tion. Cells were conditioned with three formation cycles of 3.2-mA/cm^2-20 h charges and 10-mA/cm^2 discharges. Cycling tests were then run at C/3 discharge and C/5 charge rates. With all the supported liquid membrane separators, the cells cycle at normal current densities, although slightly higher internal cell resistances were noted. Cells with one layer of separator have been cycled from 50 to 100 cycles without dendrite shorting problems. In comparison, cells with one layer of Celgard alone formed dendrite shorts after three cycles.

The accelerated tests run thus far favor dendrite growth on the zinc electrode. The supported liquid membrane outperforms one layer of Celgard 3501 under these conditions. Tests are currently being run on multiple layers of Celgard 3501 for further comparison. An accelerated test, closer to commercial tests, is being developed to maximize dendrite growth and shape change failure modes. This will better be able to demonstrate any positive effects of the supported liquid membrane separator.

The following are planned as part of the continuing research effort during 1983 on supported liquid membranes:

- Optimization of nickel/zinc test cells for direct comparison with state-of-the-art technology;
- Continued fundamental transport studies of the five candidate supported liquid membrane systems including the effect of concentration changes on transport, measurement of transference number for the OH^- ion, and spectroscopic measurements to help understand bonding mechanisms within the organic; and
- Long-term chemical and electrochemical stability tests on new combinations.

TEMPERATURE LIMITATIONS OF PRIMARY AND SECONDARY ALKALINE BATTERY ELECTRODES

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The objectives of this research program are to determine the mechanisms of increased irreversibility of Ni associated with deep discharge at elevated temperatures, quantify the extent of Fe(II) and Fe(III) dissolution at elevated temperatures, and quantify dissolution and conduct further studies of passivation and current oscillation phenomena at Zn electrodes.

SRI has sought to apply 'high information' electrochemical techniques to nickel oxide, iron, and zinc electrodes in an attempt to understand kinetic limitations, or mechanisms leading to increased irreversibility, that may impair iron/nickel oxide and zinc/nickel oxide alkaline batteries. The most important of these techniques are a.c. impedance, potentiodynamic sweep voltammetry and coulometry, rotating ring disk, rotating cylinder collector electrode studies, and semiconductor electrochemistry techniques (photoeffect and measurement of the space charge capacitance as a function of d.c. bias).

Particular emphasis has been directed toward understanding the beneficial effect of lithium hydroxide on the capacity, potential, and life of the nickel oxide electrode. Both the discharged and charged states of the nickel positive electrode may be considered as semiconductors, and the benefits of Li have been ascribed to a doping effect. It has been shown that depending on potential, an n-type or p-type semiconducting oxide can be present, giving rise to anodic or cathodic photocurrents under illumination. Impedance measurements show that a solid state diffusion process, presumably of protons through the oxide film, dominates the impedance behavior for the charged electrode. In the discharged state, the impedance behavior is determined by the space charge inside the p-type oxide. A semiconductor/electrochemical model is able to give a clearer understanding of the mechanisms of charge and discharge of the nickel oxide positive electrode in the presence and absence of Li.

It was demonstrated that an adequate model for the semiconductor properties of nickel oxide in its discharged and charged state is useful in interpreting reaction mechanisms and limitation for the nickel positive electrode. It is intended that further studies be performed on deposited nickel oxide films to determine the influence of possibly beneficial additives in addition to Li. These will be selected from the predictions of SRI's semiconductor model to increase electrode stability or capacity.

Zinc oxide and a number of the oxides of iron formed in alkaline environments also have semiconducting properties. Techniques and theories will be extended to these electrodes. The effect of dopant additives on these electrodes will be studied if applicable.

Recent publications

1 M. J. Madou and M. C. H. McKubre, Impedance measurements and photoeffects on Ni-electrodes, submitted to *J. Electrochem. Soc.*

2 M. C. H. McKubre and M. J. Madou, The dissolution and passivation of iron in concentrated alkali, to be submitted to *J. Electrochem. Soc.*

3 M. C. H. McKubre and M. J. Madou, The dissolution and passivation of zinc in concentrated KOH, to be submitted to *J. Electrochem. Soc.*