Recent publications

1 H. L. Chum, Executive summary, *Proc. Thermally Regenerative Electrochemical Systems Workshop*, Alexandria, VA, SERI/CP-234-1577, v-x, 1982.
2 H. L. Chum and S. Black, Solution redox couples for electrochemical energy storage, to be published.
3 H. L. Chum and R. F. Fahlsing, Copper/copper(II) carboxylate thermogalvanic cell, to be published.
4 H. L. Chum, R. F. Fahlsing and T. S. Jayadev, Analysis of the application of thermogalvanic cells to the conversion of low grade heat to electricity, *Proc. 15th Intsoc. Energy Conversion Eng. Conf., 1980*, pp. 1603 - 1609.
5 H. L. Chum and R. A. Osteryoung, *Review of Thermally Regenerative Electrochemical Systems — Volume 1: Synopsis and Executive Summary*, SERI/TR-332-416, 1980.
6 H. L. Chum and R. A. Osteryoung, *Review of Thermally Regenerative Electrochemical Systems — Volume 2: Survey*, SERI/TR-332-416, 1981.

OXYGEN CATHODES FOR ENERGY CONSERVATION AND STORAGE

Electrolytic Systems Division, Diamond Shamrock Corporation, Painesville, OH 44077 (U.S.A.)

The purpose of this research program was to develop unifunctional air/oxygen cathodes capable of operating at high current densities over commercially significant periods and to develop a basic understanding of the thermodynamic and kinetic limitations of the catalyst and electrode systems.

In the area of catalysis, several classes of materials were closely examined to determine their suitability as long-term catalysts in a chloralkali cell. Included in the studies of catalytic activities were underpotentially deposited (UPD) adatoms on gold and silver, nickel intermetallic catalysts, and transition metal macrocyclic catalysts. An evaluation of a series of carbons for use in oxygen cathodes was also conducted to determine the most appropriate carbons of those currently available.

Underpotential deposition on gold and silver

The UPD of bismuth on gold was studied utilizing cyclic voltammetry and the ring-disk method. The effect of bismuth in solution containing Bi(III) and pretreatment with Bi(III) followed by operation in bismuth-free electrolyte was studied. In both cases, an enhancement of the oxygen reduction with respect to pure electrolyte was observed. In the pretreated sample, the enhancement was observed primarily in the kinetic region. In the

bismuth-containing electrolyte, the catalytic effect is explained by a catalysis of the peroxide reduction process. In similar experiments, the addition of thallium(I) to the electrolyte caused a marked increase in the oxygen reduction current, though the half-wave potential did not shift appreciably. Platinum and palladium adatoms on silver surfaces enhanced the catalytic activity of the silver electrode for oxygen reduction.

Nickel intermetallics

To determine whether the catalytic activity of nickel could be enhanced, intermetallic compounds of nickel with molybdenum, vanadium, zirconium, hafnium, titanium, and niobium were prepared. Voltammetry results for most of the compounds were similar to pure nickel except for the molybdenum and vanadium compounds, which each displayed an additional anodic wave due to metal dissolution. The zirconium, hafnium, and titanium compounds gave small voltammetric peaks, possibly due to anodic film formation.

Transition metal macrocyclics

The catalytic activity and stability of transition metal macrocyclics, both adsorbed and solution phase, has been studied. In general, it was observed that with solutions of 1E-05 M, only the redox properties of the surface phase species are observed, while at concentrations of 1E-03 M, solution phase redox processes are seen. Cyclic voltammetry measurements of metal-free, iron(III), cobalt(II), and copper(II) tetrasulfonated phthalocyanines and iron and cobalt phthalocyanines were obtained as a function of pH. It was found that all voltammetry peaks exhibited a slope of 59 mV/pH, but not through the entire pH region studied. Some peaks showed the dependence only in acid, others only in alkaline regions. All peaks were due to surface redox processes, except the metal-free and copper tetrasulfonated phthalocyanines, which also exhibited solution phase processes. Generalizations in areas other than pH dependence cannot be made, however, because other factors differ significantly between compounds.

Carbon studies

While carbon blacks appear to be more stable than active carbons, they do not have high activity for oxygen reduction. The active carbons, however, suffer from rapid rates of morphological deterioration. Thermally modified RB carbons do not appear to be greatly different from the native material, but modified Shawinigan black and XC-72R carbons exhibit more anodic half-wave potentials and higher peroxide elimination rates than the native materials. Lifetimes continue to be a problem for these materials.

Modified Ketjenblack exhibited vastly different properties from the native material. An anodic shift of more than 400 mV in oxygen reduction half-wave potential and a greater than two order of magnitude enhancement of peroxide elimination was observed. Lifetimes of platinum-catalyzed gas-fed electrodes were also superior to any other modified materials tested.

Electrolyzer scale-up

The success of the DOE-funded electrode development effort allowed the scale-up of the process from bench scale, through pilot scale, to commercial prototype size. A commercial-sized device has operated for 103 days on line. During its operation, a cell voltage as low as 2.33 V at 2.5 kA/m^2 has been observed. This corresponds to a voltage savings of over 25 percent compared to conventional technology.

Recent publications

1 R. Amadelli, J. A. Molla and E. Yeager, Offsetting impurities in O_2 electroreduction on platinum with adsorbed metal ions, *J. Electroanal. Chem., 126* (1981) 265 - 271.

2 A. B. Anderson, R. Koetz and E. Yeager, Theory for CN^- and Ag–C vibrational frequency dependence on potential: cyanide on a silver electrode, *Chem. Phys. Letters, 82* (1981) 139 - 144.

3 R. Koetz and E. Yeager, Potential dependence of vibrational frequencies of adsorbates on a silver electrode, *J. Electroanal. Chem., 123* (1981) 335 - 344.

4 D. Scherson, S. B. Yao, E. B. Yeager *et al., In situ* Mössbauer effect spectroscopy of adsorbed species on high surface area electrodes, *Applications of Surface Science, 13*, 1982, in press.

5 E. Yeager, Recent advances in the science of electrocatalysis, *J. Electrochem. Soc., 128* (1981) 160C - 171C.