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Determining Extent of Ion-Exchange in Various Counterion Nafion Membranes Using Prompt Gamma Neutron Activation Analysis (PGAA)

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Abstract

Researchers have performed structural evaluations on Nafion membranes for many years. Various research groups have published a large volume of data; however, much of the work done by these groups is contradictory. One important aspect of the membranes is the chemical uniformity and quantity of water within the membrane under investigation. A new technique that has shown its usefulness for providing accurate and fast quantitative measurements of chemical composition quickly is prompt gamma neutron activation analysis (PGAA). In this work, a sulfonyl fluoride-form membrane, an as-received membrane from the manufacturer, and several differently pretreated H^+-form Nafion membranes were examined using PGAA. The evaluation showed the necessity for pretreatment of membranes to eliminate contamination. A series of counterion-exchanged membranes were also examined to determine maximum conversion achieved and to identify possible limitations to complete conversion. The results show that it is possible to obtain nearly complete or complete conversion to the counterion from the H^+-form Nafion samples. Water content can be limited within the membrane but not eliminated. In samples that were not pretreated, complete ion exchange was limited by the contamination.

Acknowledgments

The authors would like to acknowledge the use of the facilities at the National Institute of Standards and Technology (NIST) Center for Neutron Research in performing all of the prompt gamma neutron activation analyses. The post-doctoral program, under the auspices of the American Association for Engineering Education, is acknowledged for financial support of Sandra K. Young. Dr. Donald Rivin of the U.S. Army Natick Soldier Center is also acknowledged for his helpful technical input.

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1. Introduction

Nafion is a perfluorosulfonate ionomer (PFSI), consisting of a tetrafluoroethylene main chain and a perfluoroether sulfuric acid side chain [1] (Figure 1). Coulombic interactions between the ions in Nafion result in aggregation of the sulfonate groups into tightly packed ionic regions referred to as "clusters." Ionic clustering in Nafion improves the material's mechanical, thermal, and transport properties. The relationship between these properties and the membrane's structure have made Nafion the focus of many structural studies [1–8].

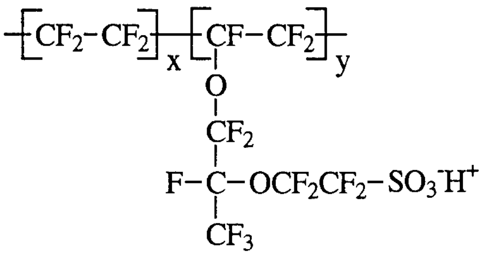

Figure 1. Nafion PFSI.

Critical to any property analysis of Nafion membranes is chemical knowledge of the counterion associated with the perfluorosulfonic acid group and the quantity of water within the membrane. The sulfonic group ($-SO_3-$) is the sole site for variation in the membrane through simple chemical manipulations. The counterion, whether a proton, alkalai metal, or other metal cation, has an effect on the interactions of the sulfonic acid or sulfonic acid salt groups, which, in turn, affects the strength of the ionic aggregates. The presence of small amounts of ion exchange, while altering the chemical structure, can also change the interaction of the aggregates. Therefore, a method for identifying the ion(s) at the exchange site is needed to fully characterize the membranes.

To date, changes regarding the sulfonic acid site, the resulting molecular structure, and molecular motions in addition to the presence and effect of water (and other solvents) regarding Nafion have been characterized through many means of chemical analysis. Research groups [9, 10] have utilized Fourier transform infrared (FTIR) spectroscopy for identification of the sulfonic acid side chains, the inter-associations with water, and the intra-associations between waters within the Nafion membrane. Proton and deuterium nuclear magnetic resonance (NMR) have been used by many researchers [11–15] for quantitative measurements of water and investigating the molecular motions within Nafion by monitoring relaxation times of the molecules. Dynamic mechanical analysis

(DMA) has long been used to follow the change in molecular motions within Nafion as a result of changes of the atom [16] associated with the sulfonic acid, mobility [17] on the sulfonic site, and solvent effects [18, 19] on the membrane. Wide-angle x-ray diffraction (XRD) has been used to determine the crystallinity of Nafion membranes [20], which affects mobility within the polymer chains. Following the significant theories reported in the field of ionomers [21, 22], many researchers performing small-angle scattering (SAS) experiments continue discussions about the morphology of Nafion, counterion effects, and solvent effects on the morphology [23–27].

Cold-neutron-capture prompt gamma neutron activation analysis (PGAA) is a new, ideal method for the evaluation of composition on Nafion membranes due to its nondestructive nature and sensitivity to trace ions, especially hydrogen. The technique for PGAA is described in detail elsewhere [28–29]; the basics are as follows (see Figure 2):

- When a sample is placed in a neutron beam, nuclei of many elements in the sample absorb neutrons and are transformed to an isotope of higher mass number in an excited state.
- Prompt gamma rays, emitted by de-excitation of the compound nuclei, are then measured using a high-resolution gamma-ray detector.
- Qualitative analysis is accomplished by identification of the gamma-ray energies, while comparison of gamma-ray intensities with those emitted by a standard yields quantitative analysis. The use of "cold" neutrons enhances the sensitivity.

