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OXYGEN ELECTRODES FOR RECHARGEABLE ALKALINE FUEL CELLS — II

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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. Approximately six support materials and five catalyst materials have been identified to date for further development.

Introduction

Viable candidate materials for moderate temperature, single-unit, rechargeable alkaline fuel cells must meet the following requirements:

(i) good electrical conductivity (a more demanding requirement for supports than 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 requires 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.

Candidate support materials have been drawn from transition metal carbides, borides, nitrides (Ti, Zr, Hf, Nb) and oxides (La, Sr, Cr, Mo, W, Mn, Ni) that have high conductivity (> 1 Ω^{-1} cm^{-1}). Candidate catalyst materials have been selected largely from metal oxides of the form ABO_x (where A = Pb, Cd, Mn, Ti, Zr, La, Sr, Na, and B = Pt, Pd, Ir, Ru, Ni, Co) that, typically, have been investigated and/or developed for one function only, either O_2 reduction or O_2 evolution. The electrical conductivity requirement for catalysts may be lower, especially if integrated with a higher conductivity support. For initial evaluation, materials have been purchased when available; subsequently, in-house preparations have been attempted, to affect surface area and composition, if necessary.

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Candidate materials of acceptable conductivity are typically subjected to corrosion testing in three steps. Preliminary corrosion testing consists of exposure to 30% KOH at 80 °C under oxygen for about 5 days. Materials that survive chemical testing are examined for electrochemical corrosion activity: 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 μA mg^{-1} of material. For more stringent corrosion testing, and for further evaluation of electrocatalysts (which generally show significant O_2 evolution at 1.4 V), samples are held at 1.6 V or 0.6 V for about 100 h. The surviving materials are then physically and chemically analyzed for signs of degradation (visual examination, electron microscopy, X-ray diffraction).

To evaluate the bifunctional oxygen activity of candidate catalysts, Teflon-bonded electrodes are fabricated and tested in a floating electrode configuration [1]. Many of the experimental materials being studied have required development of a customized electrode fabrication procedure. 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, the goal is to reduce the polarization to about 300 - 350 mV.

Materials investigated

Candidate supports

$LaNiO_3$, $LiNiO_x$, NbO_2, MoO_2, WO_2, HfB, HfN, TiN, ZrN, ZrC.

Candidate electrocatalysts

$PbPdO_2$, $Pb_2(Ir_{2-x}Pb_x)O_{7-y}$, $Pb_2(Ru_{2-x}Pb_x)O_{7-y}$, $Na_xPt_3O_4$, $La_{0.5}Sr_{0.5}CoO_3$, $La_{0.5}Sr_{0.5}MnO_3$, $YBa_2Cu_3O_x$, $PtTi_{23}O_x$, $RuTi_{12}O_x$, $RuMn_{10}O_x$, $RuMn_2O_x$.

Reference materials

O_2 reduction: 10% Pt/Au (Johnson-Matthey, 11 m^2 g^{-1}); 10% Pt/ Vulcan XC-72 Carbon (Johnson-Matthey, Pt: 130 m^2 g^{-1}).

O_2 evolution: Pt black (Englehard, 25 m^2 g^{-1}).

Sources of candidate materials

Candidate materials for both catalysts and supports were purchased, if commercially available in powder form, as the most efficient approach for preliminary evaluation (electrical conductivity, chemical and electrochemical stability). Such materials offer the advantage of an economical purchase of a material of known purity in a quantity (5 - 25 g) sufficient for preliminary qualification, and particularly for disqualification. The disadvantage is that most of the commercially available materials have surface areas in the range from low (< 10 m^2 g^{-1}) to very low (< 1 m^2 g^{-1}).

Consequently, most commercial materials that survive preliminary screening must be prepared in a higher surface area form, in-house or by a custom fabricator, for effective evaluation as potential catalysts and/or supports.

In many cases, especially for candidate catalysts, commercial materials were not available. Preparation methods described in the literature, either specific for the material or as a general model, were used when deemed appropriate to the material requirements in terms of electrical conductivity, surface area, etc.

