OXYGEN ELECTRODES FOR ENERGY CONSERVATION AND STORAGE

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This project involves a joint effort of the Diamond Shamrock Corporation (prime contractor) and Case Western Reserve University (subcontractor) to develop high performance O_2 cathodes and anodes for alkaline and acid electrolytes with emphasis on high activity, stable O_2 electrocatalysts of reasonable cost. Such improved O_2 electrodes will have major impact on energy conversion and storage.

Fuel cells and other air-consuming batteries. The irreversibility of air-consuming O_2 electrodes imposes serious restrictions on fuel cells and other air-consuming batteries in conversion and storage applications, including peak shaving–load leveling in the electric utilities, waste H_2 utilization in the industrial electrolytic industry, and vehicle propulsion (*e.g.*, aluminum–air cells).

Water electrolyzers. Water electrolyzers coupled with fuel cells offer promise for energy storage provided the O_2 electrode voltage losses can be reduced to a small fraction of those with present commercial electrolyzers and fuel cells.

This project is expected to require four years and was initiated in October 1977. Project management is the responsibility of Diamond Shamrock Corporation as prime contractor with Case Western Reserve University as subcontractor. The specific tasks include the following:

(1) Catalyst synthesis and characterization (CWRU). Choice of catalyst systems, catalyst preparation, physical and chemical characterization of catalists, screening for electrocatalytic activity for O_2 reduction.

(2) Electrode surface structure (CWRU). (a) *Optical:* assembly of u.v.–visible reflectance spectroscopic equipment; measurements on electrosorbed transition metal complex electrocatalysts on various substrates. (b) *LEED–Auger studies:* assembly of hardware for studies of single crystal catalytic surfaces; electrochemical properties of single crystal Au and Pt; measurements on underpotential deposited (UPD) metals on single crystal gold. (c) *E.s.c.a.:* all promising catalysts from Task 1 are being examined with e.s.c.a. (d) *Interpretative aspects:* the catalytic aspects are being related to surface electronic and morphological properties.

(3) Electrode kinetics and mechanisms (CWRU). Assembly of additional rotating disk-ring apparatus and supporting electronic instrumentation; kinetic studies of O_2 reduction on Pt, carbon, UPD metals, transition metal oxides and electrosorbed transition metal complexes; voltammetry studies on these same surfaces; interpretative aspects — particularly development of predictive base for O_2 electrocatalysis.

(4) Electrode structures (CWRU). Development of small gas-fed electrodes for evaluation of catalysts and various structural features; short term testing of such in concentrated caustic; analysis of polarization characteristics; recommendation of catalysts and structures for longer term testing by Diamond Shamrock.

(5) Electrode fabrication (Diamond Shamrock). Development of fabrication techniques; fabrication of air cathodes using catalysts provided by CWRU under Task 1, in sizes suitable for testing for chlor–alkali and other applications; characterization of structural and chemical properties of these electrodes.

(6) Electrode evaluation (Diamond Shamrock). Measurement of polarization curves for electrodes evaluated under Task 5; screening tests involving conditions similar to those expected for the chlor–alkali cell application; in-cell tests; life tests; evaluation for other promising applications.

During 1978-9, work has proceeded on all of the above tasks. The work has been closely correlated between Diamond Shamrock and CWRU with not only the testing by Diamond of many catalysts prepared by CWRU but also much interchange of ideas. Some of the accomplishments of this past year in the development of high performance O_2 cathodes have included:

(1) the identification of highly effective transition metal macrocyclic catalysts for alkaline electrolytes with activity comparable with or better than that of highly dispersed platinum at reasonable loadings;

(2) the preparation of highly dispersed Pt catalysts on high area carbon supports by electrocrystallization techniques and also chemical reduction methods;

(3) the fabrication of gas-fed test electrodes at both CWRU and Diamond Shamrock which use either the CWRU macrocyclic catalysts or CWRU highly dispersed metal catalysts such as Pt or Pt alloys. These electrodes operate in short term tests at 1 A/cm^2 at 0.80 V *vs.* RHE (air free) at 85 °C in 9.2M NaOH and more than meet the short term performance requirements for the chlor–alkali application; *i.e.*, 300 mA/cm^2 at 0.80 V *vs.* RHE *on air* at 85 °C in 9.2M NaOH (membrane cell grade).

Some of the more important developments in the supporting fundamental studies at CWRU have included:

(1) the identification of certain electrosorbed transition metal macrocyclics as highly effective catalysts for the overall 4-electron reduction of O_2 in alkaline and acid electrolytes, and the first detection of the O_2 adducts

with these adsorbed molecules through the use of optical reflectance spectroscopic techniques;

(2) the identification of certain underpotential deposited metals on gold as catalysts for the reduction of O_2 to OH^- in alkaline electrolytes by the overall 4-electron pathway;

(3) direct evidence that the underpotential deposition (UPD) of metals (Pb on Au) depends strongly on the surface morphology in studies of UPD on single crystal Au using LEED and Auger spectroscopic techniques together with thin-layer cell electrochemistry;

(4) the preparation of spinels which are highly effective as peroxide elimination catalysts in alkaline solutions and the characterization of the kinetics of the peroxide elimination reaction on these surfaces;

(5) the characterization of platinum and binary metal catalysts involving Pt, using high resolution electron microscopy, and the identification of platelet-type structures in some instances.

The research during the coming year is expected to continue in the same overall direction. The emphasis at CWRU will be on the question of catalyst stability as well as activity, the relation of electrode structures to polarization characteristics for various catalysts, the electrochemistry of carbon (particularly its electrochemical oxidation), and the further development of the predictive base for O_2 electrocatalysis in both alkaline and acid electrolytes.

Recent publications

1 E. Yeager, J. Zagal, B. Nikolic and R. Adzic, Optical and electrochemical studies of adsorbed transition metal complexes and their O_2 electrocatalytic properties, *Proc. Third Symp. Electrode Processes*, The Electrochemical Society, Princeton, NJ, in press, 1979.

2 E. Yeager, Oxygen electrodes for electrochemical energy storage systems, *Proc. Int. Assembly on Energy Storage*, National Academy of Sciences — Yugoslav Council of Academies, Dubrovnik, in press, 1979.

3 Diamond Shamrock/Case Western Reserve University, Oxygen electrodes for energy conversion and storage, *Annu. Rep., Contract No. EC-77-C-02-4146, 1 October 1977 to 30 September 1978*, in press.

ANALYSIS OF THE EFFECT OF ENERGY STORAGE POWER SYSTEMS ON NATIONAL TRANSPORTATION

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The objective of this subcontract is to conduct the work of the Electrochemical Storage Panel by selecting and directing panel members to fulfill objectives and schedules of the study; to assist in adding electrochemical storage data to the National Energy Storage Data Base; to provide additional support to other study panels as needed.