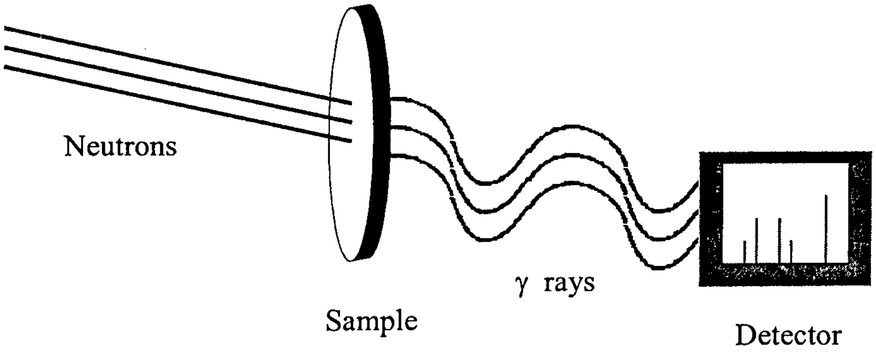

Figure 2. Sample undergoing prompt gamma analysis.

The limit of detection or the smallest possible detectable amount for prompt gamma analysis varies from element to element [28, 29]. Limits of detection for many elements measured are summarized in Table 1. The table gives the range in which the detection limit for each element lies. These ranges do not represent the range of detectable quantities for these elements, as, for example, quantities

Table 1. Elements and detection limits for PGAA.

Range (μg)	Elements
0.01–0.1	B, Cd, Sm, Gd
0.1–1	Eu, Hg
1–10	H, Cl, In, Nd
10–100	Na, S, K, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Ge, As, Se, Br, Mo, Ag, Te, I, Au
100–1000	Mg, Al, Si, P, Ca, Fe, Zn, Ga, Rb, Sr, Y, Zr, Nb, Sb, Ba, La
1000–10,000	C, N, F, Sn, Pb

of hydrogen at concentrations much greater than 10 μg/g can be detected. The limit of detection for any given element is not an absolute, but depends on the matrix of the sample (i.e., the detection limit for hydrogen measured in silicon is different from the detection limit for hydrogen measured in titanium).

PGAA has many advantages to other experimental techniques. The real usefulness for prompt gamma is its ability to detect the light elements (such as hydrogen and carbon), which are not readily detectable by other methods. Other advantages of PGAA over other experimental techniques are: (1) the analysis is performed in situ (the element not extracted from matrix, i.e., nondestructive); (2) the signal arises from a nuclear rather than chemical process, hence results are not dependent on the chemical form of the element present; and (3) neutrons and gamma rays penetrate the whole sample, hence the bulk of the sample is analyzed and not just the surface, which is especially important in thicker films.

When starting work on the Nafion program, several samples consisting of acid-form, potassium-form, and calcium-form Nafion were analyzed using small angle neutron scattering (SANS). These samples were both samples made at the U.S. Army Research Laboratory (ARL) and samples received from an external collaborator. When the SANS data was reduced, very different SANS patterns were observed for same counterion samples made at ARL when compared to the externally received samples. This was of some concern since it was not obvious why this would occur, whether it was due to contamination or other possible heat treatments incurred during transport of the samples. During deliberations of this problem with several National Institute of Standards and Technology (NIST) colleagues, the facile and practical use of PGAA in analysis of materials was discussed. While the SANS data will be discussed in a separate report, the PGAA analysis was used to elucidate these problems and work on other counterion issues involving Nafion.

In this investigation, we apply PGAA to the characterization of ion and water content in Nafion membranes that have been subjected to a variety of drying, pretreatment, and counterion exchange conditions. These measurements are used to evaluate the effectiveness of various treatments for removing water and contaminants in the membranes and confirm the efficiency of ion-exchange reactions.

2. Experimental

2.1 Materials*

PFSI membranes (1100 equivalent weight, 7 mil thick) in the SO_3H-form (Nafion 117) were obtained from C. G. Processing, Inc. Concentrated hydrochloric acid (HCl), concentrated nitric acid (HNO_3), potassium chloride (KCl), cesium chloride (CsCl), calcium chloride ($CaCl_2$), zinc chloride ($ZnCl_2$), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$), aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$), and ferrous chloride ($FeCl_3$) were all obtained from VWR Scientific and used as received. All water utilized was distilled and deionized (DI/DS).

2.2 PFSI Membrane Pretreatments

Pretreatment 1 [30]: The membranes were cleaned in boiling concentrated nitric acid for 1 hr, rinsed several times with pure water, and dried overnight at 110 °C.

Pretreatment 2 [31]: The membranes were refluxed in 2 normal (N) HCl for 3 hr at 80 °C and then rinsed with H_2O for 3 hr.

