electrolyte composition. This film prevents the catastrophic corrosion of the metal.

Stability diagrams were computed for the following half-cell reactions.

$$LiOH + e^- \longrightarrow Li + OH^- \tag{1}$$

$$Li^+ + e^- \longrightarrow Li \tag{2}$$

$$LiOH \longrightarrow Li^+ + OH^- \tag{3}$$

It has been observed in previous studies, and for these reactions also, that the thermodynamic equilibrium relationships for metals in concentrated hydroxide media are expressed better in the form of E *versus* log m_{MOH}, than as the more traditional E *versus* pH equations. The cell potential was plotted for reaction (1) as a function of LiOH concentration and temperature. These plots delineate the region within which different species (Li, LiOH) are stable, i.e., below the line the reduced species (Li) is stable, whereas above the line the oxidized species (LiOH) is stable. It was found that the stability region for the oxidized species increases with an increase in temperature, while that of reduced species is reduced.

The research will be completed by the end of 1982.

Recent publications

1 B. K. Sundararaj, Thermodynamics of lithium/lithium hydroxide/water system, M.S. Thesis, The Ohio State University, 1982.
2 B. K. Sundararaj, R. P. Singh and D. D. MacDonald, The thermodynamics of alkaline battery system, *Proc. 16th Intsoc. Energy Conversion Eng. Conf.*, Am. Soc. Mech. Eng., 1981.

AN ELECTROCHEMICAL AND MORPHOLOGICAL STUDY OF THE EFFECT OF TEMPERATURE ON THE RESTRUCTURING AND LOSS OF CAPACITY OF ALKALINE BATTERY ELECTRODES

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The objectives of this research program are to investigate the effect of temperature on the restructuring of porous alkaline battery electrodes and to determine the mechanisms of degradation of charge capacities of the electrodes on repetitive cycling. The original objectives included study of porous iron, nickel, and zinc electrodes. However, later redefinition of the program goals restricted the work to porous nickel electrodes in concentrated potassium hydroxide solutions.

The loss in charge capacity of porous nickel electrodes due to restructuring phenomena on cyclic charging and discharging has been investigated over the temperature range 0 to 100 °C. The effect of the restructuring processes on the electrode performance is under study using electrochemical techniques, particularly the a.c. impedance method.

In the initial stage of this work, the growth kinetics of oxides on planar nickel electrodes in buffered phosphate and borate solutions at ambient temperature were examined using both impedance and ellipsometric techniques. On passive nickel, the impedance data exhibit two high frequency relaxations, but at low frequencies, diffusion dominates the electrochemical behavior. In the case of a film-free nickel surface on which hydrogen evolution occurs, two well-defined relaxations are observed. These can be attributed to coupling between the discharge reaction and subsequent recombination reaction and double layer charging.

In order to interpret the a.c. impedance data for porous electrode studies, a transmission line model of finite length has been adopted. The model takes into account the resistance of the 'metal' phase, which includes the resistance resulting from the degradation of metal particle–particle contacts due to restructuring of the electrode. The analysis of a discretised or quantized transmission line model has yielded analytical functions for the current and potential distributions and the impedances in terms of system parameters including the resistance of the 'metal' phase. A computer program has been written to generate theoretical impedance spectra, and the model has been shown to reproduce the essential features of the experimental impedance data.

The experimental study has now been extended to rolled and bonded $Ni(OH)_2$ electrodes in 8 M KOH containing 1 percent LiOH. Potential/time charging and discharging curves at constant current have been obtained for up to 40 cycles and at temperatures of 0, 25, 45, and 100 °C. It was found that charge efficiencies of almost 100 percent were achieved for all cycles at 0 and 25 °C, but became much smaller at the higher temperatures.

Impedance spectra were measured at selected cycle numbers for both charged and discharged electrode conditions. At all temperatures, the impedance of the $Ni(OH)_2$ electrode was substantially larger in the discharged $(Ni(OH)_2)$ condition relative to the charged (NiOOH) condition. This may be due partly to better electrolyte access to the active material in the NiOOH condition, and partly to changes in the conductivity of the active material under the above conditions. The spectra at all temperatures except 100 °C showed two high frequency relaxations in the discharged condition compared with one when charged. At 0 °C, the spectra for both conditions show very little dependence on cycle number. In contrast, the impedance at higher temperatures was observed to increase significantly with cycle number, indicating progressive degradation on cycle charging and discharging, and demonstrating also that the extent of degradation becomes more severe with increasing temperature. Changes in the impedance spectra at 45 °C also reflected incomplete reduction on discharge of the electrode.

Further consideration has been given to the transmission line model. The model contains an impedance for the active material $(NiOH)_2$ or $(NiOOH)/$ solution interface. In order to provide an adequate equivalent circuit for this component, impedance data have been obtained over a range of potentials for planar nickel electrodes in 8 M KOH with 1 percent LiOH at ambient temperature. However, to assist in the interpretation of the data, it was necessary first to identify the potential regions for both the conversion of $Ni(OH)_2$ to NiOOH, and also for oxygen evolution under the experimental conditions. Cyclic voltammetry was used to obtain current/potential curves over a range of sweep rates from 10 to 100 mV/s. These curves showed two clearly defined peaks, one associated with the oxidation of $Ni(OH)_2$ to NiOOH and the other with the conjugate reduction reaction.

Impedance spectra were then measured at various potentials and were found to have several features in common for both the $Ni(OH)_2$ and NiOOH regions. Although not well defined in some cases, the data indicate, for example, that diffusion may be prominent in both potential regions. At potentials corresponding to oxygen evolution, the impedance spectra are characteristic of a charge transfer reaction (probably $2OH^- \rightarrow O_2 + 2H^+ + 4e^-$) in which diffusion is not involved to any significant extent.

The specific tasks that will be undertaken in this study in 1983 are as follow:

● Obtain cyclic voltammograms for planar nickel electrodes in 8 M KOH (1 percent LiOH) at higher temperatures to allow identification of the $Ni(OH)_2$ and NiOOH potential regions in order to explain the impedance data;

● Measure impedance spectra for planar nickel at various potentials for the four temperatures in the range under study, and determine the equivalent circuits(s) for the active material/solution interface; and

● Substitute the above equivalent circuit into the transmission line model and compare the theoretical impedance spectra with experimental spectra, and if necessary, incorporate refinements into the model.

Recent publications

1 S. J. Lenhart, C. Y. Chao and D. D. MacDonald, An electrochemical and morphological study of the effect of temperature on the restructuring and loss of capacity of alkaline battery electrodes, *Proc. 16th Intsoc. Energy Conversion Eng. Conf.*, Am. Soc. Mech. Eng., 1981.