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AN OXYGEN ELECTRODE BASED ON NICKEL/COBALT SPINEL, (U)
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by

William A. Armstrong



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REPORT NO. 845

AN OXYGEN ELECTRODE BASED ON NICKEL/COBALT SPINEL

by

William A. Armstrong
Energy Systems Section
Energy Conversion Division

**PROJECT NO.
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ABSTRACT

It has been demonstrated that nickel/cobalt spinel, NiCo_2O_4 , can be prepared simply and inexpensively by the thermal decomposition of cobalt nitrate on sintered nickel plaque. Electrodes suitable for use in metal/air batteries and fuel cells have been developed which will reduce oxygen from the air at room temperature and a current density of $50\text{mA}/\text{cm}^2$ for more than a year. A modification of this electrode will perform satisfactorily for more than 200 cycles of oxygen reduction/oxygen evolution at $50\text{mA}/\text{cm}^2$.

RÉSUMÉ

On a démontré la formation de l'oxyde mixte de cadmium et de nickel du type "spinelle" par la décomposition thermique du nitrate de cadmium se déposé sur une plaque poreuse de nickel. Nous avons mis au point une électrode propre à être utilisée dans une pile à combustible ou un générateur métal/air avec la capacité pour la réduction de l'oxygène de l'air en utilisant un courant d'une densité de $50\text{mA}/\text{cm}^2$ pendant plus d'une année. Une modification de cette électrode s'était subie à plus de 200 cycles composés d'une période de la réduction de l'oxygène suivie par une période de l'évolution de l'oxygène à $50\text{mA}/\text{cm}^2$.

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INTRODUCTION

The oxygen electrode is a critical component in a number of devices which generate electrical power. In fuel cells and metal/air batteries oxygen, either pure or from the air, is electrochemically reduced at the oxygen electrode as part of the process which generates electricity. When a metal/air battery is electrically recharged or an electrolyzer is used to generate hydrogen, oxygen is evolved at the oxygen electrode. A critical problem is the effectiveness and duration of life of the electrocatalyst which promotes these reactions.

Electrodes prepared by impregnating sintered nickel plaques with silver or silver oxide catalysts have operated for more than 1000 hrs in the oxygen reduction mode (1) but have failed after about 40 cycles of oxygen reduction/oxygen evolution (2). Most carbon catalysts and platinum are also destroyed on cycling (3).

Metal oxide catalysts of the spinel or perovskite structure offer the possibility of high catalytic activity and extended life under a variety of operating conditions. Tseung and co-workers (4,5) have shown that perovskite oxide electrodes prepared by doping LaCoO_3 with strontium perform better than platinum black at 170°C but are limited to very low current densities ($\sim 2\text{mA}/\text{cm}^2$) at room temperature. A large number of semiconducting oxides have been compared in terms of electrical conductivity, resistance to corrosion and catalytic activity for both oxygen reduction and evolution. The results suggested that the nickel/cobalt spinel, NiCo_2O_4 , was worthy of further study (6).

A variety of methods have been developed for the preparation of NiCo_2O_4 . These include thermal decomposition of the mixed nitrates, coprecipitation by the addition of mixed nitrate solution to either hot potassium hydroxide or ammonium oxalate followed by heat treatment and a cryochemical method (7) which consists of spraying a solution of the mixed nitrates into liquid nitrogen followed by vacuum sublimation and heat treatment. All of these procedures result in a powdery product which must be mixed with a binder and pressed onto a current collector.

In our previous studies on the preparation of oxygen electrodes we concluded that the catalyst should be in intimate contact with the substrate or the current collector and that the formation of a catalyst directly on a substrate gave a better electrode than the pressing together of a catalyst powder and binder. The present investigation was undertaken to develop a simple method of preparing more effective electrodes catalyzed with NiCo_2O_4 for use in metal/air batteries, fuel cells and electrolyzers.

EXPERIMENTAL

MATERIALS

Sintered nickel plaque of the type commonly employed in Ni/Cd batteries was used as the substrate. Electrodes 3.18 x 3.18 cm square with a 1.27 x 1.27 cm tab extending from one corner were cut from this plaque which was 0.071 cm thick, contained a nickel screen current collector and had a porosity of 84.7%. Each piece of plaque was cleaned thoroughly prior to impregnation by first soaking in trichloroethylene for ten minutes to remove any grease and then rinsing in methanol to remove the trichloroethylene. After drying at room temperature surface oxides were removed by covering the plaque with a dilute solution of nitric acid (20 ml of conc. HNO_3 diluted to 100 ml with distilled water) for 2 min., washing in flowing distilled water for 15 minutes, draining and drying in an oven at 125°C for not more than 10 minutes. Plaques were impregnated immediately following this cleaning procedure.

