Solution Casting, Characterization, and Performance Evaluation of Perfluorosulfonic Sodium Type Membranes for Chlor-Alkali Application

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ABSTRACT: This investigation describes solution casting, characterization and performance evaluation of perfluorosulfonic sodium (PFSS) type membranes prepared by three different methods from Nafion solution and Nafion-117 for Chlor-Alkali (CA) application. A Chlor-Alkali experimental set-up was designed and constructed for performance evaluation of the recast membranes. The chemical structure of solution cast films was studied and confirmed by FTIR (Fourier Transform infrared spectroscopy) and ATR (Attenuated total reflection) techniques. The physical properties of solution cast films including mechanical strength, thermal behavior, water sorption, ion-exchange capacity (IEC), morphology, and crystallinity were also evaluated. All the recast polymeric films behave like elastomers with low modulus but high elongation at break. Differential scanning calorimetric (DSC) thermograms of solution cast films showed two endothermic peaks at 180°C and 250°C attributed to matrix glass transition (T_{gm}) and ionic cluster glass transition (T_{gc}) of the Nafion polymer, respectively. The water uptake of polymeric films was reasonable in comparison with Nafion-117. Solution casting has no significant effect on ion exchange capacity of the recast films. The scanning electron microscope (SEM) micrograph showed that the morphology of recast films is reasonably similar with Nafion-117. However, the as-cast films have some micro pores, which are produced during solution casting. The crystallinity of annealed film, because of the heat treatment was slightly high due to local ordering. According to the experimental results, which obtained from performance evaluation in CA cell, the properties of recycled films are similar to commercial membranes such as Nafion-117 and can be used in CA process. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3469–3476, 2011

Key words: perfluorosulfonic sodium membrane; nafion; cell performance test; chlor-alkali membrane; solution casting

INTRODUCTION

Polymers that are functionalized with ionic groups (usually anionic sites) attached along the polymeric backbones are called ionomers.[1] They exhibit a wide range of interesting and useful physical and chemical properties because of their unique features such as chemical structure and morphology. Perfluorosulfonic acid ionomers (PFSI) have been used widely as polymeric membranes, because of their special properties such as mechanical strength, chemical stability, process abilities at low temperatures, and excellent ion exchange capacity.[2] During the past few years, methods of obtaining different equivalent weight of Nafion solution for thin film formation have been reported.[3]

The perfuorinated ion exchange membranes should have high chemical stability, reasonable mechanical strength extremely low permeability to reactant species, selective with high ion conductive, and ability to provide electronic insulation.[1] Industrial applications of these membranes include mainly brine electrolysis e.g., chlor-alkali cells, salt splitting, clean power generation by solid polymer electrolyte fuel cells, batteries, gas separation, gas sensors, and electro dialysis.[4]

A simplified flow diagram of the CA membrane cell is depicted in Figure 1. The figure shows the role of the multifunctional per-fluorinated membrane in the CA process.[5] The application of membrane is separation of the acidic anolyte from the highly alkaline catholyte, and the passage of solvated cations (Na$^+$) companion with water molecules whereas anions are not allowed to transfer through the membrane (Cl$^-$ and OH$^-$). The Nafion® (Dupont) cation exchange membrane used in CA cell is a flat multilayer composite membrane with unique structure and different functions for each layer (Fig. 2). The multilayer-sandwiched membrane comprises a major perfluorosulfonated layer facing
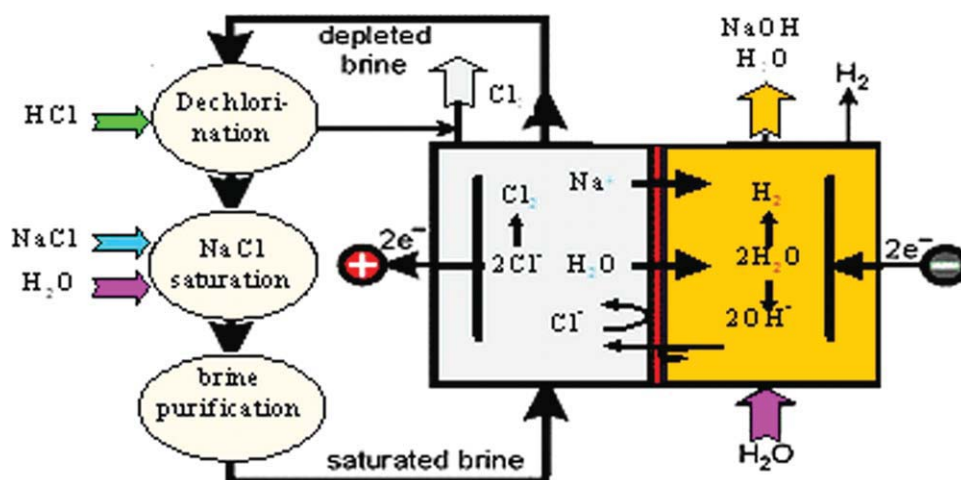
Figure 1 A simplified flow diagram of the Chlor-Alkali membrane cell. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the anode, perfluorocarboxylated layer facing the cathode in the cell, a reinforcing PTFE cloth in between, and surface modification layers on outer sides to improve gas release properties of the membrane.

