

PROCEEDINGS OF THE SYMPOSIUM ON

# DIAPHRAGMS, SEPARATORS, AND ION-EXCHANGE MEMBRANES

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*INDUSTRIAL ELECTROLYTIC, BATTERY, AND PHYSICAL  
ELECTROCHEMISTRY DIVISIONS*

Proceedings Volume 86-13

ELECTROCHEMICAL SOCIETY, INC., 10 South Main St., Pennington, NJ 08534-2896

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## PREFACE

This proceedings volume consists essentially of papers presented at the Symposium on Diaphragms, Separators, and Ion-Exchange Membranes which was held during the Spring 1986 Meeting of The Electrochemical Society in Boston, Massachusetts. The symposium was sponsored jointly by the Industrial Electrolytic, Battery, and Physical Electrochemistry Divisions of the Society. Thus, most of the papers contained herein cover the applications of separator technology in these electrochemical areas.

The papers were submitted in camera-ready form which limited the amount of editing possible. The editing philosophy was that the content of the material and its rapid dissemination were more important than its form. Thus even though misspellings and major grammatical errors were corrected, there was no attempt to revise the material to correct solecisms. However when possible technical errors were found, the authors were contacted and the errors corrected. In general inexplicit Tables and Figures are qualified in the text, but sometimes corrections to these were required also. A comprehensive index is also provided. Page numbers indicate the specific page where the key word appears.

The editors would like to thank the authors for their contributions, their patience in following the camera-ready guidelines, and the care they took preparing their work. Also, the editors would like to thank Ms. Laura A. Lucas for typing parts of this volume and for her help in preparing the index.

J.W. Van Zee  
R.E. White  
K. Kinoshita  
H.S. Burney

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## NAFION®\* AS A SEPARATOR IN ELECTROLYTIC CELLS

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### ABSTRACT

The availability of perfluorinated ion exchange membranes of exceptional chemical stability and electrochemical properties has opened new opportunities for the application of electrochemical technology in the chemical process industry. Examples are provided in the area of manufacturing chemicals, in mineral extraction (hydrometallurgy), in the regeneration of plating and metal finishing solutions and in the reclamation of chemicals from effluents. Membrane selection and design of laboratory and industrial cells will be discussed.

It is certainly a pleasure and an honor to address this distinguished group. I would like to use this opportunity to give credit to our many customers, whose vision and continued belief in the future of membrane technology was an important factor in the commercial application of ion exchange membrane technology in the production of chlorine and caustic. This commercial success of NAFION® is the foundation on which our plant in Fayetteville, North Carolina, was built.

The development of NAFION® is briefly reviewed in Figure 1. It took many years of intensive research work to develop a structure which met the unique and demanding requirements of chloralkali service.

Figure 2 shows the composition of NAFION®. A vinyl ether comonomer is copolymerized with TFE to form a melt-fabricable precursor polymer. After fabrication into the desired shape, the sulfonyl fluoride group is hydrolyzed to the ionic sulfonate form. The comonomer ratio,  $n$ , is selected to tailor the properties of the polymer for a given application. A similar polymer containing carboxylate functions is used as a barrier layer to achieve the high degree of  $\text{OH}^-$  ion rejection needed for chloralkali applications. Several Japanese companies have made important contributions toward the recognition of the unique advantages of carboxylate polymers for this application.

The hydrophilic fluorocarbon component and the hydrophobic ionic groups are incompatible. It is, therefore, not surprising that a

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degree of phase separation occurs, leading to the formation of interconnected, hydrated ionic clusters which determine the electrochemical properties of the polymer. The function of the fluorocarbon phase could be compared to that of divinyl benzene in polystyrene based ion exchange resins because it controls the swelling and prevents the ionic phase from dissolving. As the temperature is increased, these restraining forces are weakened. The fluorocarbon chains develop enough mobility to adjust to a more highly swollen state. This is why it is so important to condition a membrane before use. At even higher temperatures, the fluorocarbon phase melts and permits the ionic phase to dissolve in a mixture of alcohol and water (Figure 3). We believe that the liquid obtained is not a true solution, but that the incompatibility of the fluorocarbon phase with the solvent causes the formation of micelles surrounded by ionic groups. The continuous fluorocarbon phase in solid NAFION® has been converted into a dispersed phase. The temperature necessary to dissolve NAFION® is then simply the temperature necessary to achieve phase inversion.