Reagent grade nickel nitrate hexahydrate and/or cobalt nitrate hexahydrate were dissolved in distilled water to make up the impregnation solutions. A polytetrafluoroethylene (PTFE) suspension, Teflon 30, was employed for wet-proofing and the PTFE semi-permeable membrane applied to the air side of the electrode was Zitex E606-223. Potassium hydroxide electrolyte of the desired concentration (6.2M unless otherwise stated) was prepared by the dilution of "Certified" 45% W/W potassium hydroxide with distilled water.

ELECTRODE PREPARATION

The basic method of preparation was as follows:

- (a) A clean piece of Ni plaque was immersed in the catalyst impregnation solution.
- (b) The plaque was drained, partially dried over a hot plate and left to dry for a predetermined time in an oven at 125°C.

- (c) The dry impregnated plaque was heat treated for a set time in a furnace at a given temperature.
- (d) If the catalyst impregnation solution did not contain suspended PTFE, the plaque was first washed in flowing distilled water for 10 minutes, drained, dried in an oven at 125°C for 10 minutes and then immersed in a PTFE suspension of the desired concentration. The plaque was drained, dried in an oven at 125°C for 1 hour and then placed on a hot plate at 250°C for 3 min.
- (e) One side of the electrode was covered with a piece of semi-permeable PTFE membrane, which was pressed onto the electrode at 125°C and 112 kg/cm².

With this procedure, the composition of the catalyst impregnation solution, the drying time at 125°C, the temperature and duration of the heat treatment and the amount of wet-proofing could all be varied.

In a variation of this basic method of preparation the composition of the side of the electrode next to the electrolyte was controlled by blocking this side of the electrode with a PTFE film (Zitex) during critical steps of the electrode preparation (2). Using this technique it was possible to prepare an electrode having a hydrophilic catalyzed layer of nickel next to the electrolyte at which the oxygen evolution reaction could take place whereas the hydrophobic interior of the catalyzed plaque provided the active sites for oxygen reduction.

ELECTRODE EVALUATION

Electrodes were mounted as previously described (8) and operated in a half-cell with a piece of nickel screen as the counter electrode. The potential of the oxygen electrode was measured with respect to a mercury/mercuric oxide reference equipped with a Luggin capillary. The electrode to be evaluated was first driven in the discharge mode (oxygen reduction) with the impressed current being increased from 0 to 100 mA/cm² over a period of 1 hour. For cycling experiments the current density was reduced to 50 mA/cm² and a regime initiated consisting of 2 hours of oxygen reduction followed by 4 hours of oxygen evolution with a 10 min period on open circuit between each current reversal. The electrolyte was replaced with fresh solution once a week.

RESULTS AND DISCUSSION

FORMATION OF Ni/Co SPINEL

Initial attempts to form the NiCo_2O_4 spinel were made by impregnating the nickel plaque with an aqueous solution of the mixed nickel and cobalt nitrates and then subjecting the plaque to a heat treatment. Electrodes prepared from this plaque gave encouraging results. In one experiment only cobalt nitrate was used in the impregnation solution and the resulting electrode performed in much the same way as one impregnated with the mixed nitrates (Fig. 1). In order to determine whether the nickel/ cobalt spinel was formed in either or both of these cases, x-ray diffraction studies were arranged.

Samples were prepared by impregnating one piece of plaque with a solution of the mixed nitrates and a second with a solution containing cobalt nitrate in the same concentration as in the mixed solution. Both plaques were dried overnight in an oven at 125°C and then placed in a furnace at 250°C for four hours. Surface material was scraped from each plaque and x-ray diffraction patterns were examined. As expected most of the material was nickel but in each case a mixed Ni-Co oxide with lattice parameters corresponding to NiCo_2O_4 was detected. One extra line was found which could not be identified. It did not conform to any known oxide of nickel or cobalt. From this analysis it was concluded that NiCo_2O_4 can be formed by thermally decomposing cobalt nitrate on sintered nickel plaques. All further electrodes were prepared in this manner.

TWO STEP PROCESS

At the beginning of the investigation electrodes were prepared by a two step process. During the first step the nickel/cobalt spinel was formed

on the plaque and the effects on electrode performance of the concentration of cobalt nitrate in the impregnation solution, the duration of the drying period at 125°C and the duration and temperature of thermal decomposition were investigated. In the wet-proofing step only the concentration of the PTFE was varied, this process having been thoroughly investigated previously (8).

The results, recorded in Table I, are average values obtained from two or more electrodes. Provided the nickel plaque was well cleaned and impregnated immediately after cleaning, good reproducibility was obtained.