Characterization of candidate support materials

Candidate material preparations are typically analyzed by X-ray diffraction (XRD) for chemical characterization. The objective of preparing fine powder materials, however, is generally in conflict with obtaining sharp XRD patterns (because of the line-broadening characteristic of high surface area powders); thus the quality of these results is sometimes compromised. Firing materials for a longer time or at a higher temperature usually increases the crystallinity and improves XRD results, but at the expense of decreased surface area and some uncertainty about the composition of the higher surface area material. In some instances, materials of interest have been re-analyzed by XRD and/or scanning electron microscopy (SEM), after extended corrosion testing, to check for changes in composition, reaction products, and changes in morphology. SEM has also been used occasionally to observe the particle size range of powders.

The electrical conductivity of candidate materials is estimated by compressing a small volume (*e.g.*, 0.5 - 1 cm^3) of the powder at about 12 000 psi between metal pistons within an insulating cylinder; the resistance of the powder is measured directly, across the metal pistons, with an ohmmeter. If the resistivity thus measured is low (<5 Ω cm), the resistance is redetermined by measuring the voltage drop across the powder under the flow of sufficient current to generate easily measured current and voltage signals. The more accurate 4-point method of measuring resistance has not been used because of the larger sample volume requirement.

Surface areas of candidate materials are determined by the BET nitrogen adsorption method using a Micromeritics Flowsorb II 2300 instrument. The samples are typically outgassed at 150 °C in the vent stream of the instrument, or at ~ 100 °C under vacuum. All measurements reported have been made with 30% N_2 in He.

A summary of the measured physical characteristics of candidate materials is presented in Table 1. As a result of these measurements, the following materials were eliminated from further consideration due to *inadequate electrical conductivity*: NbO_2, $PtTi_{23}O_x$, $RuTi_{12}O_x$, $RuMn_{10}O_x$, and possibly $La_{0.5}Sr_{0.5}MnO_3$. The $La_{0.5}Sr_{0.5}CoO_3$ sample had a very low surface area but good electrical conductivity and thus remained a candidate for further testing. The $LiNiO_x$ sample had both low surface area and

TABLE 1

Physical characterization of candidate materials

Material	Source [Reference]	Surface area ($m^2 \, g^{-1}$)	Elect. conduct. ($\Omega \, cm^{-1}$)
$PbPdO_2$	Giner, Inc. #4	4	0.74
$Na_{0.8}Pt_3O_4$	Giner, Inc. #1 [5, 6]	21	50
	Giner, Inc. #2 [5, 6]	17	56
$Pb_2(Ir_{1.33}Pb_{0.67})O_{7-y}$	Giner, Inc. #1 (400 °C) [7]	24	40
$Pb_2(Ru_{1.35}Pb_{0.65})O_{7-y}$	Giner, Inc. #1 [8]	55	41
	Giner, Inc. #2 [8]	35	30
	Giner, Inc. #3 [8]	73	33
	Giner, Inc. #3 (400 °C) [8]	30	26
$PtTi_{23}O_x$	Giner, Inc. #1 [9]	79	(poor)
$RuTi_{12}O_x$	Giner, Inc. #1 [9]	73	(poor)
$RuMn_{10}O_x$	Giner, Inc. #1 [9]	38	(poor)
$RuMn_2O_x$	Giner, Inc. #1 [9]	62	2.9
$La_{0.5}Sr_{0.5}CoO_3$	CheMaterials (Basic Vol.)	0.1	105
$La_{0.5}Sr_{0.5}MnO_3$	CheMaterials	9	0.14
$YBa_2Cu_3O_x$	Duke University	0.04	1.3
$LaNiO_3$	CheMaterials	5	5 - 10
	Giner. Inc. #1 [2]	4	46 - 109
	Giner, Inc. #2 [3, 4]	6	(poor)
$LiNiO_x$	CheMaterials	0.8	0.4
NbO_2	Alfa Prod. (Morton-Thiokol)	N/M[a]	(poor)
MoO_2	Alfa Prod.	N/M	3.4
WO_2	Alfa Prod.	N/M	3.5
HfB	Aesar (Johnson-Matthey)	N/M	2.1
HfN	Aesar	N/M	1.7
ZrN	Alfa Prod.	0.3	91
ZrC (2% Hf)	Aesar	1	125
TiN	Alfa Prod.	N/M	390
	Giner, Inc.	2.3	440
	Univ. of California #2	56	0.34
	Univ. of California #3	38	N/M
	Univ. of California #5	21	14
Au/TiN	Giner, Inc./U. Calif. #3	51	0.37