Pretreatment 3 [32]: A common membrane pretreatment where the membranes were refluxed in 3% H_2O_2 for 1 hr, refluxed in DI H_2O for 1 hr, refluxed in 0.5 molar (M) H_2SO_4 for 1 hr, and refluxed in DI H_2O for 1 hr.

Pretreatment 4 [33]: As-received membranes were exchanged to the acid form by refluxing in 50% HCl:50% HNO_3 solution (v:v), leaching out excess acid in deionized water reflux (3×), and finally vacuum drying at 125 °C. All membranes were exchanged to this standard initialized state prior to counterion exchange and prompt gamma analysis in order to assure maximum sample reproducibility.

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[*] Certain commercial products are identified in this report in order to specify the experimental procedures in adequate detail. This identification does not imply recommendation or endorsement by the authors or by NIST, nor does it imply that the products identified are necessarily the best available for the purpose.

2.3 Formulation of Ion-Exchanged Nafion Membranes

2M and 0.01M solutions of each salt were made in 1-liter volumetric flasks. Samples of initialized, H^+-form Nafion were cut to approximately 3-cm × 3-cm squares.

2M Salt Solutions. Membranes were soaked in an excess of the 2M salt solutions for 24 hr (step 1). The solution was then brought to reflux and held at reflux temperature for 4 hr; afterwards, the membranes in the salt solution were allowed to cool overnight (step 2). The ion-exchanged samples were then refluxed twice in DI/DS H_2O to flush the membrane of excess salts (step 3).

0.01M Salt Solutions. Three separate ion exchanges were performed using the 0.01M solutions. The ion exchanges used three different mole ratios of salt to acid group in Nafion, 1:2, 1:1, and 2:1. The membranes were preweighed, dried in a vacuum oven for 24 hr at 120 °C and 4 kPa to remove atmospheric water, cooled in a dessicator, and reweighed. This procedure allowed for the most accurate determination of the moles of sulfonic acid groups and subsequent calculation of the appropriate moles of salt used to exchange the sample. Nafion samples were then soaked in the dilute salt solution at room temperature for 24 hr, removed from the solution and patted dry, placed back in the vacuum oven for 24 hr at 120 °C and 4 kPa to remove atmospheric and excess water, cooled in a dessicator, and reweighed. In the limited mole-ratio exchanges, we did not reflux the membranes in the salt solutions. This will be explained in detail in section 3.

2.4 Atmospheric Water Diffusion Into Nafion Analysis

A piece of initialized H^+-form Nafion was weighed and placed in an oven at 125 °C and 4 kPa for 24 hr to dry. The membrane was then removed from the oven, allowed to cool in a dessicator, and placed on an OHAUS GA200 analytical balance in a room at 22 °C and 55% relative humidity. The diffusion of atmospheric water into the membrane was observed and recorded over time until the amount of atmospheric water absorbed reached a plateau, typically at 6.5 weight-percent uptake. Figure 3 describes the time dependence of this process.

2.5 PGAA

Teflon bags were prepared by cutting a Teflon sheet and heat sealing the edges; the precut ion-exchanged Nafion samples were placed in the bags. The sample and bag were then weighed and placed in an oven at 125 °C and 4 kPa for 24 hr to dry. Upon removal from the oven, the sample and bag were placed in a dessicator to cool and then reweighed before sealing the bag to obtain a measure of the overall atmospheric water loss. The sealed bags were stored in a dessicator prior to analysis. Figure 4 shows a typical spectrum from a sample of

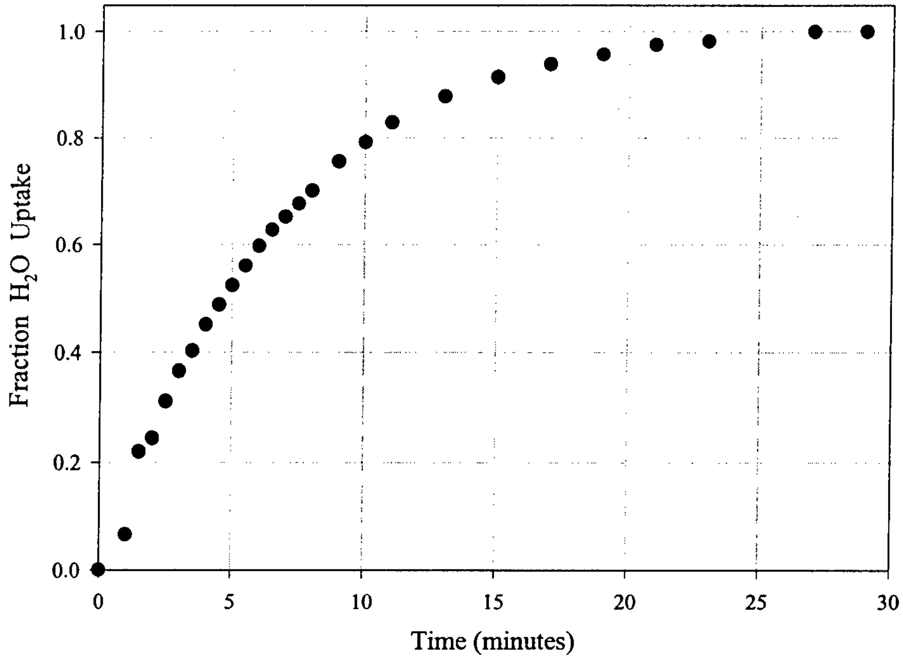

Figure 3. Atmospheric water uptake into dry, initialized H^+-form Nafion.