Certain trends are evident, particularly with respect to the performance of the electrodes during oxygen reduction. The duration of the drying time is important which conforms to the findings of Tseung and King (9) that mixtures of nickel and cobalt oxides must be very dry in order to form the spinel on heating. It is also clear that temperatures greater than 250°C have deleterious effects on electrode performance. The effects of catalyst and PTFE concentrations are not as pronounced.

A number of electrodes were prepared using a 20h drying period at 125°C followed by 4h of thermal decomposition at 250°C, the conditions judged most suitable based on the results in Table I. Only the concentration of PTFE in the wet-proofing solution were varied. These electrodes were subjected to cycles consisting of 2h of oxygen reduction followed by 4h of oxygen evolution each at a current density of 50mA/cm². Cycling was terminated when the electrode potential became more negative than -200mV with respect to the mercury/mercuric oxide reference electrode during oxygen reduction.

The results (Table II) show that the electrode life varied from 5 to 26 cycles with no simple dependence on the parameters which had been varied.

ONE STEP PROCESS

Although the results obtained with the two step process, i.e. separate steps for impregnation with catalyst and wet-proofing, were encouraging the limiting current density for oxygen reduction and the cycle life were too low for most applications. During a previous investigation (8) on the introduction of a manganese dioxide catalyst into a porous nickel plaque, it was found that combining the catalyst impregnation and wet-proofing steps into a single process resulted in a more reactive electrode. The same technique was attempted in the present investigation. Concentration of cobalt nitrate and PTFE in the single impregnation solution, drying time at 125°C along with the temperature and duration of thermal

TABLE I

Performance of Nickel/Cobalt Spinel Electrodes
Prepared by the Two-Step Process

Electrode Number	[Co(NO ₃) ₂ ·6H ₂ O] (mg/ml)	Drying at 125°C (h)	Temp & Duration Thermal Decomp. (°C) (h)	[PTFE] (mg/ml)	Potential* on O ₂ Reduction at Various CD's		Potential* on O ₂ Evolution at Various CD's	
					26	53	26	53
1	600	1	250 4	79	-96	-168	622	635
2	600	4	250 4	79	83	135	625	642
3	600	20	250 4	79	81	135	618	630
4	600	20	250 2	79	86	138	628	655
5	600	20	250 4	102	82	131	625	635
6	600	20	250 4	54	93	150	622	638
7	600	1	350 4	79	149	257	632	640
8	800	20	250 4	79	68	129	610	628
9	800	20	250 4	102	96	166	630	645

*v.r.t. to Hg/HgO Ref.

TABLE II

OXYGEN REDUCTION/OXYGEN EVOLUTION CYCLING OF ELECTRODES
PREPARED BY THE TWO-STEP PROCESS

[Co(NO ₃) ₂ ·6H ₂ O] (mg/ml)	[PTE] in wet proofing Soln (mg/ml)	Potential w.r.t. Hg/HgO Ref on O ₂ reduction at 50mA/cm ² cycle (mV)	Potential w.r.t. Hg/HgO Ref on O ₂ evolution at 50 mA/cm ² (mV)	Number of Cycles*
600	79	-155	644	5
800	79	155	658	22
800	144	155	651	9
1000	54	158	635	26
1000	79	159	640	20
1000	144	156	627	22

*Cycling stopped when electrode potential during oxygen reduction became more negative than -200 mV with respect to the Hg/HgO reference electrode.

decomposition were varied. The results are listed in Table III and a comparison of the performance of the electrodes prepared by the one and two step processes is illustrated in Fig. 2.

In all cases the electrodes prepared by the one step method exhibited lower polarization during oxygen reduction than similar electrodes prepared by the two step method. With oxygen evolution there was not such a distinct difference. Once again the importance of a long drying period before thermal decomposition was demonstrated as were the negative effects of thermal decomposition at 350°C.

Electrode No. 10, Table III exhibited the best performance of any electrode during oxygen evolution. This electrode was prepared using an impregnation solution containing 800mg/ml $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 130 mg/ml PTFE; was dried for 20h at 125°C and cured for 4h at 250°C. Based on the increase in weight of the plaque and the composition of the impregnation solutions it was calculated that the electrode contained 18 mg/cm² NiCo_2O_4 and 7 mg/cm² PTFE.

Electrodes prepared in an identical way to No. 10, Table III were driven in the oxygen reduction mode continuously at a current density of either 53 mA/cm² or 106 mA/cm². Figure 3 shows that an operational lifetime of more than a year at 53 mA/cm² was obtained. This is about eight times as long as the best electrode previously developed at DREO (1). At 106 mA/cm² the life was shortened to about 1300h and increasing the concentration of PTFE in the impregnation solution from 130 mg/ml to 173 mg/ml had little effect on performance at this current density.