[a]N/M = Not measured.

marginal conductivity; XRD analysis, however, indicated a second phase of lithium carbonate (which might be leached out), consequently, this material was also retained for further testing.

Stability testing

A preliminary assessment of the *chemical stability* of the candidate support materials is made by exposing the as-prepared powder to 30% KOH at 80 °C under an oxygen atmosphere. Indications of chemical reaction between the support material and the KOH are: color change of the solution or powder, evolution of gas, dissolution of the powder, weight change, and combinations of these phenomena. After exposure for up to 5 days, the remaining powder is filtered out and weighed to determine weight change, if any; small weight changes (*e.g.*, <5%) have an equal probability of being within experimental error for the measurement (weighing, filtering, washing, drying, weighing), and need to be evaluated in conjunction with other observations.

For an initial assessment of the *electrochemical 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 30% KOH at 80 °C. The powder to be tested is blended with polytetrafluoroethylene (PTFE, DuPont type 30 Teflon™* suspension) at about 10 - 20% by weight and heated to 275 - 325 °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 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 (~100 h), 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 electrochemical 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 (5 - 10 μA cm^{-2}). Consequently, the anodic current values measured must be combined with other observations such as weight loss or gain, color changes, microscopic examination (SEM, TEM) and analysis (EDAX, XRD, etc.).

Observations on chemical stability are summarized in Table 2. Electrochemical stability measurements are recorded in Tables 3 and 4.

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*TM - Teflon is a trademark of E.I. DuPont Corp.

TABLE 2

Results of stability tests of selected candidate materials

Material	Source [Reference]	Weight change (%)	Observations
$PbPdO_2$	Giner, Inc. #4	+0.7	NVR
$Na_{0.8}Pt_3O_4$	Giner, Inc. #1 [5, 6]	N/M	NVR
	Giner, Inc. #2 [5, 6]	N/M	NVR
$Pb_2(Ir_{1.33}Pb_{0.67})O_{7-y}$	Giner, Inc. #1 (400 °C) [7]	N/M	NVR
$Pb_2(Ru_{1.35}Pb_{0.65})O_{7-y}$	Giner, Inc. #1 [8]	N/M	SR-C
	Giner, Inc. #2 [8]	N/M	SR-C
	Giner, Inc. #3 [8]	−20	SR-C
	Giner, Inc. #3 (400 °C) [8]	N/M	NVR
$RuMn_2O_x$	Giner, Inc. #1 [9]	−14	SR-C
$La_{0.5}Sr_{0.5}CoO_3$	CheMaterials	−28	NVR
$La_{0.5}Sr_{0.5}MnO_3$	CheMaterials	−15	NVR
$YBa_2Cu_3O_x$	Duke University	N/M	SR-C
$LaNiO_3$	CheMaterials	N/M	NVR
	Giner, Inc. #1 [2]	−25	NVR
$LiNiO_x$	CheMaterials	−29	NVR
MoO_2	Alfa	N/M	NVR
WO_2	Alfa	N/M	NVR
HfB	Aesar	−100	D-C/G
HfN	Aesar	−100	D-C/G
ZrN	Alfa	−9	NVR
ZrC (2% Hf)	Aesar	N/M	SR-G
TiN	Alfa	N/M	NVR
	Giner, Inc.	N/M	NVR
	Univ. of California #2	N/M	SR-C

NVR: No Visible Reaction.
SR: Slight Reaction (C = Color, G = Gas).
D: Dissolved.
N/M: Not Measured.