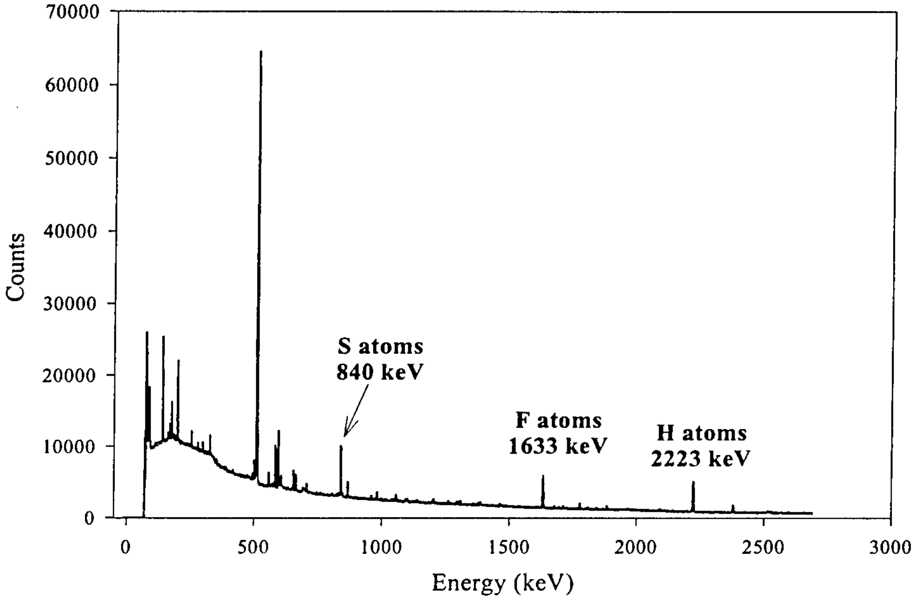

Figure 4. Prompt gamma spectrum for N117—H^+ form.

Nafion 117 that was exchanged to the H^+ form. Spectrum is the plotted number of counts vs. energy in kiloelectronvolts (keV). Samples were analyzed for all ions present (K^+, Ca^{2+}, Cl^-, etc.), including Cs (308 keV), Fe (352 and 7634 keV), K (770 keV), Cl (787 and 1165 keV), S (841 keV), Zn (1077 keV), Al (1778 keV), Ca (1942 keV), H (2223 keV), Co (230, 277, and 556 keV), Cu (278 and 7614 keV), and Mg (585 keV). Each line in the spectrum is a signature for a specific element. In addition to the gamma-ray peaks due to neutron capture in the sample, there are peaks at low energies in the prompt gamma-ray spectra resulting from neutron capture by germanium (in the detector), aluminum (in the sample holder, shielding, and detector endcap), cadminum (shielding), copper (shielding), and fluorine (from the Teflon bag). The background for these experiments was measured with an empty Teflon bag. For simplicity, only the peaks of interest relating to the sample were labeled.

To quantify the elemental composition of the samples, the peak intensity for each atom detected is normalized to the peak intensity of sulfur. For these samples, sulfur is the internal sample reference because it is assumed that one sulfur atom would be present for each monovalent counterion, two sulfur atoms would be present for each divalent counterion, and three sulfur atoms would be present for each trivalent counterion. The uncertainties (2 sigma or 2σ) on the molar ratios were calculated from the uncertainties in the counting statistics and are equal to the square root of the total counts minus the background counts for a given peak. To calculate the uncertainties on the element ratios, we then add the uncertainties of the two elements and then take the square root of the sum of the squares.

The raw results (see Table 2 for raw data from as-received H^+-form Nafion) yielded information on any contamination present in the samples and a measure of the extent of counterion exchange achieved in each of the procedures previously mentioned.

Table 2. Raw data from prompt gamma analysis.

Sample	H/S	H/S Error	K/S	K/S Error
H^+ As-Received	2.27	0.07	0.05	0.01
H^+ Pretreatment 2 [31]	2.29	0.03	0	0

Note: 2σ uncertainties were evaluated based on counting statistics.

