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

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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.

To implement this factorial study, a series of model membranes was synthesized from ethylene glycol dimethacrylate, 4-vinylpyridine, and ethyl hexylmethacrylate. Membranes were rendered porous by carrying out the polymerization in the presence of isobutanol. The use of ethyl hexylmethacrylate as a diluent allowed the adjustment of all three structural parameters independently.

It was found in these studies that increasing the ion exchange capacity had a beneficial effect on all three membrane properties. Thus, increasing the ion exchange capability reduced the initial resistance, permeation, and fouling. In the case of initial resistance, an interaction was observed between ion exchange capacity and porosity. At low porosity, increasing the ion exchange capacity resulted in a dramatic tenfold decrease in resistance; in contrast, at high porosity, the effect of ion exchange capacity was negligible.

Although the effect of crosslinking on initial resistance was negligible, beneficial trends were noted with respect to selectivity and fouling. The relationship of crosslinking to these latter membrane responses was rather complex as evidenced by the existence of multiple interactions.

The main effect of increasing porosity was to decrease membrane resistance and fouling at the expense of higher iron permeation. Again, multiple interactions were detected between porosity and the other structural variables when permeation and fouling were the properties monitored.

The trends described above suggest that it should be possible to make improved membranes by increasing the ion exchange capacity and degree of crosslinking while holding the porosity at some optimum intermediate value. To date, however, difficulties have been encountered in synthesizing high ion exchange membranes that are leakproof.

It is noteworthy that one of the model membranes, the one with high ion exchange capacity and crosslinking and low porosity, had better selectivity and fouled less than the membrane that is currently used in the NASA battery.

The Zn/ferricyanide redox storage battery developed by Lockheed requires an inexpensive cation exchange membrane that is stable to the combined influence of ferricyanide and sodium hydroxide for long time periods. During 1983 we plan to synthesize new membranes that embody structural features that should enhance stability against oxidative attack by ferricyanide. Ferricyanide attack occurs at the most activated hydrogen and initiates a free radical chain reaction, which results in scission of the backbone and attack on neighboring chain molecules. In the membranes that are to be synthesized, these unstable hydrogens will be eliminated.