Three candidate materials were eliminated from consideration due to evidence of *chemical instability* when the sample powders were exposed to KOH at 80 °C under O_2: HfB, HfN, and $YBa_2Cu_3O_x$. Two additional materials were eliminated due to *dissolution* during electrochemical stress testing at 1.6 V: MoO_2 and WO_2. As a result of these screening tests, the following materials remain as potential candidates for further investigation, and may be classified as follows:

Supports: TiN, ZrC, ZrN.

TABLE 3

Electrochemical stability measurements on selected candidate materials

Material	Source [Reference]	Anodic current ($\mu A\ mg^{-1}$) at 1.0 - 1.4 V (vs. RHE)				
		1.0	1.1	1.2	1.3	1.4
$Na_{0.8}Pt_3O_4$	Giner, Inc. #1 [5, 6]	1.5	1.0	1.3	2.3	800
$Pb_2(Ir_{1.33}Pb_{0.67})O_{7-y}$	Giner, Inc. #1 (400 °C) [7]	23	—	32	50	—
	Giner, Inc. #2 (500 °C) [7]	—	—	0.4	2.0	6.0
$Pb_2(Ru_{1.35}Pb_{0.65})O_{7-y}$	Giner, Inc. #1 [8]	—	1.1	4.9	530	2400
$RuMn_2O_x$	Giner, Inc. #1 [9]	—	—	4.0	—	600
$La_{0.5}Sr_{0.5}CoO_3$	CheMaterials	0.8	—	—	—	3.5
$LaNiO_3$	CheMaterials	—	—	—	0.1	18
	Giner, Inc. #1 [2]	—	—	—	—	0.9
$LiNiO_x$	CheMaterials	0.1	0.1	0.1	0.2	4.0
MoO_2	Alfa	16	—	—	—	0.7
		0.2	1.5	2.0	1.5	2.0
WO_2	Alfa	2.5	—	—	—	0.3
		—	—	—	—	0.4
		20	—	—	—	—
ZrN	Alfa	0.4	0.4	0.4	0.4	0.2
ZrC (2% Hf)	Aesar	0.5	1.1	1.2	0.7	0.7
TiN	Alfa	0.2	0.2	0.2	0.2	0.2
	Giner, Inc.	0.4	0.4	0.6	0.5	0.6
	Univ. of California #2	1.0	2.0	2.0	1.0	3.5
	Univ. of California #3	0.4	0.9	1.3	0.5	1.5
	Univ. of California #5	1.3	1.3	1.2	0.5	0.2

TABLE 4

Electrochemical stress tests on selected candidate materials

Material	Source [Reference]	Stress test (hours at 1.6, 0.6 V)		Observations (Wt. change)
		1.6 V	0.6 V	
$Na_{0.8}Pt_3O_4$	Giner, Inc. #1 [5, 6]	120	70	No signif. deterior.
$Pb_2(Ir_{1.33}Pb_{0.67})O_{7-y}$	Giner, Inc. #1 (400 °C) [7]		112	Cracking, shrinkage
	Giner, Inc. #2 (500 °C) [7]	24	72	Delamin. at 0.6 V
$Pb_2(Ru_{1.35}Pb_{0.65})O_{7-y}$	Giner, Inc. #1 [8]	50	2.5	Color in soln. (−40%)
$RuMn_2O_x$	Giner, Inc. #1 [9]	70		Color in soln. (−17%)
$La_{0.5}Sr_{0.5}CoO_3$	CheMaterials	64		NVR[a] (−7%)
$LaNiO_3$	CheMaterials	75	46	XRD-No evidence of react.
$LiNiO_x$	CheMaterials	114	3.5	Mat. loss (−72%)
MoO_2	Alfa	20		Delamin. at 1.6 V
		1		Dissolved at 1.6 V
WO_2	Alfa	48		Delamin. at 1.6 V
		37	6	Dissolved at 1.6 V
		(16 h at 1 V)		Dissolved at 1.0 V
ZrN	Alfa	169	17	No signif. deterior.
ZrC (2% Hf)	Aesar	48	17	Mat. loss (−38%)
TiN	Giner, Inc.	105		Surf. color change (0%)
	Univ. of California #3	46		Part. dissolved
	Univ. of California #5	3		XRD anal. K_2TiO_3? (+5%)

[a]No visible reaction.