To separate hydrogen contributions due to water from those due to acid the following calculations were used. The acid hydrogens per sulfur (H^+/S) ratios were calculated using equation (1) for samples in the acid form and equation (2) for samples in the ion-exchanged form:

$$\frac{acidH^+}{S} = 1 - [\text{Total ions/S}]; \qquad (1)$$

$$\frac{acidH^+}{S} = 1 - [\text{Total ions/S} - \left(\frac{\left(\frac{Cl^-}{S}\right)}{n}\right)], \qquad (2)$$

where

the total ions/S is the ratio of total moles of all other ions measured to moles of sulfur,

Cl^-/S is the chlorine-to-sulfur molar ratio, and

n is the charge of the contaminating ion or ion used in the ion-exchange procedure.

For example, if K^+ is the contaminant ion, such as in the case of the as-received sample, the charge is 1. For samples in the ion-exchange form, incomplete exchange would result in the presence of acid hydrogens and residual unassociated salt would result in the presence of chlorine. This equation is straightforward unless there is more than one metal ion involved and they are of different charges. For samples containing hydrogen plus two counterions, a different calculation was required for the reported H^+/S ratios. Equation (3) was used:

$$\frac{acidH^+}{S} = 1 - [\text{Total ions/S} - \left[\left(\frac{\left(\frac{Cl^-}{S}\right)}{n1} * \left(\frac{\frac{M1}{S}}{\frac{M1}{S}+\frac{M2}{S}}\right)\right) + \left(\frac{\frac{Cl^-}{S}}{n2} * \left(\frac{\frac{M2}{S}}{\frac{M1}{S}+\frac{M2}{S}}\right)\right)\right]], \qquad (3)$$

where

the total ions/S is the ratio of total moles of all ions except hydrogen measured to moles of sulfur,

Cl^-/S is the chlorine-to-sulfur molar ratio, which must be taken as a percent of the ions with which it is associated,

$n1$ is the charge of the ion $M1$, and

$n2$ is the charge of the ion $M2$.

Once the acid H^+/S ratio has been calculated, it is assumed that the remaining hydrogen is due to water, and equation (4) is used to calculate the H_2O/S ratio:

$$\left(\frac{H_2O}{S}\right)=\left[\frac{\left(\frac{H}{S}-\frac{acidH^+}{S}\right)}{2}\right], \tag{4}$$

where

H/S is the molar ratio of total hydrogen to sulfur, and

$acidH+/S$ has been calculated using equations (1), (2), or (3).

3. Results and Discussion

3.1 Atmospheric Water Diffusion

Because the diffusion of atmospheric water into Nafion could influence the results of the prompt gamma analysis, an evaluation of the atmospheric water absorbed by the membrane was conducted. The plot in Figure 3 shows the fraction of atmospheric water uptake in Nafion over time until the uptake reached a plateau of 6.508% atmospheric water uptake at about 27 min. The diffusion coefficient can be estimated from this curve by determining the time to attain half-time sorption equilibrium [34, 35]:

$$\mathrm{D}=\frac{0.0492*l^2}{t_{1/2}}, \tag{5}$$

where

the half-time sorption value is the time it takes for half equilibrium sorption weight to be achieved,

$t_{1/2}$ is the half-time in seconds, and

l is the thickness of the membrane in centimeters. From the original data, D can then be calculated to be 2.1486 E-7 m/s. This value is in agreement with the other researchers [36].

3.2 Nafion Pretreatments

Prompt gamma data was collected for a series of H+-form Nafion membranes. Several H+-form membranes were prepared using each of the four pretreatment techniques for as-received membranes described in the previous section. In addition, two other samples were analyzed for comparison: a SO_2F precursor and a SO_3H as-received. The results are shown in Table 3. The prompt gamma analysis yielded information on the composition of the membranes—the only elements detected within the membranes were H, K, and S. Oxygen cannot be detected using the technique, and carbon and fluorine cannot be quantified because the samples were analyzed in Teflon.

Table 3. Prompt gamma comparison of H^+-form Nafion membranes.

Sample	Acid H^+/S	% Neutralization (Other Counterions)	H_2O/S
Pretreatment 1 [30][a]	1 ± 0.022	0	0.685 ± 0.014
Pretreatment 2 [31][b]	1 ± 0.013	0	0.635 ± 0.008
Pretreatment 3 [32][c]	1 ± 0.034	0	0.645 ± 0.023
Pretreatment 4 [33][d]	1 ± 0.029	0	0.056 ± 0.016
$-SO_2F$ Precursor	0 ± 0	0	0 ± 0
Nafion, As-Received	0.95 ± 0.033	5	0.660 ± 0.019

[a] Boil in concentrated nitric acid; rinse with pure water.
[b] Reflux in 2N HCl; rinse with H_2O.
[c] Reflux in 3% H_2O_2; reflux in DI H_2O; reflux in 0.5M H_2SO_4; reflux in H_2O.
[d] Reflux in 50% HCl:50% HNO_3 solution (v:v); reflux in DI/DS H_2O (3×).
Note: 2σ uncertainties were evaluated based on counting statistics.