Another electrode prepared in an identical manner to No. 10 was subjected to the cycle regime described in the preceding section. The performance on oxygen reduction decreased as the cycling continued from an initial potential of -93mV with respect to the Hg/HgO reference to -120mV after 25 cycles, -133mV after 50 cycles, -147mV after 100 cycles and -200mV at 129 cycles. During this period the performance on oxygen evolution improved somewhat from an initial potential of 632mV to a final value of 584mV.

The results can be explained by a loss of hydrophobicity by the electrode. When a new electrode was removed from the electrolyte solution it was observed that the electrolyte drained off almost completely but that after a number of cycles the electrode remained wet. The electrochemical reduction of oxygen takes place only at catalytic sites at a three-phase boundary and, therefore, requires a fairly hydrophobic electrode surface. During oxygen evolution, however, only the surfaces of solid catalytic particles in contact with the electrolyte will be active. Thus the reactivity for oxygen evolution increase as the surface of the electrode becomes less hydrophobic.

As electrodes had been driven in the oxygen reduction mode for several thousands of hours without undue loss of hydrophobicity (Fig. 3) it was assumed that oxygen evolution played the major role in reducing the water repellency of the electrode.

TABLE III

PERFORMANCE OF NICKEL-COBALT SPINEL ELECTRODES PREPARED BY THE ONE STEP PROCESS

Electrode Number	$(\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ (mg/ml)	PTFE (mg/ml)	Drying at 125°C (h)	Temp and Duration of Thermal Decomp. (°C) (h)	Potential on O_2 Reduction at Various CDs (mV)			Potential on O_2 Evolution at Various CDs (mV)		
					26	53	106mA/cm ²	26	53	106mA/cm ²
1	600	86	1	200	4	-84	-128	-217	612	700
2	600	86	1	250	4	74	87	127	618	685
3	600	86	1	300	4	67	96	128	620	655
4	600	86	1	350	4	131	195	-	610	650
5	600	86	20	250	4	63	83	114	612	658
6	600	130	20	250	4	55	80	131	606	660
7	600	173	20	250	4	62	86	129	605	646
8	800	86	1	250	4	56	77	128	612	655
9	800	86	20	250	4	56	76	116	610	652
10	800	130	20	250	4	46	62	88	605	659
11	800	173	20	250	4	50	67	95	614	648
12	800	259	20	250	4	56	77	115	610	642

*w.r.t. Hg/HgO Ref

Following this line of reasoning, it was decided to prepare an electrode in such a manner that a thin layer of the catalyzed nickel plaque next to the electrolyte would be hydrophilic while the interior of the electrode would be hydrophobic. It was predicted that oxygen evolution would take place almost entirely on the hydrophilic surface with a minimum of disruption to the hydrophobicity of the main back of the electrode where the reduction of oxygen would occur.

The method for preparing this type of electrode is similar to one described previously (2). The clean nickel plaque was dipped in an aqueous solution containing 800 mg/ml of cobalt nitrate hexahydrate, drained, dried overnight in an oven at 125°C and then transferred to a furnace at 250°C where it was left for 2 hours. A piece of Zitex was cold-pressed to one side of the plaque and a solution containing 800 mg/ml of cobalt nitrate hexahydrate and 130 mg/ml PTFE was added drop-wise to the bare side of the plaque until the plaque was saturated. Then it was drained, dried in an oven at 125°C for 1h, the Zitex removed and the plaque placed in a furnace at 250°C for 3h. This resulted in an electrode catalyzed evenly throughout with nickel/cobalt oxide but wet-proofed with PTFE on only one side. The wet-proofed side was covered with a piece of Zitex membrane which was pressed onto the electrode at 125°C and 112 kg/cm².

The performance of this electrode (Fig. 4) was such that 240 cycles were obtained, nearly double the life of the electrode uniformly wet-proofed. Increasing the concentration of PTFE in the second impregnation solution from 130 mg/ml to 173 mg/ml resulted in an electrode with a slightly reduced cycle life (192 cycles).