Catalytic supports: $LaNiO_3$, $LiNiO_x$, $La_{0.5}Sr_{0.5}CoO_3$.

Electrocatalysts: $PbPdO_2$, $Na_{0.8}Pt_3O_4$, $Pb_2(Ir_{1.33}Pb_{0.67})O_{7-y}$, Pb_2-$(Ru_{1.35}Pb_{0.65})O_{7-y}$, $RuMn_2O_x$.

The following observations were made on these materials:

TiN. The coarse commercial powder (40 μm) and the low surface area Giner, Inc. preparation (1 μm, 2.3 m^2 g^{-1}) appeared to be quite stable up to 1.4 V *versus* RHE. The latter material, held at 1.6 V for more than 100 h, had a slight surface discoloration, but otherwise showed no evidence of reaction (*e.g.*, no weight change). Post-test XRD analysis indicated a strong TiN pattern ($a = 4.240$ Å), no TiO_2, and a few lines possibly due to a silicate, phosphate or carbonate.

The higher surface area material (TiN_x, Univ. of Calif.), similarly, appeared relatively stable in the chemical test (very small amount of white floc visible, quantitative weight change measurement not successful), and anodically up to 1.4 V. Post-test XRD analysis showed a strong TiN pattern and three additional lines that might be attributed to a phase such as potassium titanate. When the electrode was held at 1.6 V, however, the material was largely lost, apparently by dissolution. A gold-catalyzed TiN electrode was also found to be very reactive. After electrochemical testing, the surface of the electrode had degraded to a refractory, non-conductive material. Post-test XRD analysis again showed a second phase (much stronger) consistent with the first analysis (potassium titanate?). Based on these results, it appears that the non-stoichiometric TiN_x ($x = 0.72$ - 0.86), although promising in terms of the high surface area achieved, is unstable at anodic potentials. Based on other results, TiN remains a candidate support material under investigation.

ZrC. The commercially available material was a coarse (40 μm), low surface area powder with about 2% Hf impurity. During the initial period of the chemical stability test, gassing was observed; this was attributed to dissolution of the Hf impurity (weight change measurements were not successful). In three repetitions of electrochemical testing, the anodic currents measured at 1.4 V were very low, 0.2 - 0.7 μA mg^{-1}, equivalent to the background current measured on the gold current collector. In testing at 1.6 V *versus* RHE from 50 to 100 h, there was a visible loss of material, as well as a measurable weight loss (*e.g.*, ~40%), but this could not be distinguished from physical shedding during oxygen evolution, and there was no other evidence of reaction. This material remains a potential candidate support under development with emphasis on higher surface area preparations.

ZrN. The commercially available material, a coarse, low surface area powder, also appeared to be fairly inert in all stability tests. A weight loss

of about 9% was recorded for a 14-day chemical exposure test. The anodic current at 1.4 V was at a background level (0.2 μA mg^{-1}) and there were no signs of degradation after a week of oxygen evolution (1.6 V in 30% KOH at 80 °C). This material also remains under development, primarily to produce high surface area powder.

LaNiO$_3$. The commercial material has proven to be quite stable in all corrosion testing. Since LaNiO$_3$ is also catalytic [2] oxygen evolution currents were measured at 1.4 V *versus* RHE. After extended testing at 1.6 V and 0.6 V, XRD analysis still indicated a strong, unchanged pattern for LaNiO$_3$. Attempts to prepare materials with surface areas greater than ~ 5 m^2 g^{-1} have been unsuccessful to date.