If the solvent is evaporated at room temperature, the morphology of the discontinuous fluorocarbon phase is largely preserved. Such a film is weak and will readily redissolve in alcohol. If, however, the solvent is evaporated hot or if the cast film is heated to 100 to 120°C, the dispersed fluorocarbon phase will to some extent fuse together and the film will become insoluble.

Figure 4 shows the forms of NAFION® which are available for a broad range of applications. Du Pont supplies the first two items on this list; the other three are available through other companies.

This paper reviews only the first two items, particularly the second one, and Figure 5 lists the types of NAFION® supplied by Du Pont for these applications. We start with NAFION® 117, an unreinforced film of the sulfonate polymer. For many industrial applications, a reinforcing fabric made of TEFLON®\* is added to produce NAFION® 435. NAFION® 324 contains an additional higher EW barrier layer for improved anion rejection. It can be used over the entire pH range. Even better anion rejection is achieved in NAFION® 901 through the use of a carboxylate barrier layer. This membrane, however, cannot be used at low pH.

Figure 6 shows the general reactions at the three-phase boundaries of a divided electrolytic cell: Oxidation and Reduction where the electronic and ionic conductors meet and cation transport if a cation exchange membrane is used as a separator. In a given application, one, two or all three of these reactions may be important although, of course, all three must occur. Note that some of these reactions involve only liquids and gases; others also involve solids. This is important for the design of the cell.

Figure 7 shows some of the electrochemical reactions carried out using NAFION® separators. Most of these reactions can also be

accomplished by other means. One advantage of the electrochemical route is the absence of byproducts. This eliminates the need for extensive separation and purification steps and the resulting yield losses. An example is the conversion of a salt, such as sodium borate, to the corresponding acid. In the conventional process, addition of sulfuric acid is used, followed by separation of the byproduct sodium sulfate by fractional crystallization. It is difficult to achieve high yield and high purity at the same time. The same is true for the manufacture of the two plating chemicals shown (for gold and tin plating): The mother liquor from the crystallization of the product can be used as the electrolyte for the next batch. Note that in the case of gold, NAFION® is used on a commercial scale in both the forward and reverse reaction.

The manufacture of chlorine and caustic is, of course, the most important application for NAFION®, and Japan has been the world leader in applying this new technology on a commercial scale. The in-depth discussion of this subject is beyond the scope of this paper. I would, however, like to show you a very small cell used for providing chlorine to a swimming pool (Figure 9). Most of the apparatus is occupied by salt storage to provide unattended operation for long periods of time.

Figure 10 shows the regeneration of a chromic acid solution. The objective could be the oxidation of three valent chromium to chromic acid, the removal of some cations, or both. Three valent chromium would be present in a chrome etchant bath for plastic parts or from the chrome plating of the inside of pipes. Metal ion contamination could arise from a variety of applications, including anodizing and surface treatment of metals.

Figure 11 shows a chromic acid regeneration cell developed by the U.S. Bureau of Mines. Note the open tank design permitting easy servicing of the electrodes and membranes and minimizing the chances of spilling chromic acid.

Another cell design is shown in Figure 12. This particular installation is at the Ford Motor Company. Three cylindrical electrolytic cells are used in conjunction with a common catholyte tank. Cooling is provided by a TEFLON® Heat Exchanger installed in the catholyte tank. The general layout is shown in Figure 13. The cell uses a cylindrical NAFION® membrane. Sealing on top and bottom is provided by O-rings of VITON® elastomer (Figure 14).

Plating chemicals can be prepared by dissolving a metal anode. The membrane prevents the metal from being plated again on the cathode. The first example is potassium stannate made by dissolving tin ingots placed in an anode basket (Figure 15). The dissolved tin is two valent, and air oxidation brings it to the four valent state.

KOH is formed in the cathode compartment and is recycled to the anode compartment. If an anion exchange membrane would be used as a separator, this recycle would not be necessary. The cation exchange membrane, however, is so superior in long-term stability and other properties that it is the preferred separator.

An open tank design makes it easy to add tin ingots. The cathodes are inside a bag made from NAFION®.

Another example of the electrochemical production of plating chemicals is  $\text{KAu(CN)}_2$ . The simple chemistry, free from byproducts, reduces processing and handling and the resulting yield losses.

The reverse reaction (Figure 17) is used in gold mining. The membrane eliminates interference of  $\text{O}_2$  at the anode and corrosion of the stainless steel anode by "trouble" anions (chloride, sulfate) in the pregnant solution. In order to plate out gold effectively, even at very low concentration, a high surface area steel wool cathode is used.

