

kinetics of the  $O_2$  reduction will be examined as functions of coverage of substrate structures with the adsorbed macrocycles. This will be accomplished by following the increase in current for  $O_2$  reduction with the macrocyclic (water-soluble form) adsorption on the electrode. (Or in the case of nonsoluble forms, the coverage is varied by controlling the preapplication conditions.)

- Over the next 2 years, EXAFS studies of the most promising macrocycles on carbon will be undertaken.
- This work will be supported with molecular orbital calculations of  $O_2$  interactions with the transition metal macrocycles.

### Recent publications

- 1 R. Kotz and E. Yeager, Raman spectroscopy of cobalt phthalocyanine adsorbed on a silver electrode, *J. Electroanal. Chem.*, 113 (1980) 113 - 126.
- 2 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*, 10 (1982) 325 - 332.
- 3 B. Simic-Glavaski, S. Zecevic and E. Yeager, Study of phthalocyanines in aqueous solutions and adsorbed on electrode surfaces, *International Conference on Electronic and Molecular Structure of Electrode-Electrolyte Interfaces*, July 25 - 30, 1982.
- 4 E. Yeager, Sauerstoff-Verzehrskathoden für die Chloralkali Elektrolyse/Oxygen consuming cathodes for chloralkali electrolysis, *Chemie Ingenieur Technik*, 52 (5) (1980) 384 - 391.
- 5 E. Yeager, J. Zagal, B. Z. Nikolic and R. R. Adzic, Optical and electrochemical studies of adsorbed transition metal complexes and their  $O_2$  electrocatalytic properties, in S. Bruckenstein, J. D. E. McIntyre, B. Miller and E. Yeager (eds.), *Proc. Third Symposium on Electrode Processes, National Meeting of the Electrochemical Society, Boston, May 1979*, The Electrochemical Society, Princeton, NJ, 1980, pp. 436 - 456.
- 6 J. Zagal, P. Bindra and E. Yeager, A mechanistic study of  $O_2$  reduction on water soluble phthalocyanines adsorbed on graphite electrodes, *J. Electrochem. Soc.*, 127 (1980) 1506 - 1517.

## ELECTROCHEMISTRY APPLIED TO THERMAL CONVERSION

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The objectives of this task are to aid evaluations of the area of Thermally Regenerative Electrochemical Systems (TRES) and to carry out research to define the usefulness of TRES for conversion of low-grade heat to electricity.

A specialists' workshop on Thermally Regenerative Electrochemical Systems was organized to include a thorough critical view of past and present work on TRES. To give all participants a common background

relative to existing heat engines and those in development, two of the talks addressed the state-of-the-art of heat engines and the new concepts on condensed state heat engines. Six papers reviewed past work and four papers reviewed present work. In addition, a panel discussion addressed the perspective of TRES, materials problems, molten salts, and other aspects related to the science and technology of TRES. All of the papers, a transcription of the panel discussion, and the executive summary of the workshop are published in the *Proceedings of the Thermally Regenerative Electrochemical Systems Workshop*, H. L. Chum (ed.), SERI/CP-234-1577, 1982, (available upon request from the Solar Energy Research Institute). The executive summary addressed (1) possible applications of TRES, (2) electrochemical versus mechanical heat engines, and (3) advantages and disadvantages of TRES. Even though electrochemical heat engines have been researched for at most 25 years, the workshop was successful in identifying some types of TRES that have proven scientific feasibility and the possibility of achieving a substantial fraction of Carnot's efficiency.

The experimental part of this task investigated systems with a reversal of potential near room temperature for the low-grade heat utilization by direct conversion of that heat into electricity in an electrochemical heat engine, Carnot-cycle limited in efficiency. In addition, electrode reactions were selected that can lead to large opposite isothermal temperature coefficients of the electrode potentials  $[(dE/dT)_{\text{isoth}}]$  i.e., large opposite entropies of reactions), under practical battery operating conditions (high concentration of the couples and supporting electrolyte). Two basic types of regeneration are under consideration:

- Systems that operate generating power at  $T_1$ , and that are regenerated at higher temperature, i.e.,  $T > T_r$  spontaneously, or  $T < T_r$ , consuming a fraction of the power generated at  $T_1$ .
- Systems that operate generating power at  $T_h$ , and that are regenerated by cooling, i.e.,  $T < T_r$  spontaneously, or  $T > T_r$ , consuming a fraction of the power generated at  $T_h$ .

To vary the electrode potentials, complex formation was utilized. Twelve electrode reactions involving redox couples of iron(III)/iron(II) and copper(II)/copper and a variety of simple ligands and mixed ligands were investigated in aqueous and acid media. Several of the electrode reactions investigated displayed large and opposite isothermal temperature coefficients, but the final TRES configuration would require an ion-exchange separator. Some of the couples tested could be used as solution redox couples for electrochemical energy storage in redox regenerative batteries.

Although solution redox couples may lead to TRES, the need for separators and the limited solubility of the couples would lead to rather heavy and possibly expensive device configurations for conversion of low-grade heat into electricity. One possible way to overcome some of these problems is to use solid-state electrodes, e.g., electrodes of the second kind. Our efforts in 1983 aim to select and test viable solid-state electrodes as possible TRES components.

## 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

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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