies in alkaline fuel cells [10] and was intended to provide an external reference point; more development was required to achieve satisfactory performance with this material, therefore. The performance of both of these materials as oxygen reduction electrodes is shown in Fig. 1.

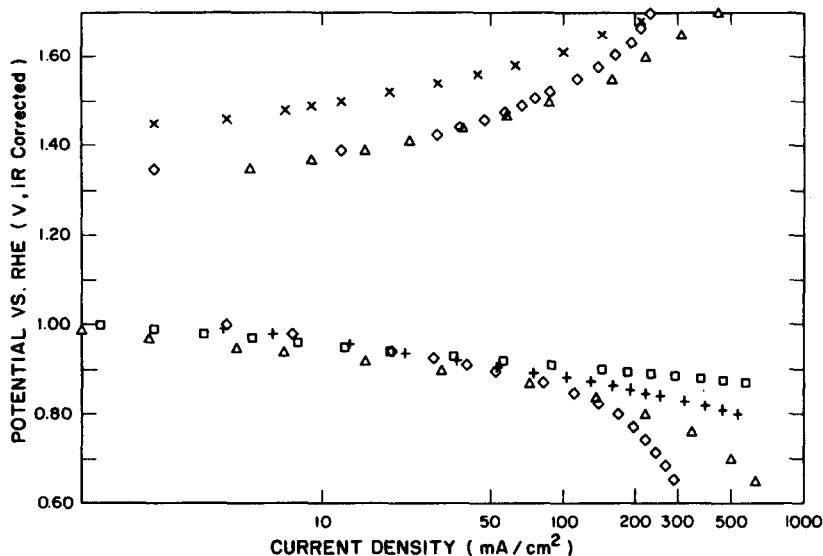


Fig. 1. Oxygen reduction/evolution in 30% KOH at 80 °C. □, 10% Pt/Au; △, $\text{Na}_x\text{Pt}_3\text{O}_4$; ◇, PbIrO_x ; +, 10% Pt/C; ×, NiCo_2O_4 .

NiCo_2O_4 purchased from Basic Volume Ltd. (CheMaterials, U.K.) has, to date, not exhibited performance levels described in the literature for this material as an oxygen evolution catalyst. Some progress has been made, however, and better performance is anticipated. The most recent performance obtained for NiCo_2O_4 is shown in Fig. 1.

Candidate catalysts

The CdPd_3O_4 preparation was tested for both oxygen reduction and oxygen evolution performance in 30% KOH at 80 °C. The results in either mode do not suggest the potential for significant catalytic activity, especially for oxygen reduction, *e.g.*, at a current density of 10 mA cm⁻² the electrode exhibited a reduction potential of about 0.6 V and an oxidation potential of about 1.5 V *versus* RHE.

The most conductive preparation of PbPdO_2 (112 k Ω cm) was still too resistive to make a practical electrode with the pure material. A sample of PbPdO_2 supported on carbon* was tested as an alternative method of evaluation. This material, as shown in Fig. 2, appears to show catalytic activity for oxygen reduction beyond the activity of carbon alone. This catalyst candidate material will be investigated further if it can be deposited successfully on a non-carbon support.

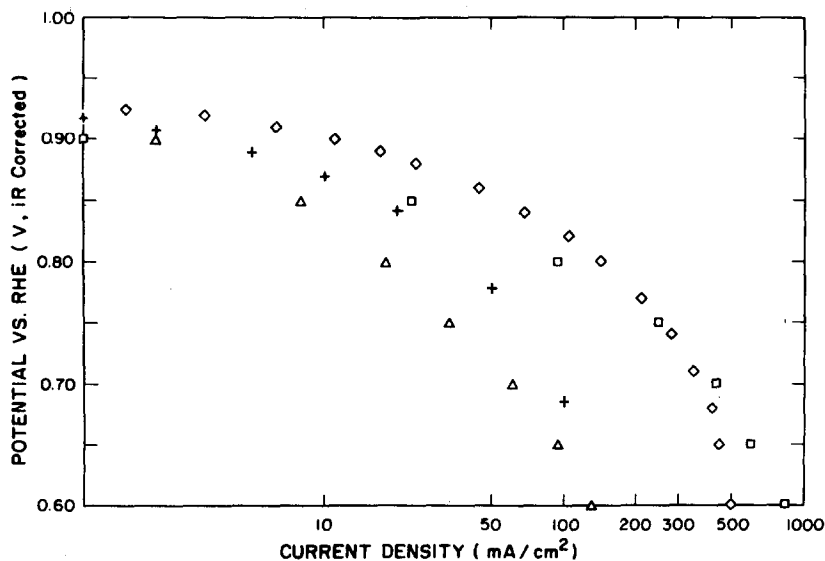


Fig. 2. Oxygen reduction in 30% KOH at 80 °C. □, PbPdO_2 on VXC72; ◇, CoTMPP on AKC; +, CoTMPP on VXC72; △, Vulcan XC-72 carbon.

*See footnote p. 407.

CoTMPP was prepared on carbon supports also, as a method of evaluation. The method described by Scherson *et al.* [11] was tried using Vulcan XC-72 carbon and a higher-surface-area carbon, Anthralur KC (Lurgi). The oxygen reduction performance, although better than carbon alone, did not approach the performance reported by Scherson. These results are shown in Fig. 2. An early attempt to deposit CoTMPP on a low-surface area, non-carbon support, Material A, was, at best, very non-uniform; X-ray dot mapping, for example, did not show evidence of cobalt. This approach will be pursued further with higher surface area, non-carbon supports.

$\text{Na}_x\text{Pt}_3\text{O}_4$ was prepared by solid state reaction of PtO_2 and Na_2CO_3 . The value of x was determined to be about 0.8*. The surface area and particle size obtained have not yet been determined. The bifunctional oxygen electrode performance, shown in Fig. 1, suggests that this material is suitable for further development.

The Pb-Ir pyrochlore preparation was based on a procedure described by Horowitz *et al.* for $\text{Pb}_2(\text{Ru}_{1-x}\text{Pb}_x)\text{O}_{7-y}$ [12]. After firing at 400 °C the material was still amorphous. Consequently, to determine the structure, a sample was fired at 500 °C for 2 h. X-ray diffraction analysis* gave broad lines for the pyrochlore pattern and a lattice parameter of $a = 10.396 \pm 6 \text{ \AA}$. The composition proposed is $\text{Pb}_2(\text{Ir}_{1.33}\text{Pb}_{0.67})\text{O}_{7-y}$. The original material (fired at 400 °C) was used to make electrodes for the testing described here. The bifunctional oxygen electrode performance, shown in Fig. 1, also suggests promise for further development. The corrosion test results described earlier may indicate some instability, however. Our initial approach will be to try a higher firing temperature, as used for the analytical sample.

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