EFFECT OF KOH CONCENTRATION ON PERFORMANCE

In all the evaluations described in previous sections of this report, the electrolyte was 6.2M KOH, the concentration commonly used in zinc/air batteries. Small changes in concentration had not been observed previously to affect significantly the performance of oxygen electrodes catalyzed with oxides of silver or manganese but were found to cause changes in the operating potential of the NiCo_2O_4 spinel electrode. In Figure 5 the effects of KOH concentration on the potential during oxygen reduction of an electrode prepared in the same manner as No. 10, Table III are plotted for a number of current densities. Over the range of concentrations studied (3.9M - 7.4M KOH) a significant increase in electrode polarization with increasing KOH concentration was observed at all current densities but was more pronounced at the higher currents. This increase cannot be attributed to changes in the resistivity of the electrolyte because the resistivity of the 3.9M KOH was somewhat greater, not less, than that of the solution of higher KOH concentration (10).

In a battery or fuel cell system the choice of electrolyte concentration would also be influenced by the minimum operating temperature required by the application. The minimum freezing point of -60°C occurs at a KOH concentration of 5.8M and the freezing point of a 3.9M solution is about -30°C (10). Other factors such as the effect of electrolyte concentration on the performance of the other electrode and the operational life of the separator material would have to be considered when choosing the optimum electrolyte composition.

CONCLUSIONS

1. Nickel/cobalt spinel, NiCo_2O_4 , can be prepared simply and inexpensively by the thermal decomposition of cobalt nitrate on sintered nickel plaque. It is important to thoroughly dry the impregnated plaque prior to the thermal decomposition which should be carried out at a temperature not greater than 300°C .
2. The best performance for oxygen reduction was obtained with electrodes prepared by a single impregnation with a solution containing both cobalt nitrate and suspended PTFE followed by an overnight period of drying at 125°C and then thermal decomposition at 250°C for 4 hours. A suitable loading of NiCo_2O_4 was found to be about 18 mg/cm^2 and of PTFE 7 mg/cm^2 . This type of electrode which was operated continuously for more than a year at a current density of 50 mA/cm^2 , would be suitable for primary (or mechanically rechargeable) alkaline metal/air batteries and fuel cells.
3. A method was developed for the preparation of an electrode catalyzed evenly throughout with nickel/cobalt spinel but wet-proofed on only one side. When subjected to a regime consisting of 2 hours of oxygen reduction followed by 4 hours of oxygen evolution, both at a current density of 50 mA/cm^2 , this type of electrode performed satisfactorily for more than 200 cycles. It could find use in alkaline secondary metal/air batteries and fuel cell/electrolyzer units.

ACKNOWLEDGEMENT

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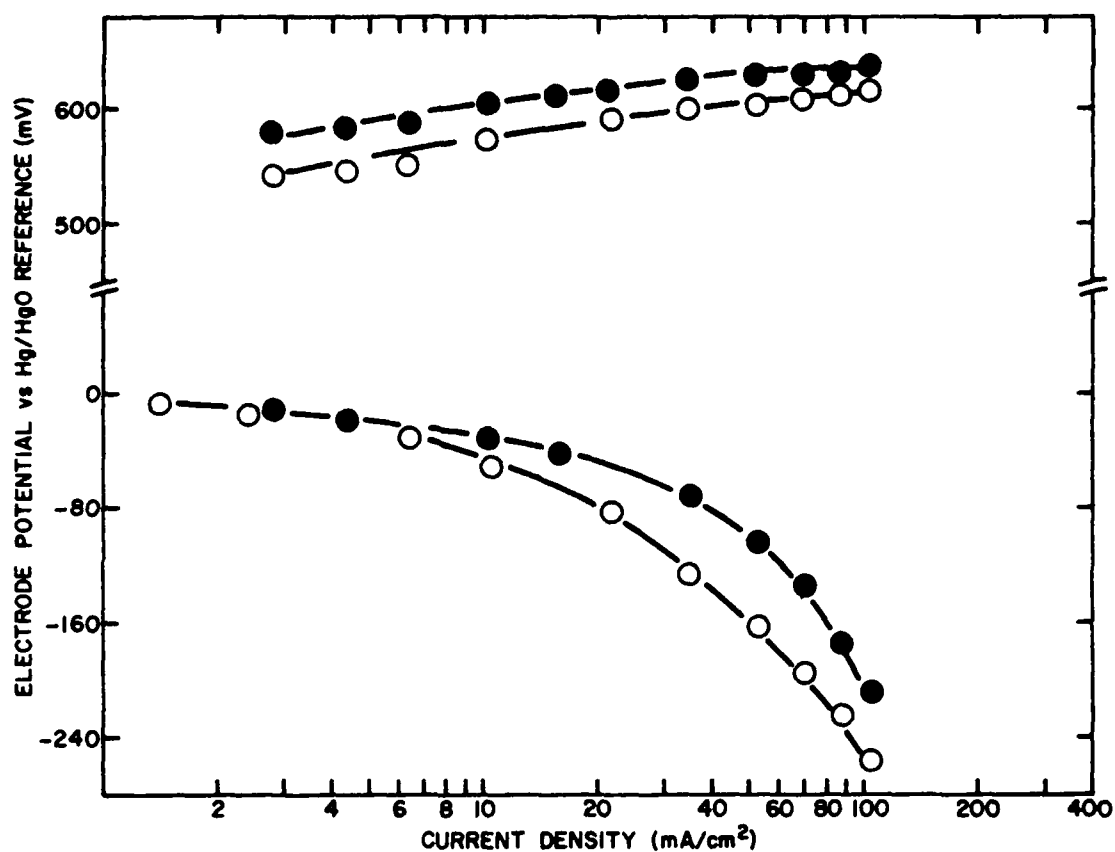


