This battery meets the requirements for these applications with cell voltages of 1.90 V on charge and 1.62 V on discharge (35 mA/cm^2, 40 °C), with a peak power density of 4.5 kW/m^2. A mean energy efficiency of 84 percent was obtained after 950 4-h cycles using a sintered nickel porous-flow-through positive electrode, a Nafion N-114 separator, and a cadmium-plated iron substrate for zinc deposition. The goal of replacement of sintered nickel by graphite felt has been successfully met with 670 4-h cycles (70 mA h/cm^2 capacity) currently logged, at an energy efficiency of 74 percent. The reduced efficiency is totally due to the use of a separator with higher resistance (Nafion N-125) in current testing, because the N-114 separator is no longer available. Zinc half-cell storage capacity has been demonstrated at 175 cycles for a capacity of 300 mA h/cm^2 and at 260 cycles for a level of 200 mA h/cm^2 with essentially the same values of coulombic efficiency. Similarly, a full-cell test is currently in progress, with 150 cycles logged at capacities between 200 and 300 mA h/cm^2.

Recent work has emphasized the assessment of criteria for scale-up to 1000-cm^2 single cells, evaluation of the solid reactant storage parameters, and definition of the random cycle switching characteristics crucial to solar photovoltaic applications. In addition, studies have focused on material compatibility with alkaline ferricyanide, separator screening, and development of a conceptual engineering design for the zinc/ferricyanide battery system.

The critical technical areas to be addressed during 1982 - 1983 include membrane technology development, critical issues in crystallizer evaluation, continued scale-up and cycle life measurements of cell components, and development of suitable electrode technology to convert the system from monopolar to bipolar configuration.

Recent publications

1 G. B. Adams, R. P. Hollandsworth and E. L. Littauer, Rechargeable alkaline zinc/ferricyanide hybrid redox battery, *Proc. 16th Intsoc. Energy Conversion and Eng.*, *Am. Soc. Mech. Eng. Conf.*, *Paper #819383*, 1981, pp. 812 - 816.

FOULING AND CONDUCTANCE OF ANIONIC PERMSELECTIVE MEMBRANES

Sandia National Laboratories, Albuquerque, NM 87185 (U.S.A.)

The objectives are to examine the fouling mechanism and to model the membrane's conductance in order to understand how the membrane's structure affects its performance. This understanding will aid in the modification of existing membranes and the synthesis of new membranes.

The NASA iron/chromium redox battery being developed for photovoltaic and utility load-leveling applications uses an anionic permselective membrane to provide electrical continuity while keeping the reactants separate. The membrane's ability to successfully perform these two functions directly affects the battery's lifetime and efficiency. The membrane resistance increases as a function of time when exposed to a ferric chloride solution. This increase in resistance is termed fouling. The first task was to understand the fouling mechanism.

The principle characteristics of fouling are that (1) the resistance increases slowly when exposed to ferric chloride but decreases rapidly when exposed to hydrochloric acid, (2) the fouling resistance of a membrane having both sides exposed to ferric chloride is much greater than twice the fouling resistance of a membrane having only one side exposed to ferric chloride, and (3) the fouling resistance is a nonlinear function of the amount of iron associated with the fouled membrane. These characteristics could be explained by assuming that the highest concentration of iron is at or near the surface of the membrane analogous to the fouling of reverse osmosis membranes by contaminants. This hypothesis was tested and found to be false by quantitative electron microprobe analysis, which showed a uniform distribution of iron throughout a membrane that had been exposed to ferric chloride for a short time.

It was hypothesized that the iron may cause the membrane to form ionic clusters just as perfluorinated cationic membranes are known to cause metal salt formation. The formation of clusters has been shown to result in an increase in resistance. No evidence of clustering, however, could be detected by small angle X-ray diffraction of fouled membranes.

The amount of water in the membrane was found to decrease when the membrane becomes fouled. The water loss was shown to be related to both an osmotic effect from placing the membrane in an ionic solution and a displacement effect when the ferric chloride enters the membrane. The next objective was to characterize the resistive behavior of the fouled membrane in terms of its water loss using percolation theory. Percolation theory describes the resistance of a system consisting of conducting particles embedded in a nonconducting matrix. The ion-containing aqueous phase of the membrane corresponds to the conducting 'particles', while the polymer resin corresponds to the nonconducting matrix. The model successfully fits the observed data, and the fitting parameters were shown to be physically reasonable. Although the model makes use of adjustable parameters and does not consider details of the conductance process, it is successful in establishing the fouling mechanism. Fouling is a function primarily of the quantity of water available to provide a conductance path. Specific chemical interactions or changes in the polymer structure do not appear to be of importance.

Although our study of fouled membranes established the importance of water, a fouled membrane could not be modeled in detail because the equilibria governing the formation of ferric chloride complexes are not known. The second task was to calculate the properties of membranes in 1N

HCl from first principles. The membranes modeled were those prepared by C. Arnold, Jr., for his factorial synthetic program. The resistances were represented as a product of three factors: the concentration of ions in the membrane, the mobility of the ions in a dilute aqueous solution and, the effect of the membrane on the ions' pathway. The agreement between theory and experiment is excellent. The model predicts that increasing the percent water in the membrane provides a trade-off between resistivity and selectivity, and increasing the ion exchange capacity can provide both characteristics. C. A. Arnold is synthesizing membranes incorporating these ideas.

A low-cost, stable cationic exchange membrane is required by the Lockheed zinc/ferricyanide redox storage battery. During 1983 membranes that are offered commercially or have been prepared specifically for severe environments will be screened and tested. Selected membranes will be analyzed in detail to elucidate the degradation mechanism. Procedures by which uniform distributions of ionic sites can be prepared by radiation grafting with the least amount of radiation damage will be examined.

STRUCTURE–PROPERTY RELATIONSHIPS OF ANIONIC PERMSELECTIVE MEMBRANES

Sandia National Laboratories, Albuquerque, NM 87185 (U.S.A.)

Our primary objective was to define the relationships between structure and properties of anionic permselective membranes and use this knowledge to develop improved membranes for use in NASA's Fe/Cr redox storage battery. A secondary objective was to develop statistical models that could be used to predict membrane performance.

Membranes with lower resistance, higher selectivity, and reduced susceptibility toward fouling are required to improve the efficiency and lifetime of the Fe/Cr redox storage battery developed by NASA. The relationships between these properties and such structural parameters as the degree of crosslinking, ion exchange capacity, and porosity were not adequately understood. To gain a better understanding of the structure-property relationships of anionic permselective membranes, each of the aforementioned structural parameters was varied over rather wide ranges in a factorial study. The advantages of using a factorial experimental design as opposed to the classical 'one-factor-at-a-time' approach are two-fold: (1) the effect of each structural variable is determined at different levels of the other variables — in this way the effect of a single variable can be isolated and interactions identified and (2) main effects and interactions can both be quantified — this allows one to develop predictive models.