

DEVELOPMENT OF A HIGH RATE INSOLUBLE ZINC ELECTRODE FOR ALKALINE BATTERIES

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The objectives are to prepare doped oxides, determine the effect of electrolyte additives in lowering zinc solubility, and characterize electrode/electrolyte combinations that exhibit lowered zinc solubility.

Activated ZnO samples have been formulated that singly, or in combination with dilute electrolyte formulations, result in partially insoluble discharge products. Activated ZnO (prepared by alloy vaporization or by thermally accelerated diffusion of metallic dopants into the ZnO lattice), which had proved to be less soluble than pure ZnO, also proved to be less electrochemically active. This resulted in reduced efficiency, higher degrees of polarization and passivation, and decreased conductivity. These properties are known to be detrimental to the performance of secondary Zn/NiOOH batteries, and this approach was abandoned.

For the above reason, a new approach to electrode material formulation was adopted. Active material was mixed dry with materials that would provide an insoluble matrix after initial reaction in the cell electrolyte. These electrodes are expected to exhibit improved performance in two ways. First, there is an even distribution of permanent, highly conductive nucleation sites along the apparent electrode surface, providing for even Zn deposition and distribution during charging. Second, the increase in effective surface area decreases actual current densities, thereby decreasing overvoltages. This should decrease dendrite formation and gas evolution and allow the use of higher apparent current densities.

Problems posed by the development of this type of electrode material are, for the most part, material-selection problems. Materials must be chosen carefully, not only to fulfill their given function within the electrode system, but also to provide for minimal counter-productive interaction with each other. Electrochemical evaluations of these types of materials show generally favorable behavior.

The electrochemical properties of the ZnO lattice can be altered by insertion of metallic dopants making it less soluble. Decreased solubility also results in a decrease of other types of electrochemical activity, which in turn causes low efficiency and conductivity and increased polarizability. These effects make this an unacceptable approach for the formulation of exclusive anode materials, although use of such formulations as additives may be helpful in combating counter-productive hydrogen evolution.

A more workable approach has been found in the use of pure ZnO in conjunction with other materials, which after initial hydration and charging form a highly conductive and insoluble matrix. This matrix provides in-

creased actual surface area and an evenly distributed network of permanent nucleation sites for Zn deposition.

Full-scale cell tests of some of these anode materials have shown them to form substantially more stable anodes than pure ZnO alone. Performance decay with the repetitive oxidation and reduction of secondary battery cycling has been shown to be minimal.

SUPPORTED LIQUID MEMBRANE BATTERY SEPARATORS

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The purpose of this research program is to develop supported liquid membrane battery separator technology as it applies to the nickel/zinc battery, in particular, to provide a separator that will prevent zinc dendrite growth from shorting out the cell and alleviate capacity loss due to zinc shape changes.

Supported liquid membranes use a highly specific organic transport reagent contained in a microporous membrane support to transport hydroxyl ions while rejecting zincate ions. Five organic reagent-solvent-support systems that meet these criteria have been tested for hydroxyl ion transport using d.c. resistance measurements. Separator resistances are in the range of 15 to 80 ohm cm². These membranes exhibit hydroxyl ion transport and resistance levels adequate for testing in nickel/zinc cells when used as a separator. The five supported liquid membranes when tested for zincate transport in KOH solutions show very low zincate transport rates and are therefore highly specific for hydroxyl ions.

Recent tests using higher concentrations of transport agents indicated the possibility of lowering separator resistance and a value of 7 ohm cm² was measured with one combination.

A number of membrane materials have been tested for use as supports of liquid membranes. Loaded membranes were tested for chemical compatibility with both organic components and KOH solutions and resistivity. Polyvinyl chloride (PVC), PVC copolymer, and nylon membranes all undergo slight chemical attack or swelling when used as a support. Nonwoven polypropylene supports have low resistivity but are not hydrophobic and may gradually allow displacement of organic by KOH solution. Thus far, Celgard 2500 works well, but tests indicate that a similar material with larger pores could improve supported liquid membrane performance. Use of Teflon membranes may be feasible if organic wetting can be improved.

All five combinations of transport reagent-solvent-supports have been tested as separators in nickel/zinc tests cells. The cells used sintered nickel electrodes and polymer bound zinc oxide electrodes in a flooded configura-