The as-received sample revealed some contamination due to K^+ ions, possibly as a result of processing. The pretreated samples were all completely converted to the sulfonic acid form; the contamination was removed from the membrane in the pretreatment processes. In addition, the drying procedure appears to be effective in removing most of the water from the membrane. Chemically, all of the pretreated membranes are the same.

3.3 Complete Counterion Exchanged Nafion

In addition to the H^+ form membranes, several other counterion forms were prepared, including K^+, Cs^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Al^{3+}, and Fe^{3+}. In the ion-exchange procedure, three different membrane samples were prepared for each counterion using the following procedure: in the first step, samples were soaked in an excess of the 2M salt solution for 24 hr, and one sample was taken after step 1 was completed; in the second step, the two remaining samples were refluxed in the salt solution for 4 hr and one sample was taken after steps 1 and 2 were completed; in the third step, the last sample was refluxed two times in DI H_2O and the sample was taken after steps 1, 2, and 3 were completed. All samples were dried before prompt gamma analysis according to the procedure in section 2. The different ion-exchange samples were taken to determine what would be the maximum percent exchange for the ion, whether different conditions produced different degrees of exchange, how rigorous the conditions for exchange would need to be for maximum exchange, and whether there was any indication of reverse exchange back to the proton form due to refluxing with DI water, perhaps simulating some application processes such as in fuel cells.

The results from the counterion exchange procedure are shown in Table 4. The H^+/S ratios were the same regardless of the sample preparation (i.e., step 1 only, steps 1 and 2, or steps 1–3). Samples from step 1 and from steps 1 and 2 of the treatment processes showed small amounts of chlorine within the membrane, while samples from steps 1–3 processes showed no residual chlorine. While this was taken into account for the calculation of the H^+/S—the degree of neutralization and the H_2O/S—the presence of chlorine shows that there are still excess salts within the membrane before the final rinsing process. The final step in the neutralization process is necessary to remove these excess ions.

Table 4. Prompt gamma results from the counterion exchange procedures.

Sample	Counterion Radius Size [37] (pm)	Acid H^+/S	Neutralization (To Counterion) (%)	Amount H_2O/S
K	227	0.059 ± 0.004	94	0.060 ± 0.012
Cs^+/Step 1	265	0.065 ± 0.006	93.5	0.033 ± 0.017
Cs^+/Steps 1 and 2	265	0.060 ± 0.005	94	0.060 ± 0.022
Cs^+/Steps 1–3	265	0.060 ± 0.005	94	0.040 ± 0.023
Mg^{2+}	160	0	100	0.725
Ca^{2+}	197	0.008 ± 0.0002	98.6	0.626 ± 0.010
Co^{2+}	125	0.020 ± 0.001	98	0.700 ± 0.015
Cu^{2+}	128	0.022 ± 0.002	97.9	0.709 ± 0.030
Zn^{2+}/Step 1	134	0	100	0.565 ± 0.024
Zn^{2+}/Steps 1 and 2	134	0	100	0.675 ± 0.015
Zn^{2+}/Steps 1–3	134	0	100	0.669 ± 0.029
Fe^{3+}	126	0	100	0.599 ± 0.031
Al^{3+}	143	0	100	1.605 ± 0.036

Notes: 2σ uncertainties were evaluated based on counting statistics.
pm = picometers.

Taken together, the results show that excess salts are picked up by the membrane but can be flushed out of the membrane through refluxing with DI/DS water. A rigorous procedure for exchange is not necessary since allowing the membrane(s) to sit in the saturated solution at room temperature is sufficient to allow for exchange, and a long-term, vigorous reflux in DI water does not appear to influence a reverse exchange to the protonated sulfonic groups.

Furthermore, a shortened procedure might be used to achieve the same results: soaking the membranes for 24 hr in the saturated salt solution (step 1) and then refluxing the ion-exchanged membranes in DI/DS water to remove excess ions (step 3).

Because the acid H+/S, percent neutralization, and H2O/S data are similar for the three ion-exchange procedures, only one set of results for the membranes soaked in the salt solutions (steps 1–3) are shown in Table 4 for all membranes other than cesium and zinc. The amount of H_2O/S in the sample fluctuated slightly from sample to sample, but showed less than one water molecule per sulfonic acid group remaining for membranes exchanged with all ions except for the Al^{3+}. All membranes were free from contamination except those exchanged with calcium, which revealed some potassium contamination. Because the membranes used were all pretreated, it is presumed that the potassium contamination originated from the calcium salt, which has potassium listed as a minor component. The reported H^+/S ratios did require a different calculation than the one previously discussed for the calcium samples since there were two metal ions present and the ions contained different charges. The following equation was used:

$$\frac{acidH^+}{S} = 1 - [\text{Total ions/S} - \left[\left(\frac{\left(\frac{Cl^-}{S}\right)}{n=1} * \left(\frac{\frac{K}{S}}{\frac{K}{S}+\frac{Ca}{S}}\right)\right) + \left(\frac{\frac{Cl^-}{S}}{n=2} * \left(\frac{\frac{Ca}{S}}{\frac{K}{S}+\frac{Ca}{S}}\right)\right)\right]], \qquad (6)$$

where

the total ions/S is the ratio of total moles of all other ions measured to moles of sulfur,

Cl^-/S is the chlorine-to-sulfur molar ratio, which must be taken as a percent of the ions with which it is associated, and

n is the charge of the contaminating ion or ion used in the ion-exchange procedure.

