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Dehydration of nitric acid using perfluoro carboxylate ionomer membranes

Richard L. Ames[a,b,*], J. Douglas Way[b], Elizabeth A. Bluhm[a]

[a] *Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM 87575, USA*
[b] *Colorado School of Mines, Chemical Engineering Department, Alderson Hall, 1500 Illinois Street, Golden, CO 80401, USA*

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Abstract

Investigations determined the feasibility of using perfluoro carboxylate ionomer films for the dehydration of nitric acid. Motivation for this effort was the speculation of improved water selectivity (nitrate rejection) for the carboxylate film when compared to the dehydration using perfluoro sulfonate or sulfonate/carboxylate composite films. The methodology used was to generate solution cast perfluoro carboxylate ionomer films, characterize the film and to assess the film's aqueous transport performance. Experimental results suggest that the cast films had a reduction in ion-exchange capacities when compared to “as received” films by as much as 56% due to the generation of an ester form of the ionomer during the dissolution/casting process. Nitric acid pervaporation experiments showed that permeate fluxes were two orders of magnitude smaller for the cast films when compared to ionomer sulfonate films of similar thickness (sulfonated Nafion^{TM} 111). Water separation efficiencies (α) were demonstrated to be one order of magnitude higher for the carboxylate cast films when compared to sulfonated Nafion^{TM} 111.

Keywords: Composite membranes; Diffusion; Ion-exchange membranes; Membrane preparation and structure; Pervaporation; Nitric acid dehydration

1. Introduction

Current applications of perfuoro sulfonate [R–SO_3M], carboxylate [R–COOM], or sulfonate/carboxylate composite ionomers include use as cell components in batteries, diffusion rate limiting barriers in time-release drug systems, proton exchange membranes in fuel cells, and as ion exclusion partitions in acid dehydration [1–6]. Acid dehydration systems are of recent interest in commercial (acetic acid production) and federal (acid recycle and purification) entities investigating the potential of the ionomer films in acid concentration and liquid waste reduction systems [7,1,2,3]. Interest at the Los Alamos National Laboratory (LANL) in perfluoro carboxylate ionomer membranes stems from the potential of applying the technology to nitric acid dehydration. Currently the facility uses an acid recycle system designed around distillation where bottoms from the column are recycled to the plant facilities and overheads are discarded as waste.

During these investigations it was determined that thin perfluoro carboxylate ionomer films could be synthesized using solution casting, these polymers were characterized and preliminary pressure and pervaporation transport data were developed for pure water and nitric acid feeds. Investigations beyond the scope of this effort will determine if these films have potential application at the Los Alamos National Laboratory.

1.1. Perfluoro carboxylate and sulfonate membranes

Perfluoro carboxylate membranes were first synthesized by E.I. Du Pont de Nemours and Company in the 1960s from

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[*] Corresponding author. Tel.: +1 303 384 2017; fax: +1 303 273 3730.
E-mail address: rames@mines.edu (R.L. Ames).

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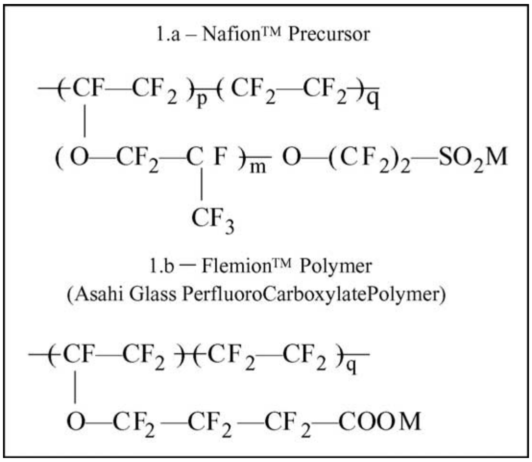

Fig. 1. Nafion^{TM} precursor and Flemion^{TM} ionomer chemical structures.