LiNiO$_x$. XRD analysis of the commercial sample (labeled "LiNiO$_2$") indicates a strong second phase of lithium carbonate. This may account for the weight loss recorded in chemical testing. It is anticipated that a more-well-defined material will be stable, somewhat catalytic, and a potential support material. Higher surface area in-house preparations will be investigated.

La$_{0.5}$Sr$_{0.5}$CoO$_3$. This commercial compound was quite conductive but very low in surface area. It showed a 28% weight loss in the chemical test but did not appear to be reactive (or very catalytic) at anodic potentials. Higher surface area preparations will be attempted for further investigation as a support.

PbPdO$_2$. The classical preparations of this material, by high temperature firing of the mixed oxides [10] or hydroxide co-precipitates, have generally resulted in fairly non-conductive powders [11], limiting our ability to evaluate the material. It remains of interest because it has shown catalytic activity on a carbon support [11]. A recent preparation by a novel method has yielded a quite conductive material with the correct XRD pattern for PbPdO$_2$. In the limited chemical test performed to date, the material showed no weight change or other signs of reaction, and will be investigated further.

Na$_{0.8}$Pt$_3$O$_4$. Prepared at Giner, Inc. (Batch #1), this compound had moderately high surface area and good conductivity. After 17 days of corrosion testing, primarily at 1.6 V *versus* RHE, there were no signs of degradation or changes in appearance (no XRD data) and the electrode showed a similar level of anodic polarization at 200 mA cm^{-2} (~ 400 mV) as that of a freshly-prepared electrode (~ 385 mV). This material continues to show promise as a bifunctional oxygen electrode catalyst, as discussed in the next section.

Pb$_2$(Ir$_{1.33}$Pb$_{0.67}$)O$_{7-y}$. In our initial investigation of this material [11] it was found to be unstable in 30% KOH at 80 °C (*e.g.*, 23 μA mg^{-1}

at 1.0 V *versus* RHE); at 1.6 V, the material showed substantial physical changes. More recently, this same material was refired at 500 °C. This had the effect of improving its crystallinity and decreasing its reactivity below 1.4 V. The test electrode survived 24 h at 1.6 V, but delaminated from the current collector at 0.6 V. It is anticipated that this material will be prepared in different compositions and by alternative methods for further investigation.

$Pb_2(Ru_{1.35}Pb_{0.65})O_{7-y}$. This material, prepared in several batches by a method [8] different from that of the Pb–Ir pyrochlore above, was obtained in a crystalline form at low temperature. The resulting materials, however, were unstable under most test conditions, as evidenced by yellow coloration of all test solutions. Heat treating the 3rd batch of this compound at 400 °C resulted in a substantial reduction in surface area ($73 \rightarrow 30$ m^2 g^{-1}) and stabilized the compound in the chemical test (no coloration of the solution). This material is under active investigation.

$RuMn_2O_x$. This material, to date, has been subjected to very limited investigation; it shows evidence of instability similar to that observed for the Ru pyrochlore discussed above. Efforts are now concentrated on stabilizing this catalyst by thermal treatments and alternative preparations.

Oxygen electrode performance testing

Oxygen electrode performance testing is implemented in a floating electrode cell [1] in 30% KOH at 80 °C using a 1 cm × 1 cm electrode sample. Pure oxygen is fed to the cell through a water presaturator. To fabricate a test electrode, a powder sample is blended with PTFE (DuPont type 30 Teflon suspension) in the range 15 - 40% by weight, as an approximate function of surface area. The Teflon catalyst blend is then applied to a gold-plated Ni mesh with a porous Teflon backing (1 μm pores), dried, and thermally processed at 330 - 360 °C. It is frequently necessary to try other Teflon-catalyst compositions and fabrication procedures to achieve an adequate balance in the hydrophobic/hydrophilic properties of the electrode.

