

TEMPERATURE LIMITATIONS OF PRIMARY AND SECONDARY BATTERY ELECTRODES

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The purpose of this project is to assess electrochemically the features of Ni, Fe, and Zn in concentrated NaOH which may impair the performance of primary or secondary batteries in the temperature range -20 to $+120$ °C. Such temperatures may arise either from ambient temperature variations or from ohmic heating at high charge or discharge rates.

The parameters of interest and the major avenues of our experimental approach are listed below.

(1) The specific energy: the influence of T on the potential at which charge storage processes occur and on the utilization of active material.

(2) Specific power: the influence of T on the rate of charge storage reactions.

(3) Electrode life and charge storage ability: the influence of T on the nature and extent of irreversible electrode processes.

The experimental approach has been bifurcate. Objective 1 above is primarily associated with the thermodynamics of metal/aqueous hydroxide systems, and has been accomplished by an extensive set of potential-concentration calculations as a function of temperature, for each metal of interest.

As a means of checking the thermodynamic predictions and to accomplish Objectives 2 and 3, electrochemical kinetic studies have been performed, as a function of temperature, in 5, 6 and 7 molal NaOH. Principal tools and methods used in this study have been a rotating ring disk electrode to detect electrode dissolution products, cyclic voltammetry to determine the mechanisms and position of charge storage, and potential step and potential sweep coulometry to determine the extent of reversible and irreversible electrode processes.

In the period to June 30, 1979 covered by this review, experiments have been essentially completed on Ni and Fe. Preliminary analysis of the data obtained has revealed the following.

(i) Rotating ring disk studies of Ni electrodes have shown that, despite the predicted thermodynamic stability of the HNiO_2^- ion, no significant electrode dissolution occurs at any temperature within the normal potential range of the Ni positive electrode.

(ii) Rotating disk and rotating ring disk studies of Fe electrodes have indicated the presence of three distinct dissolution phenomena at elevated temperatures. Reductive dissolution occurs within a narrow potential range during charging, producing an Fe(II) species which can be reoxidized on the Pt ring. During discharge, anodic dissolution of exposed Fe(0) was observed to produce HFeO_2^- (or a similar ion), and at a condition of high discharge

(potentials > -500 mV *vs.* Hg/HgO), dissolution of formed oxide occurs, producing an Fe(III) ion. All three dissolution processes increase with both temperature and hydroxide concentration. In 7-molal NaOH, significant reductive dissolution was observed at temperatures above approximately 40 °C, and anodic dissolution at temperatures above $80 - 100$ °C.

(iii) For Ni and Fe, the total reversible charge and the rate of reversible processes generally increase with increasing temperature.

(iv) At full charge, the extent of coulombic inefficiency due to oxygen evolution on the Ni electrode and hydrogen evolution on Fe was observed to increase roughly with e^T/T , consistent with Tafel's law. Hydrogen evolution on Fe at elevated temperatures detracts significantly from the performance of this electrode, and occurs at a significant rate at potentials more positive than the Fe/Fe(OH)₂ couple.

In addition to experimental studies, calculations have been completed from which a complete set of potential-concentration diagrams (analogous to potential-pH diagrams) can be constructed covering the temperature range -20 to $+120$ °C.

Within the schedule duration of this project, SRI intends to complete experimental studies of Zn, to construct potential-concentration diagrams for metal/NaOH solutions, to analyze and collate all experimental data, and to incorporate these in the final report. In further experimental studies of Zn, we intend to concentrate primarily on temperature limitations associated with dissolution and passivation, utilizing a rotating, vitreous carbon ring, Zn disk electrode.

ENERGY STORAGE SYSTEMS FOR AUTOMOBILE PROPULSION

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This project continues the ongoing multi-DOE laboratory analytical study to evaluate the updating of energy storage devices and their suitability in energy storage propulsion systems for automobiles. The study this year includes: (a) updating the previous projections of energy storage device characteristics and the technical analysis of their utilization in propulsion systems; (b) the preparation of these data for addition to a national data base; (c) the analysis of the technical and economic tradeoffs for new systems; (d) an energy impact analysis of these systems; (e) an examination of the financial and infrastructure requirements of selected energy storage vehicles (ESV's); (f) an investigation of ESV specialty markets. The ultimate goal of the project is to determine which energy storage devices and power systems are most