chemistry developed for the perfluoro sulfonate ionomer [1]. An ionomer film precursor is made by the copolymerization of tetrafluoroethylene (TFE) and a functionalized form of TFE which allows the introduction of an ionic side chain. Both the sulfonate and carboxylate (Nafion^{TM}) products are made from the resulting perfluoro precursor polymer film shown in Fig. 1a, where *m* is 0, 1 or 2, *p* is from 1 to 10, *q* is from 3 to 15, and M is either F or H [8,9]. For example, for the perfluoro sulfonyl fluoride precursor shown in Fig. 1a having the pendant chain

$$-\mathrm{O}-(\mathrm{CF}_2)_2-\mathrm{SO}_2\mathrm{F} \qquad (1)$$

reaction with an oxidizing agent will convert the pendant chain to

$$-\mathrm{O}-\mathrm{CF}_2-\mathrm{COOH} \qquad (2)$$

This reaction takes place at an elevated temperature (50–60 °C) or in the presence of a metal catalyst (salts of iron, vanadium or copper) at room temperature. Conversion to the ionic sulfonate (Nafion^{TM}) membrane pendant side chain

$$-\mathrm{O}-(\mathrm{CF}_2)_2-\mathrm{SO}_3\mathrm{H} \qquad (3)$$

is achieved by the hydrolysis of the precursor. In addition, films with a mixture of both the carboxylate and sulfonate pendant chains (Eqs. (2) and (3)) can be synthesized by controlled exposure of the precursor film to oxidizing and reducing reagents [10]. Finally, Asahi Glass Corporation has developed a perfluoro carboxylate ionomer (Flemion^{TM}) with the short pendant chain (when compared to those films manufactured by Du Pont) shown in Fig. 1b, where *q* is from 3 to 15 and M is either CH_3, F, a metal salt or H [11,12]. Solution cast membranes tested in this study were synthesized from Asahi Flemion^{TM} feed material.

2. Experimental

The ultimate purpose of this effort was to determine the ability of solution cast perfluoro carboxylate ionomer membranes to dehydrate nitric acid. Characterization of cast films was useful in attempting to explain film behavior and to compare results with similar ionomer films and with results from previous investigations. Described below are characterization techniques and equipment used, general descriptions of dissolution/casting procedures, as well as descriptions of transport systems and operating procedures.

2.1. Ionomer film generation

Preliminary pressure transport tests conducted with 162 μm thick, "as received" Flemion^{TM} carboxylate ionomer film indicated that pure water permeation rates were too low to measure even at trans-membrane pressures up to 900 psig. Sportsman also discovered that permeate fluxes could not be measured through this film for pure water, 50 wt.% or concentrated nitric acid feeds during pervaporation tests with permeate pressures of 11×10^2 Pa (8 Torr) [3]. By producing solution cast perfluoro carboxylate materials in-house we had the ability to synthesize thin films with measurable fluxes that could be the subject of nitric acid dehydration studies. Polymer dissolution and casting procedures used were developed based on the techniques reported in literature using perfluoro sulfonate films [13–18].

2.2. Solution casting

Because commercial manufacturers offer limited film thickness options, procedures were developed to dissolve and recast perfluoro sufonate films [16–18]. Solution casting of perfluoro carboxylate films has not been reported prior to this work, yet, using reagents, equipment and procedures similar to those described by Moore et al., successful dissolution and solution casting of thin films was accomplished with "as received" Flemion^{TM} carboxylate ionomer membrane feed (K^+ form, EW of 1.25 mmol eq^{-1}, membrane thickness 162 μm). The procedure consisted of dissolving the feed Flemion^{TM} in a 50:50 mixture of de-ionized (Milli-Q^{TM} processed) water and propanol for 4 h at 190 °C [17]. The resulting solution was clear to slightly cloudy (colloidal) containing approximately 1–3 wt.% ionomer. Dissolution was accomplished at pressure in a Parr Instrument^{TM} acid digestion bomb (model 4766) fitted with a custom made Teflon^{TM} block liner, in turn lined with a 60 ml, glass dissolution vessel.

Solution casting of perfluoro carboxylate films (solcast films) was carried out in a National Appliance Co. model 5831, vacuum oven in three 3 h stages (at temperatures of 100, 130 and 150 °C) at 2 in. Hg vacuum. The dissolved ionomer solution was mixed with *N*,*N*-dimethylformamide (DMF), placed in a level, 7 cm diameter, tempered glass, flat-bottom casting vessel, and held at temperature and vac-