The testing sequence is usually an oxygen reduction polarization test followed by an oxygen evolution polarization test, applying small potential steps sufficient to yield a few data points in each log-decade of current density from 1 to 1000 mA cm^{-2}. The potentials are controlled and compensated for *IR* loss with a Princeton Applied Research model 173 potentiostat. Collecting oxygen evolution data entails frequent interruptions to remove trapped gas bubbles. After an oxygen evolution test, electrodes are sometimes too flooded to re-run an oxygen reduction test. Development of an electrode structure adequate for bifunctional operation with these candidate electrocatalysts is an independent research task; some
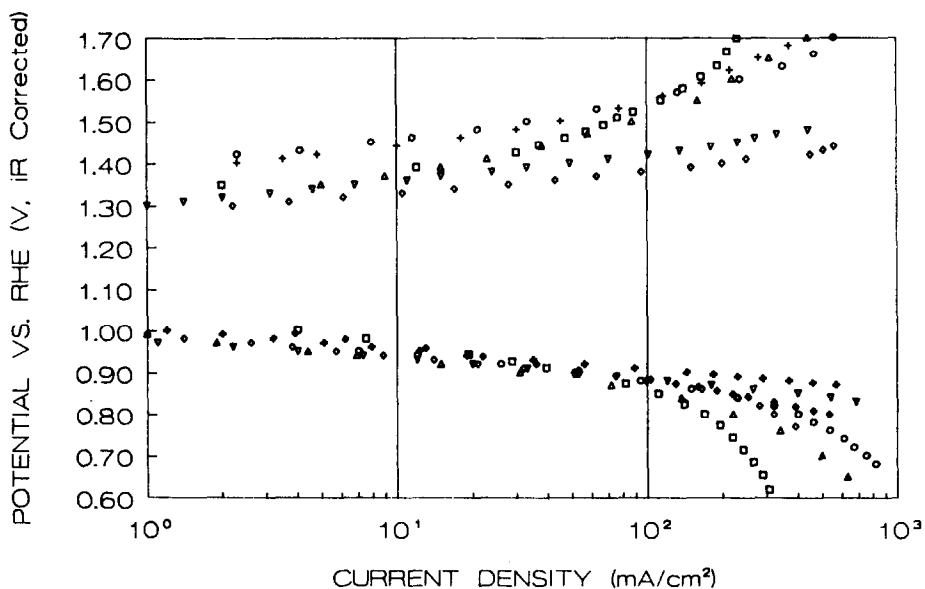
Fig. 1. Bifunctional oxygen catalyst performance in 30% KOH at 80 °C. ✦, 10% Pt/Au (15 mg cm^{-2}); +, Pt black (10 mg cm^{-2}); ◆, 10% Pt/C (1 mg Pt cm^{-2}); ◇, RuMnO$_x$, #1 (26 mg cm^{-2}); □, PbIrO$_x$ (19 mg cm^{-2}); ○, PbRuO$_x$ (20 mg cm^{-2}); △, Na$_{0.8}$Pt$_3$O$_4$, #1 (20 mg cm^{-2}); ▽, Na$_{0.8}$Pt$_3$O$_4$, #2 (20 mg cm^{-2}).

experience, gained in the development of Pt black bifunctional hydrogen electrodes, will be beneficial to this effort.

The best performance data for each of the catalysts, as well as data for the reference materials (10% Pt/Au, 10% Pt/C and Pt black), are shown in Fig. 1. The following observations were recorded:

$RuMn_2O_x$. This compound exhibited exceptional oxygen evolution performance and moderate oxygen reduction performance in the limited testing performed to date. Unfortunately, this batch of material was not stable, as evidenced by the reddish coloration of the test solutions in this test and in the earlier corrosion tests. We are currently investigating methods of stabilizing this catalyst by thermal treatment and/or doping.

$Pb_2(Ir_{1.33}Pb_{0.67})O_{7-y}$. The material (fired at 400 °C) gave a good performance at lower current densities for both oxygen reduction and evolution, but polarized rapidly above 100 mA cm^{-2}, suggesting a poor electrode structure. This preparation was also unstable, as discussed under stability testing. The sample refired at 500 °C was corrosion tested but not performance tested. Further preparation and testing of this catalyst is planned.