This concept is important not only in the electrowinning of metal in hydrometallurgical operations, but also in the removal of metals from waste streams. Special consideration has to be given to the potential distribution in such a three-dimensional electrode (Figure 18). While the potential of the metal is nearly constant throughout the thickness of the electrode, the potential of the electrolyte is not. The thickness,  $d$ , the current density and the conductivity of the electrolyte must be selected so that an excessive potential difference at the front of the electrode is avoided. Otherwise, excessive  $\text{H}_2$  evolution would reduce current efficiency.

A high surface area cathode may also consist of a packed bed (Figure 19), in this case of graphite particles. The recovered metal may be removed from the cell either by exchanging the packing or by current reversal. In this example, the metal is recovered as a concentrated solution free from other contaminants of the original waste stream and possibly associated with a different anion. Note that in this design the right-hand electrode is always idling, making oxygen during metal deposition and hydrogen during dissolution. A symmetrical cell design, with high surface area electrodes on both sides, could combine deposition and dissolution in a single operation.

Figure 20 illustrates the conversion of a salt to its corresponding acid. A pair of conventional anion exchange columns is used to remove chromate ions from the rinse water. Regeneration with sodium hydroxide results in a concentrated solution of sodium chromate or dichromate. This is converted to chromic acid in the electrolytic cell. The chromic acid can then be returned to the plating bath. Note that other contaminants in the rinse are not returned. Sodium hydroxide generated in the cathode compartment is used for the regeneration of the ion exchange columns. In this application the electrode reactions are incidental and only the ion transport through the

membrane is important. The example relates to the clean-up of a rinse water from a plating operation, but similar chemistry could be used for the manufacture of weak or moderately strong acids such as boric acid. If the acid is sensitive to oxidation, a three-compartment cell is used.

Work on NAFION® was carried out at the Experimental Station, which is located at the same site where the Du Pont Company was founded as a manufacturer of black powder more than 180 years ago. A development of this magnitude is possible only through the contributions of many individuals, whom I wish to acknowledge in closing.

FIGURE 1  
CHRONOLOGY OF NAFION<sup>®</sup>

1962	Discovery of NAFION
1964	First demonstration as a separator in a chloralkali cell
1966	Use of NAFION in H <sub>2</sub> /O <sub>2</sub> fuel cells
1970	Development of fabric reinforced NAFION
1971	Introduction of barrier layer to improve OH ion rejection
1972-76	Selection of optimum barrier layer chemistry
1977-79	Construction to start-up of plant at Fayetteville, NC

FIGURE 2  
SYNTHESIS OF NAFION<sup>®</sup> COPOLYMERS

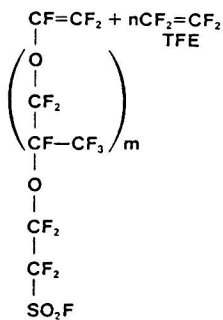


FIGURE 3

# Phase Inversion of NAFION®

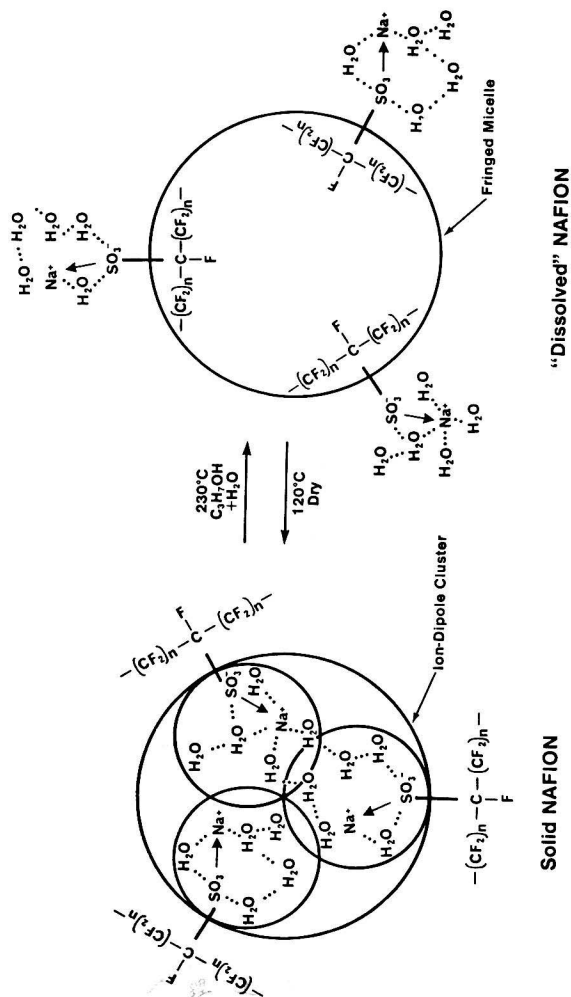


FIGURE 4

**Applications for NAFION®**

Form	Application
Film	Fuel Cells, Batteries
Membrane	Electrolytic Cells
Tubing	Gas Drying, Dialysis
Powder	Catalysis
Solution	Coated Electrodes