The experiments show that the exchange procedures, used successfully, result in replacement of 94–100% of acid protons. Conversions are slightly lower for monovalent cations than for di- and trivalent cations. Monovalent K^+ and Cs^+ ions exhibited the most difficulty in achieving maximum conversion. These ions are the largest in size and it is a possibility that in the membrane aggregates there is a limit to the accessibility of the ion for exchange. The accessibility limitation in the aggregates seems to be supported by solubility and diffusion measurements. Monovalent cations reduce the solubility and diffusion coefficients for water and simple alcohols much more than di- and trivalent ions [37].

3.4 Limited Counterion Exchanged Nafion

The effects of stoichiometry on the exchange procedure were evaluated with the 0.01M salt solutions. Three separate ion exchanges were performed using mole ratios of salt to reactive group in Nafion of 1:2, 1:1, and 2:1. These experiments were used to determine (1) whether a dilute solution having half the salt cations needed could force a partial exchange and if some control over the extent of exchange could be achieved, (2) whether an equal mole ratio of ions to sulfonic groups would yield the same extent of conversion as that of a saturated solution, and (3) what the limitations on the concentration of the exchange solution might be to obtain complete exchange. Partial exchange might be useful for situations where preferential solvent sorption is needed but total exchange is too limiting on the conductivity. In addition, the 1:1 mole ratio samples and the 2× excess number of cations (2:1) were used to determine how easily the ions access the membrane, and for economic considerations, since some of the salts used for the exchange procedure are expensive, how few cations per sulfonic acid site could be used for the exchange procedure.

For these experiments, the moles of sulfonic acid groups in the membrane (assuming one per equivalent) are estimated simply from the equation:

$$\text{moles of -SO}_3\text{H groups} = \frac{W_{sam}}{EW_N}, \tag{7}$$

where

W_{sam} is the weight of the sample, and

EW_N is the equivalent weight of the Nafion sample (which, in our case, is 1100).

For this evaluation, because the previous experiments showed that no rigorous exchange procedure was required to obtain maximum sample exchange, all exchanges were performed at room temperature by soaking the membrane in the solution for 24 hr. Recall for these experiments the membrane was preweighed, the approximate moles of sulfonic acid groups calculated, and an equivalent number of moles of salt solution used to exchange the sample. These experiments were performed on a much narrower scale with only K^+, Ca^{2+}, Zn^{2+}, and Al^{3+}. The results are shown in Table 5. Focusing strictly on the data for the monovalent cation, K^+, the exchange is 33% for the 1:2 sample, 58.7% for the 1:1 sample, and 82.6% for the 2:1 sample. All samples are below the maximum exchange that was, in the other study using 2M salt solutions (which used about a 100× molar excess of salt ions), found to be 92%. An excess of greater than two times appears to be necessary to force complete exchange to occur.

Table 5. Prompt gamma results for limited molar concentration solutions.

Sample (mol salt:mol-SO_3H)	Acid H^+/S	Neutralization (To Counterion) (%)	Amount H_2O/S
1:2—K^+ Sol'n	0.661 ± 0.042	33.094	1.038 ± 0.011
1:1—K^+ Sol'n	0.437± 0.023	56.347	0.748 ± 0.015
2:1—K^+ Sol'n	0.205 ± 0.004	79.516	0.544 ± 0.008
1:2—Ca^{2+} Sol'n	0.566 ± 0.030	42.220	2.486 ± 0.012
1:1—Ca^{2+} Sol'n	0.129 ± 0.005	87.142	1.303 ± 0.017
2:1—Ca^{2+} Sol'n	0.015 ± 0.001	98.468	1.786 ± 0.042
1:2—Zn^{2+} Sol'n	0.550 ± 0.082	45.009	2.784 ± 0.034
1:1—Zn^{2+} Sol'n	0.169 ± 0.008	83.103	2.219 ± 0.021
2:1— Zn^{2+} Sol'n	0.084 ± 0.007	91.560	2.911 ± 0.044
1:2—Al^{3+} Sol'n	0.407 ± 0.041	59.253	3.019 ± 0.030
1:1—Al^{3+} Sol'n	0.083 ± 0.008	91.716	2.024 ± 0.045
2:1—Al^{3+} Sol'n	0.010 ± 0.002	100	3.694 ± 0.080

Note: 2σ uncertainties were evaluated based on counting statistics.

