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PHYSICAL CHEMISTRY OF MOLTEN SALT BATTERIES

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The objective of this project, new in 1979, is to provide studies of polarization phenomena in molten salt batteries related to current-induced composition gradients in mixed molten salt electrolytes. The kinds of battery systems considered include those consisting of: a lithium alloy negative electrode and an iron sulfide positive electrode with LiCl-KCl as the electrolyte; other active alloy (*e.g.*, calcium) negative electrodes with more complex electrolytes; Na/ β "Al₂O₃ negative electrode with SCl₃AlCl₄ positive electrode and NaCl-AlCl₃ electrolyte.

A previously described model (J. Braunstein and C. E. Vallet, Migrational polarization in high-current density molten salt battery and fuel cell analogs, *J. Electrochem. Soc.*, 126 (1979) 960) of ion flows in molten salt mixtures has now been extended to incorporate composition changes and gradients in an alloy electrode, and the way in which these gradients interact with the composition gradients in the electrolyte. Results of these computations, using available thermodynamic and transport data for LiAl alloys and for molten LiCl-KCl mixtures, can indicate conditions of current density and electrode thickness at which the composition changes at different depths in the LiAl electrode may be expected to cause phase changes in the alloy. These computations are being used also to design experiments for measuring the extent of electrolyte component separation in LiAl/LiCl-KCl/FeS_x batteries. (Such separation has been observed by Giner *et al.* during discharge of an Al/Cl₂ battery with NaCl-KCl-AlCl₃ electrolyte where AlCl₃ precipitated at the anode (J. Giner and G. L. Holleck, Report, NASA CR-1541 (March 1970), *J. Electrochem. Soc.* 119).)

Equipment has been assembled and measurements initiated of concentration polarization at LiAl electrodes in molten LiCl-KCl as a function of current, potential, time, and initial electrolyte composition. The measurements consist of electrolysis-e.m.f. relaxation measurements such as those

that have demonstrated significant electrolyte composition gradients at Ag electrodes in electrolyzed NaNO_3 - AgNO_3 mixtures (C. E. Vallet, D. E. Heatherly and J. Braunstein, *Abstract #340, 2nd Int. Symp. Molten Salts, The Electrochem. Soc., Pittsburgh, Oct. 15 - 20*, p. 921). In collaboration with G. Mamantov, University of Tennessee, a cell has been designed and constructed for electrolysis-e.m.f. relaxation measurements in the cell $\text{Na}/\beta\text{-Al}_2\text{O}_3/\text{NaCl}, \text{AlCl}_3/\text{Al}$ to determine the importance of migrational polarization involving the beta alumina membrane.

During the remainder of 1979 and 1980 we will conduct a systematic series of electrolysis-e.m.f. relaxation measurements at LiAl electrodes in LiCl-KCl mixtures, varying alloy and electrolyte compositions and current densities in order to resolve diffusional relaxations in the alloy and in the electrolyte. Scanning electron microscopic examination of quenched electrolyzed salt samples will be tested as a means of observation of composition gradients.

ELECTROLYTE DATA EVALUATION

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The objective of this project is to collect, compile and evaluate the thermodynamic data on aqueous electrolyte solutions. This project will provide for the electrochemical community a broad data reference base on electrolyte solutions as well as critically evaluated values of osmotic and activity coefficients for these solutions. Thermodynamic equilibrium properties (ionic activities, apparent and partial molal enthalpies and heat capacities) and transport properties (conductivity, transference numbers, and diffusion coefficients) are included. This project is complementary to a continuing program sponsored by the Office of Standard Reference Data of the National Bureau of Standards.

Past accomplishments include the following:

(1) Development of a comprehensive set of computer programs for the evaluation of mean ionic activity and osmotic coefficients for aqueous electrolyte solutions [3].

(2) Application of this correlational scheme to calcium chloride [4] -- both as a standard for isopiestic measurements and to demonstrate the utility of the scheme.

(3) A comprehensive literature search for sources of thermodynamic data pertinent to aqueous solutions. This search disclosed useful sources of data in the literature [2].