Fig. 1: Comparison of Electrocatalyte activity of $\text{Ni Co}_2\text{O}_4$ formed by thermal decomposition of mixed nickel and cobalt nitrates on sintered Ni plaque with that of $\text{Ni Co}_2\text{O}_4$ formed by the thermal decomposition of cobalt nitrates on sintered Ni plaque

○ mixed Ni and Co nitrates
● Co nitrate

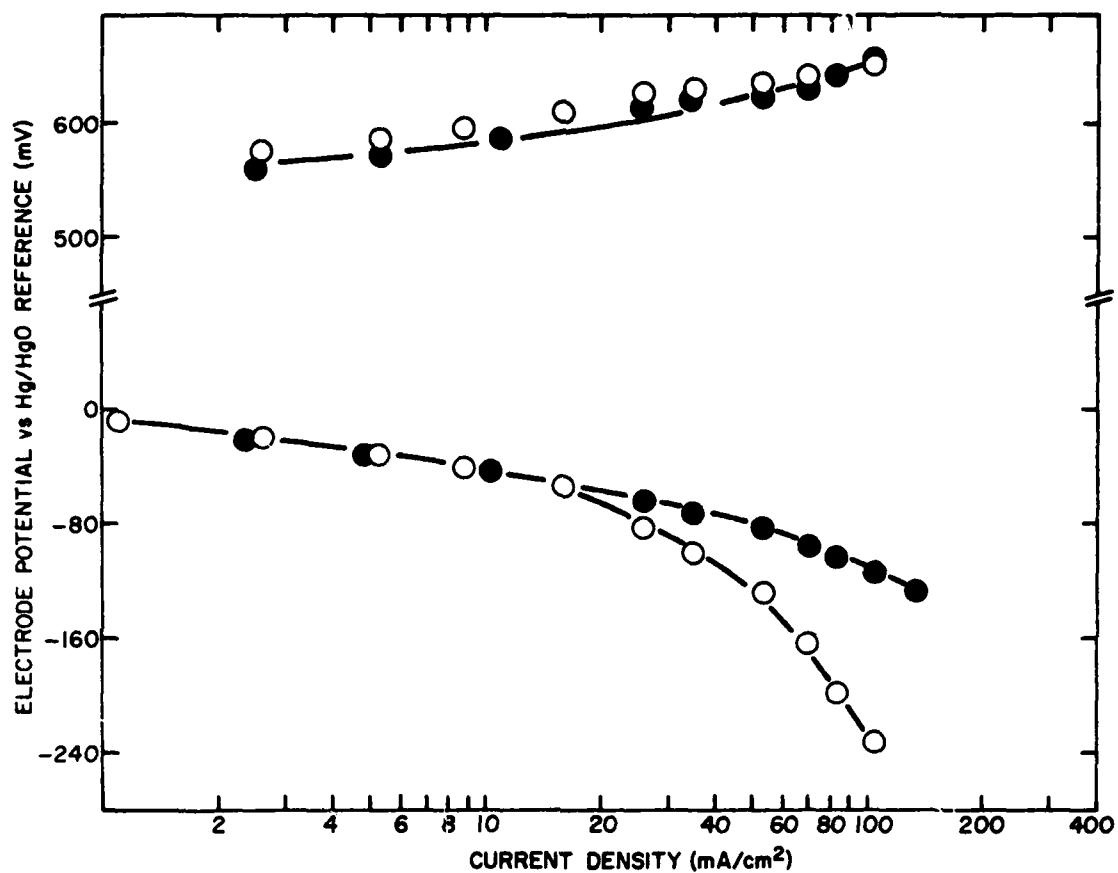


Fig. 2: Comparison of the Performance of Electrodes Prepared by the One and Two Step Processes
 ● one step (Electrode No. 5, Table III)
 ○ two step (Electrode No. 5, Table I)

