

equivalent performance to the state-of-the-art electrode for 500 cycles. These procedures and test results will be discussed.

The third area of study was involved with failure analysis of air electrodes. A series of eight air electrodes were life tested at Westinghouse. At various cycles, these electrodes were delivered to CWRU for analysis. The results of this analysis in general indicated that the silver catalyst was not lost during cycling for over 400 cycles. The details of this testing and analysis will be presented and discussed.

The program is currently oriented toward advancing the performance and life of the bifunctional air electrode. Studies have recently been initiated to investigate the nature of various carbons for use in the system. The results of some tests in this area will be presented and discussed.

The contract will be completed on December 31, 1982.

## BIFUNCTIONAL OXYGEN ELECTRODES

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The purpose of this research is to significantly improve the efficiency and life of the bifunctional oxygen electrode for use in rechargeable iron/air cells. This is being accomplished by developing the following:

- O<sub>2</sub> reduction and generation catalysts that combine good activity and stability,
- A more oxidation-resistant carbon, and
- An improved electrode structure.

Until recently, a significant amount of effort has been expended toward understanding the catalytic system and failure mechanisms of the Westinghouse bifunctional air electrode. As a fair degree of understanding has been achieved and has already led to improvements in the catalytic system, the emphasis has shifted to new catalysts, supports, and electrode structures.

### Understanding the life history of Westinghouse bifunctional air electrodes

In an attempt to understand the changes in the physical and chemical aspects of Westinghouse electrodes responsible for electrode break-in and failure, 10 identical electrodes were cycled at Westinghouse for various lengths of time. They were then examined at CWRU using X-ray energy-

dispersive spectroscopy (XEDS), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). Samples of the used electrolyte were also analyzed. The electrodes were fabricated using silver-catalyzed Shawinigan acetylene black, Teflon, NiS,  $\text{FeWO}_4$ , and WC with 12 wt.% Co in a structure consisting of four active layers and one hydrophobic layer. Cycles consisted of 4-h discharge at  $-25 \text{ mA cm}^{-2}$  and 4-h charge at  $+12.5 \text{ mA cm}^{-2}$ .

XEDS analysis showed apparent increases in levels of W, S, Fe, Co, and Ni in the electrode-active layer during break-in (10 to 20 cycles) due to an increase in dispersion of these elements. The starting materials had previously been shown to undergo irreversible electrochemical processes upon cycling. Electrolyte, which was replaced weekly, contained high levels of W and S after the first 15 cycles, while the other elements were at low levels. The break-in process involves a complex array of electrochemical reactions, which are expected on thermodynamic grounds and result in the rapid release of tungstate, the slower release of sulfate, and the formation of hydrated oxides of Fe, Co, and Ni in a high state of dispersion. The polarization on both charge and discharge decreases markedly during this period.

The Ag levels within the electrodes remained fairly constant from the unused state through to failure. The stabilization of Ag even at quite anodic potentials is thought to result from association with sulfide and possibly also hydrated nickel oxides. (The solubility product of  $\text{Ag}_2\text{S}$  is very low.) Levels of the other catalytically important elements, Fe, Co, and Ni, also remained fairly constant throughout.

XPS showed the oxygen/carbon ratio to increase significantly during cycling, indicating oxidation of the carbon surface. The fluorine/carbon ratio also increased markedly, indicating carbon loss with respect to Teflon. Weight loss and SEM also both indicated severe carbon loss.

The conclusion was that, since loss of Ag, Fe, Co, and Ni was not remarkable, the oxidation and loss of carbon were the major underlying causes of electrode failure. The actual processes involved are thought to be (1) loss of hydrophobicity, leading to increased wetting and loss of  $\text{O}_2$  transport capability; (2) decrease of electrical conductivity within the electrode; (3) degradation of mechanical stability; and (4) possible decrease in the activity of carbon to catalyze the reduction of oxygen to peroxide.

### Understanding the Westinghouse catalytic system

As noted above, the initial components of the Westinghouse formulation undergo chemical transformations during the first 15 cycles, which lead to decreases in both anodic and cathodic polarization. In an effort to pin down the formation of chemical species that are the most critical for  $\text{O}_2$  reduction and generation, a series of gas-fed electrodes was fabricated and tested under both cycling conditions and steady-state polarization. These electrodes contained Shawinigan black or silver-catalyzed Shawinigan black

and various combinations of Westinghouse-type additives and also included some of the following: Co,  $\text{Co(OH)}_2$ , FeS,  $\text{Fe(OH)}_3$ , and  $\text{Ni(OH)}_2$ . For combinations not including Ag, the findings were that, after cycling, (1) Co, whether loaded as WC/Co, Co powder, or  $\text{Co(OH)}_2$ , is active as a peroxide elimination catalyst and (2) NiS and FeS or  $\text{FeWO}_4$  form an effective  $\text{O}_2$  generation catalyst. For combinations including Ag, the results after cycling were that (1) Co, NiS, and FeS (or  $\text{FeWO}_4$ ) in various combinations do not lead to remarkable improvements in the cathodic polarization exhibited by Ag-catalyzed Shawinigan acetylene black alone; (2) the combination of NiS and FeS leads to very good anodic polarization; and (3) the combination of Ag,  $\text{Ni(OH)}_2$ , and  $\text{Fe(OH)}_3$  has superior polarization both anodically and cathodically.