$Pb_2(Ru_{1.35}Pb_{0.65})O_{7-y}$. This material, prepared by a low temperature process [8], showed from good (Batch #1) to exceptional (Batch #3)
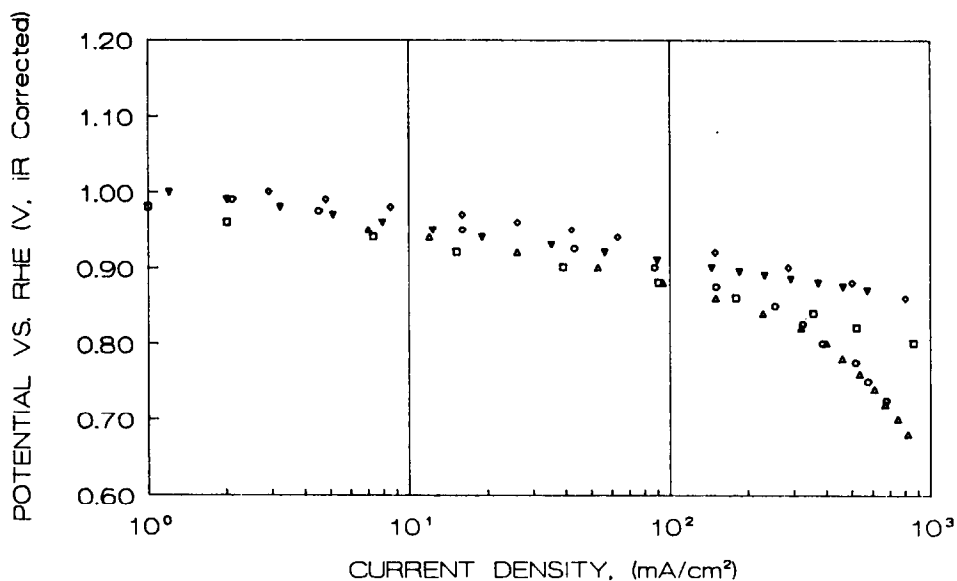
Fig. 2. Oxygen reduction performance of lead ruthenate preparations in 30% KOH at 80 °C: ▼, 10% Pt/Au; △, PbRuO$_x$ #1; ○, PbRuO$_x$ #2; ◇, PbRuO$_x$ #3; □, PbRuO$_x$ #3, 400 °C.

activity for oxygen reduction, as presented in Fig. 2. All of these preparations were unstable in KOH, however. Post-thermal treatment at 400 °C (Batch #3) stabilized the material, but resulted in a loss in performance coincident with the loss in surface area. Oxygen evolution performance was generally very poor with the exception of Batch #1, as shown in Fig. 1. Performance of all materials was typically transient and non-reproducible. This catalyst is still under investigation with emphasis on stability and oxygen evolution performance.

$Na_{0.8}Pt_3O_4$. Performance data for two separate preparations of this catalyst are shown in Fig. 1. The data for Batch #2 are the more recent and represent improvements in electrode structure as well. This material is the best candidate bifunctional oxygen electrode catalyst developed to date in terms of both stability and oxygen reduction/evolution performance. The emphasis in further development is on increasing the surface area and preparing larger quantities of material. Deposition on a support will also be attempted when a suitable, stable, high surface area support material has been developed.

Au/TiN_x. Gold was deposited on the high surface area TiN_x, by a Giner, Inc. proprietary process, to investigate the feasibility of catalyzing this support. The surface area was increased from about 38 m^2 g^{-1} to 51

$m^2 \ g^{-1}$, indicating an average particle size of about 25 nm. Electron microscopic examination of this material at NASA by Dr William Fielder indicated the presence of particles in this range as well as larger agglomerates of particles. The material could not be tested electrochemically because of the instability of the TiN_x, as discussed above, but the potential feasibility of catalyst deposition on this novel support is indicated.

Acknowledgements

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