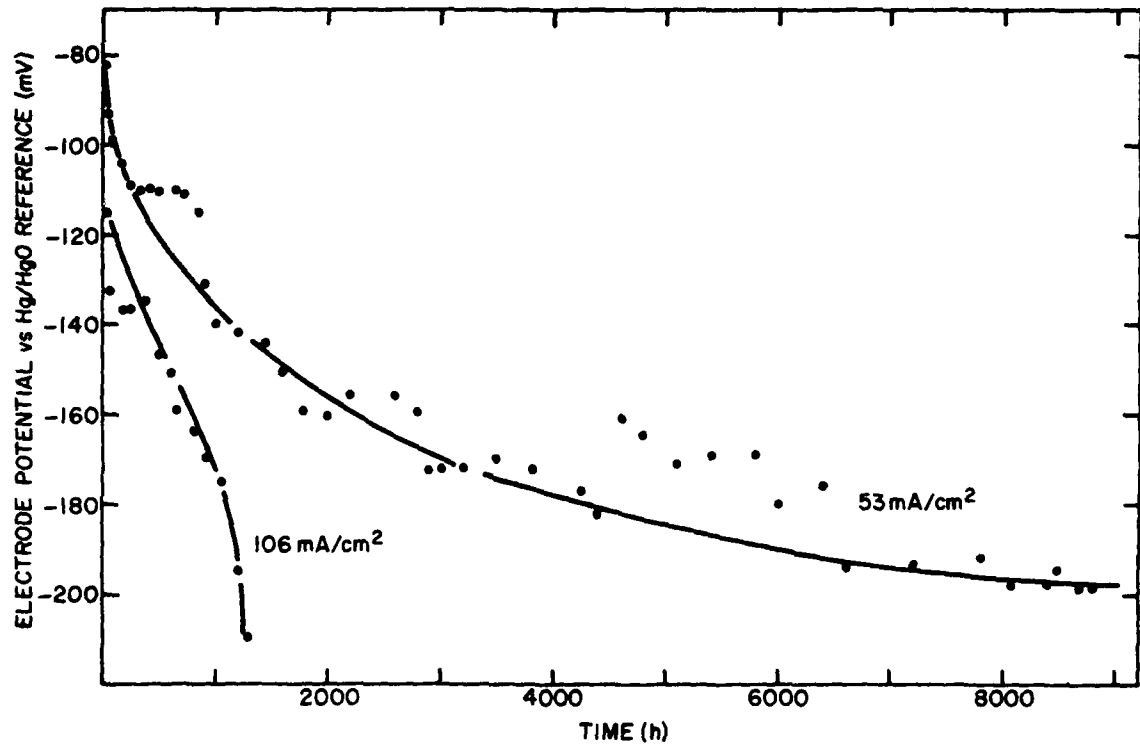


Fig. 3: Operational lifetimes of Electrodes Driven at Constant Current in the Oxygen Reduction Mode