These findings were supported by extensive work using floating-type gas-fed electrodes with steady-state polarization measurements and with the open-circuit potential decay method for determining the apparent peroxide elimination rate constants, which was developed at CWRU during 1981. This method is based on the idea that the high-area carbon within the electrode acts as a good potentiometric sensor for peroxide under open-circuit conditions, assuming that the  $\text{O}_2$  partial pressure remains constant. The technique has shown that for many catalysts, peroxide elimination appears to be second order in peroxide concentration. Large rate constants are often correlated with low cathodic polarization. Specifically, it was found that  $\text{Ni(OH)}_2$  helped to maintain the high peroxide elimination activity of Ag during extended cycling. The combination of Ag,  $\text{Ni(OH)}_2$ , and  $\text{Fe(OH)}_3$ , however, yielded smaller rate constants but showed surprisingly good cathodic polarization at moderate current density ( $25 \text{ mA cm}^{-2}$ ).

The overall conclusions were that (1)  $\text{O}_2$  reduction to peroxide occurs mainly on the carbon; (2) a form of hydrated cobalt oxide is a good peroxide eliminator; (3) Ag is a good peroxide eliminator whose activity can be maintained by the presence of  $\text{Ni(OH)}_2$ ; (4) the cathodic polarization of Ag-catalyzed carbon is improved by the presence of Ni and Fe hydroxides through a mechanism not involving peroxide elimination; and (5) Ni and Fe hydroxides are critical for  $\text{O}_2$  generation, possibly through the formation during cycling of the hydrated spinel  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ .

### New catalytic systems

There has been a continuing effort to test catalysts that have been reported in the recent literature to be promising for  $\text{O}_2$  reduction, generation, or both. These have included metal oxides (perovskites, spinels, pyrochlores, and nonstoichiometric oxides) and macrocyclics (naphthalocyanines and porphyrins). Lead ruthenate, developed at Exxon, showed promising activity for both  $\text{O}_2$  reduction and generation but was judged not to be suitable for an Fe-air cell because of corrosion problems leading to lead in the electrolyte, which could adversely affect the capacity of the Fe electrode. Although

further work is planned, none of the other metal oxide systems has approached the  $\text{Ag-Ni(OH)}_2\text{-Fe(OH)}_3$  system in polarization characteristics in bifunctional operation.

Two macrocyclic catalysts, cobalt tetramethoxyphenyl porphyrin (CoTMPP) and molybdenum naphthalocyanine (MoNc, obtained from Dr. M. Savy, Meudon, France), have shown very attractive cathodic polarization behavior and good stability during cycling if Co, NiS, and FeS are used as electrode additives. During cycling, Co forms an effective peroxide eliminator and NiS and FeS form a species that lowers anodic polarization; both help to protect the macrocyclic catalyst from oxidative attack.

At present, there are three systems that offer a significant improvement in cell voltage in both charge and discharge modes over the Westinghouse  $\text{Ag-Ni(OH)}_2\text{-Fe(OH)}_3$  formulation: Co, NiS, and FeS with either CoTMPP or MoNc. The life for electrodes using these catalyst systems remains to be established.

Fundamental studies on macrocyclics such as Co and Fe TMPP and phthalocyanine are in progress using principally surface-enhanced Raman and Mossbauer spectroscopy in both *in situ* and *ex situ* measurements together with electrochemical measurements to establish the state of the macrocyclic on the electrode surface. Work has also been initiated on macrocyclics pyrolyzed at temperatures up to 900 °C. Although the structures are drastically modified, these materials have exhibited good catalytic activity for  $\text{O}_2$  reduction and, in the reduction mode, long life.

### Improved carbons

Because of the crucial importance of carbon oxidation in the failure process, work was recently initiated to examine carbons and graphites that may have oxidation resistance superior to Shawinigan black. A graphitized carbon black obtained from Professor A. Scaroni, Pennsylvania State University, and ExCO, a highly ordered carbon produced pyrolytically from CO, have exhibited lower electrochemical oxidation rates in preliminary tests than the currently used Shawinigan black. These results tend to confirm previous work by other workers that a high degree of structural order can lead to improved oxidation resistance.

The goals for fundamental research in 1983 include the following:

- The effort to establish a predictive base between catalytic properties for  $\text{O}_2$  reduction and generation and the electronic-surface properties of the catalysts will continue.
- The effort to understand the basis for the good activity for  $\text{O}_2$  reduction and generation and stability of the macrocyclic catalysts will continue.
- The open circuit potential decay technique will be put on a sound theoretical basis so that its sphere of usefulness will be clearly de-

linedated. Also, the role of peroxide elimination in polarization behavior will be explored theoretically.