FIGURE 5

**NAFION® for Electrolytic Cells**

NAFION	Construction	Application
117	Unreinforced Film -SO <sub>3</sub> H	Batteries, Fuel Cells
324	Reinforced Bimembrane -SO <sub>3</sub> H	Improved Selectivity in Acid Medium
435	Reinforced Membrane -SO <sub>3</sub> H	General Purpose
901	Reinforced Bimembrane -SO <sub>3</sub> K/-CO <sub>2</sub> K	Chloralkali

FIGURE 6

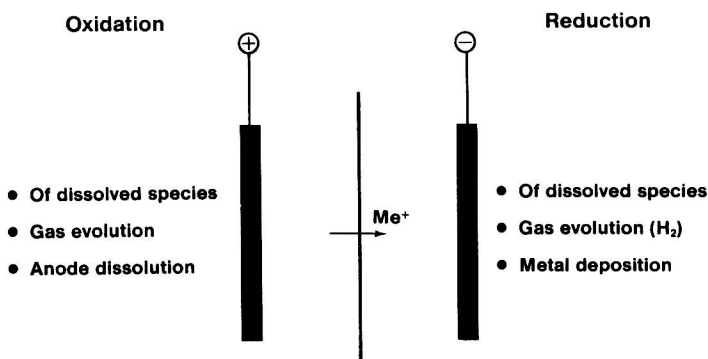
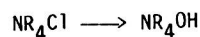
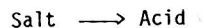
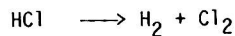
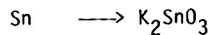
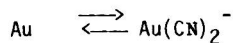
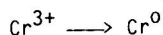
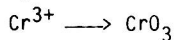
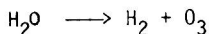
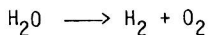
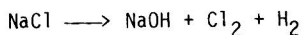
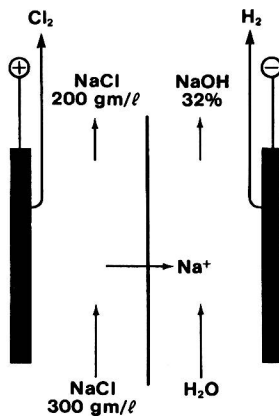
**General Processes in an Electrolytic Cell**

FIGURE 7

**SOME ELECTROLYTIC APPLICATIONS FOR NAFION®**

## NaCl Electrolysis

FIGURE 8



## Swimming Pool Chlorinator

FIGURE 9

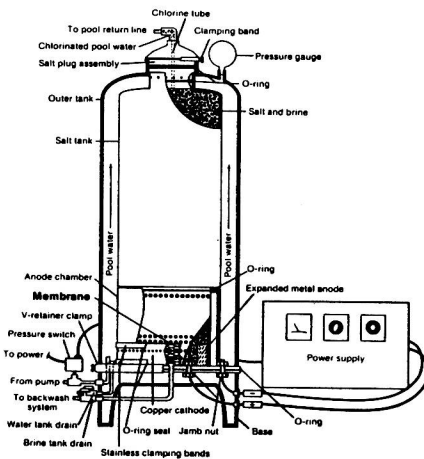




FIGURE 10

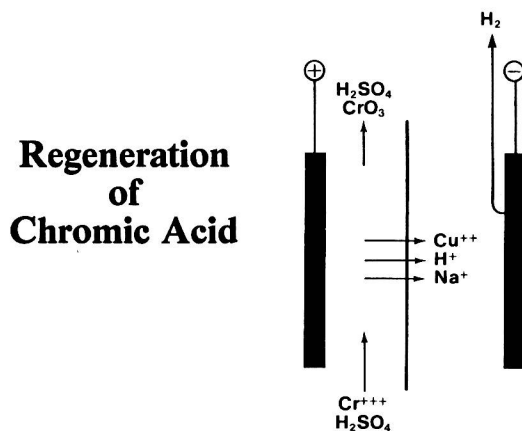


FIGURE 11