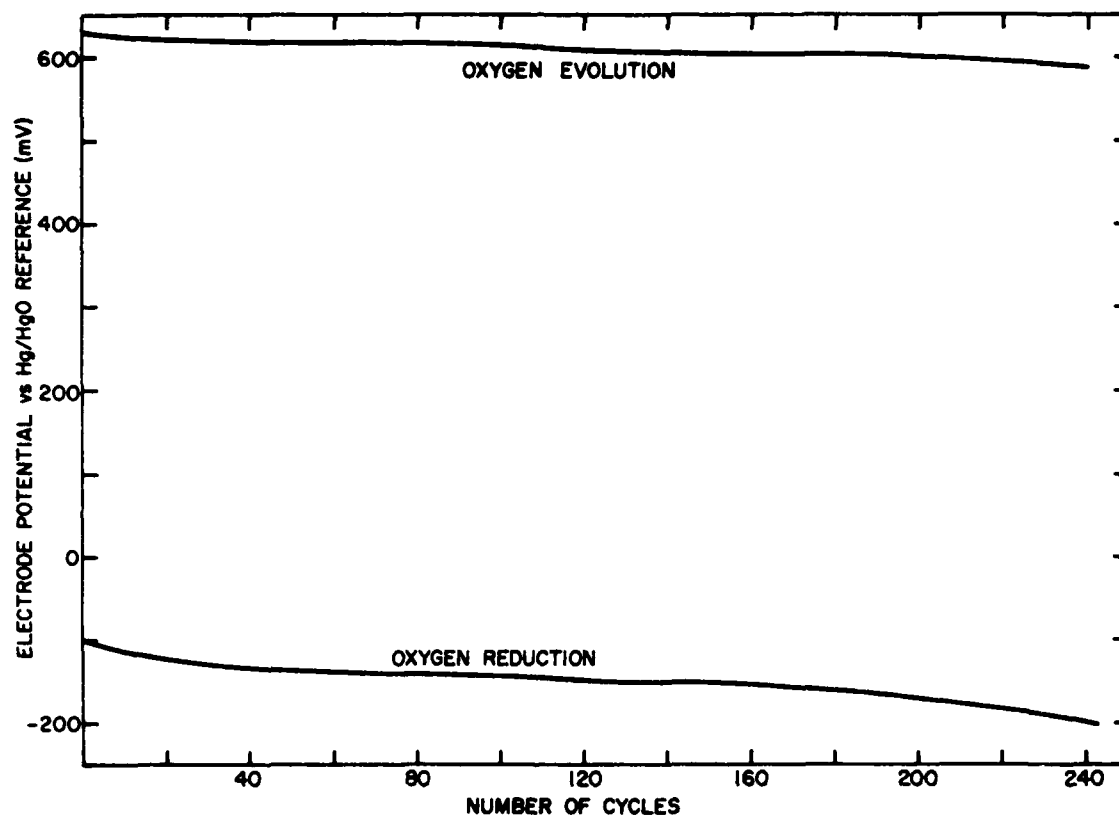


Fig. 4: Operational lifetimes of Electrodes Subjected to Cycles of Oxygen Reduction/Oxygen Evolution

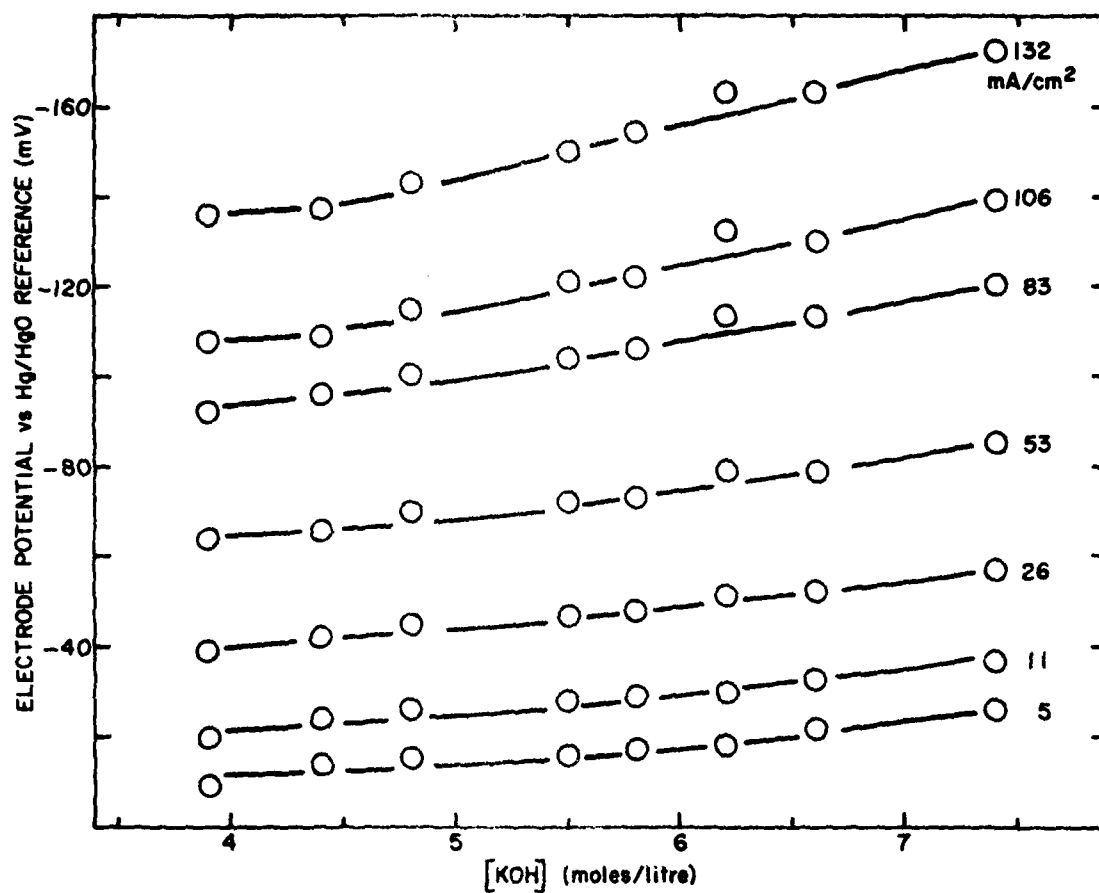


Fig. 5: Effect of Electrolyte Concentration on Performance of Electrodes during Oxygen Reduction

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