- The nature of the relationship between electrochemical oxidation resistance and carbon properties, especially bulk structure, surface composition, and impurity distribution, will be explored.

The major objective in applied work will be to develop an electrode system, including catalyst, support, and structure that will survive 1000 cycles with low polarization. Other objectives are as follows:

- The three most attractive catalytic systems developed to date will be life-tested by Westinghouse.
- Further improvements in these systems will be made on the basis of both short-term and long-term testing.
- Other members of the naphthalocyanine and porphyrin groups such as FeNc, CoNc, and FeTMPP will be studied both singly and in combination.
- Other parameters affecting the total catalytic system, such as type of carbon and pyrolysis temperature, will be varied. There is expertise along these lines at CWRU.
- Some of the thermally decomposed, nonstoichiometric metal oxides will be prepared in high-area form and tested for O<sub>2</sub> generation activity in an effort to decrease anodic polarization even further.
- Several other highly ordered carbon materials will be tested for long-term oxidation resistance. These will also be tested as catalyst supports for the more attractive catalytic systems.
- Alternative supports such as conductive metal oxides will be investigated.
- Because of the problem of progressive electrolyte penetration and eventual leakage through the hydrophobic gas-diffusion layer, new types of electrode structure based on a more stable interface between wetted and nonwetted layers will be tested.
- An effort will be made to characterize the chemical species formed in the Ag-Ni(OH)<sub>2</sub>-Fe(OH)<sub>3</sub> system as well as the mechanisms for O<sub>2</sub> reduction and generation.

### Recent publications

- 1 J. T. Lu, D. Tryk and E. Yeager, Determination of the equilibrium constant for superoxide dismutation, *Abstract No. 674, The Electrochemical Society Extended Abstracts, Montreal, Canada, May 9 - 14, 1982, pp. 1075 - 1076.*

- 2 J. T. Lu, D. Tryk and E. Yeager, Electrochemical formation of superoxide on graphite in alkaline solutions, *Abstract No. 323, The Electrochemical Society Extended Abstracts*, Detroit, MI, October 17 - 21, 1982, pp. 520 - 521.
- 3 T. Ohzuku, D. Tryk and E. Yeager, Catalytic systems for bifunctional oxygen electrodes, *Abstract No. 116, The Electrochemical Society Extended Abstracts*, Denver, CO, October 11 - 16, 1981, pp. 293 - 294.
- 4 D. Tryk, E. Yeager and T. Ohzuku, Decay of polarization on open circuit as a measure of activity of catalysts for air cathodes, *Abstract No. 36, The Electrochemical Society Extended Abstracts*, Detroit, MI, October 17 - 21, 1982, pp. 59 - 60.
- 5 E. Yeager, D. Tryk, T. Ohzuku *et al.*, The oxygen electrode in metal air batteries, *Abstract No. 105, The Electrochemical Society Extended Abstracts*, Denver, CO, October 11 - 16, 1981, pp. 265 - 267.

## ALUMINUM/AIR BATTERY PROGRAM

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The goal of the aluminum/air program is to develop and demonstrate a battery capable of providing an electric vehicle with the range, acceleration, and rapid-refueling capability of today's conventional automobile. The motivation for this goal is the prospect of a significant decrease in our dependence on liquid fuels through the use of electric vehicles capable of widespread use in the automotive market. Benchmark goals for the total cost of vehicle operation and for total energy use are to achieve equivalence with internal combustion engine vehicles using synthetic liquid fuels derived from coal.

Our approach to these goals involves parallel developments of (1) cell configurations and battery processes that are scalable to vehicle size, using as models anodes and air-cathodes adapted from existing technologies; (2) cost-effective anode and cathode materials and structures; and (3) electric propulsion systems optimized for Al/air battery characteristics and low cost. Through 1982, the program has emphasized the research and development of battery processes.

Aluminum/air cells and cell stacks have been routinely operated under conditions anticipated for automotive battery applications. Small scale (25-cm<sup>2</sup> anode) cells were operated to establish a baseline for comparison with larger cells and cell stacks. In small cell tests, peak net energy yields were over 4.0 kW h/kg Al; peak power densities were 6.3 kW/m<sup>2</sup> (0.15-cm interelectrode gap) or 5.0 kW/m<sup>2</sup> (0.32-cm gap), using an Al-0.05 Ga-0.1 Mg alloy and the Diamond-Shamrock standard air electrode, in 4 M NaOH + 1 M Al(OH)<sub>3</sub> + 0.06 M Na<sub>2</sub>Sn(OH)<sub>6</sub> at 60 °C. A large cell (0.1 m<sup>2</sup>), the MO series, was operated with a crystallizer to stabilize concentration of aluminate at 2.7 M and to establish compatibility of cell and crystallizer pro-