These limited molar concentration solutions were used in the exchange procedures to determine if partial exchange could be achieved and to gain an idea of what the limits of the solution concentration for complete exchange might be. The samples that were swollen in 1:2 (mol:mol) solutions, containing about one half the number of moles of salt needed for complete exchange, did show limited exchange of the sulfonic acid sites (see Table 5). The samples also showed repeatability in the results of the limited exchange. In addition, while the amount of exchange was nearly twofold over the 1:2 (mol:mol) solutions, the 1:1 (mol:mol) solutions do not allow all counterions to access the membrane areas needed for complete exchange at the sulfonic acid sites. The divalent and the trivalent have more sites readily exchanged than the monovalent counterion. The 2:1 (mol:mol) solution exchange for the divalent and trivalent counterions show high degrees or complete exchange and the neutralization values are nearly identical to the saturated solution samples. However, the monovalent counterion would require a more concentrated salt solution to approach the maximum amount of exchange in the sample. The amount of water in the membranes is larger than in the other samples analyzed. However, this is not significant since the membranes were not rigorously dried before analysis for this portion of the study due to its focus on stoichiometric aspects of the exchange procedure.

3.5 As-Received Counterion Exchanged Nafion

Finally, as-received membranes were analyzed, focusing on the K^+ contamination within the as-received membrane and the possibility that it could be exchanged out of the membrane when converting to a new counterion. For this study, the Zn^{2+} and Al^{3+} cations were used since both exhibited high degrees of conversion to the counterion. Results are shown in Table 6. For both counterions, the amount of K^+ ion contamination does not change significantly from the as-received H^+-form sample, 5%, for the 1:2 (mol:mol) solutions but decreases by a factor of 2 for the 1:1 (mol:mol) solutions. These results indicate that it is possible to displace some K^+ ions with Zn^{2+} or Al^{3+}. The displacement of K^+ contaminants with other counterions was not complete at the intermediate molar excess levels studied. The total ion-exchange levels achieved in these as-received membranes are very similar to the counterion conversion achieved for initialized samples under the same exchange conditions.

Table 6. Prompt gamma results for as-received H^+-form Nafion.

Sample (mol salt:mol – SO_3H)	Acid H^+/S	K^+ Ion Contamination	Neutralization (To Counterion) (%)	Amount H_2O/S
As-Received	0.95 ± 0.033	0.05 ± 0.006	5	0.660 ± 0.019
Initialized	1 ± 0.029	0	0	0.056 ± 0.016
1:2—Zn^{2+} Sol'n	0.486 ± 0.083	0.050 ± 0.009	46.426	3.094 ± 0.085
1:1—Zn^{2+} Sol'n	0.169 ± 0.025	0.025 ± 0.008	81.051	3.112 ± 0.073
1:2—Al^{3+} Sol'n	0.413 ± 0.042	0.039 ± 0.006	54.692	2.926 ± 0.051
1:1—Al^{3+} Sol'n	0.010 ± 0.001	0.013 ± 0.005	98.725	3.439 ± 0.053

Note: 2σ uncertainties were evaluated based on counting statistics.

4. Conclusions

PGAA was applied to the study of chemical composition in Nafion PFSI membranes. This technique is unique in its ability to quantitatively identify trace ion content and water content (through detection of hydrogen) in the membranes. The study was focused on identifying contamination, effectiveness of treatments to remove contamination, and extent of ion-exchange in membranes prepared using different procedures. The results established that as-received membranes contained small amounts of residual potassium contamination, which was effectively removed by any of a variety of standard pretreatments. Maximum extent of ion-exchange was also determined for a variety of mono-, di-, and trivalent counterions. Exchange levels for membranes prepared in excess ion solutions varied from 94–100%, increasing with valency. Partial exchange levels were achieved using mono-, di-, and trivalant cations introduced in ion-starved solutions. Results also indicated that ion-exchange can be used to reduce residual potassium contamination in as-received membranes.

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13. ABSTRACT*(Maximum 200 words)*

Researchers have performed structural evaluations on Nafion membranes for many years. Various research groups have published a large volume of data; however, much of the work done by these groups is contradictory. One important aspect of the membranes is the chemical uniformity and quantity of water within the membrane under investigation. A new technique that has shown its usefulness for providing accurate and fast quantitative measurements of chemical composition quickly is prompt gamma neutron activation analysis (PGAA). In this work, a sulfonyl fluoride-form membrane, an as-received membrane from the manufacturer, and several differently pretreated H^+-form Nafion membranes were examined using PGAA. The evaluation showed the necessity for pretreatment of membranes to eliminate contamination. A series of counterion-exchanged membranes were also examined to determine maximum conversion achieved and to identify possible limitations to complete conversion. The results show that it is possible to obtain nearly complete or complete conversion to the counterion from the H^+-form Nafion samples. Water content can be limited within the membrane but not eliminated. In samples that were not pretreated, complete ion exchange was limited by the contamination.

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