The chemical structure of the perfluorosulfonated layer in acid form is depicted in Figure 3. The Teflon like per-fluorosulfonated layer, which is the major embodiment of the composite membrane, consists of a pendant PFSS ion end group. The perfluorosulfonated layer, which is responsible for water sorption and ion conductivity, shows less cell voltage, therefore less energy consumption in comparison with the perfluorocarboxylated layer. This is mainly due to a higher water uptake and dissociation coefficient of sulfonic acid group with respect to carboxylic acid group.[2]
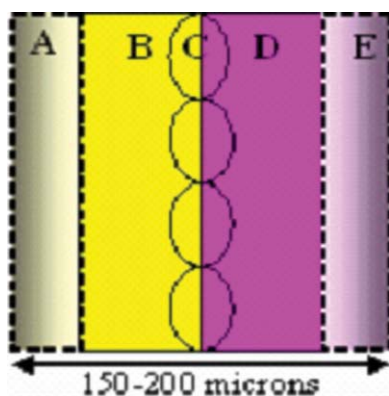
The minor impurities present in brine feed left from brine purification system (mainly divalent cations, e.g., Ca^{2+}, Mn^{2+}, … at ppb levels) precipitate gradually within the membrane structure in CA process. This is caused by high pH gradient across the thin membrane, which contributes to membrane failure in long term (within two to three years). This deficiency consequently results in plant shut down and calls for membrane replacement leading to a higher production cost and environmental problem due to the nondegradable used membrane landfill.

A systematic study was thus launched in our laboratory for recycling, regeneration and reuse of the used or failed Nafion[®] and/or Flemion[®] membranes from CA industry. However, the complexities due to the multilayer structure of the commercial CA membranes, variety of brine impurities contributing to the membrane failure and nondestructive separation of the membrane layers are numerous. Therefore, it was thus decided to initially consider and investigate a simplified unilayer membrane as the first stage of the comprehensive membrane reclaiming study.
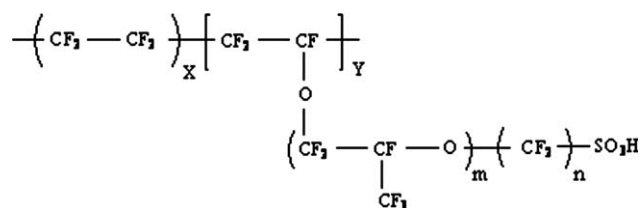

Figure 2 A cross section view of the multilayer composite membrane used in CA cell, (A) Outer MnO_2 layer for Cl_2 gas release, (B) Perfluorosulfonic layer, (C) Reinforcing PTFE cloth, (D) perfluorocarboxylic layer, (E) Outer SiC layer for H_2 gas release. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3 Chemical structure of the perfluorosulfonic layer, X, molar fraction of Tetra- fluoroethylene; Y, molar fraction of perfluoro vinyl ether, m: 0–2, n: 1–4 or 2–12).

Recycling and regeneration of the unilayer Nafion 115 membrane has already been reported for proton exchange fuel cell, but not for CA application.[6] In this study, we thus report on dissolution, (re)casting, characterization, and performance evaluation of per-fluorosulfonated layer in a CA cell. Unilayer per-fluorosulfonic acid (PFSI) end group films are to be cast from Nafion® (Dupont) solution and/or recast from Nafion® 117 membrane, converted to films with sodium salt end groups and then annealed. Conditions for good film forming are established.

The mechanical and thermal properties, water uptake, morphology, and crystallinity of the solution cast films were studied. The chemical structure of the films was characterized and confirmed by FTIR and ATR techniques, while thermal properties were studied by DSC-TG. Morphology and structure of the cast films were investigated by SEM and compared with those of a commercial membrane. The cell performance of the films obtained was also evaluated in a CA set-up similar to a scaled-down industrial electrolysis unit.

EXPERIMENTAL

Materials

Nafion-117 (Equivalent Weight (EW) = 1100) and Nafion suspension (5% w/v in alcohol/water, EW = 1100) were obtained from DuPont. Nitric acid (70%), sulfuric acid (98%), hydrochloric acid (37%), sodium chloride, and sodium hydroxide were supplied from Merck. N, N'-Dimethyl sulfoxide (DMSO) was obtained from Merck and used as received.

Apparatus

Film formation by solution casting was performed by Teflon moulds with 12 cm × 5 cm internal dimensions under nitrogen atmosphere. The casted films were dried in an oven under vacuum. A micrometer measured the thickness of films. FTIR (Fourier Transform Infrared Spectroscopy) and ATR (Attenuated total reflection) spectra were taken with a Bruker model IFS-48 spectrophotometer, taking samples in film forms. Mechanical properties were determined according to ASTM D-638 by using Instron model 6025. The speed of crosshead was 50 mm/min for all samples. The thermal properties of samples were evaluated by DSC-TG (Differential Scanning Calorimetry-Thermogravimetry) Analyzer model STA- 625 in air at a heating rate of 20°C/min in 50–360°C regions. Studies on surface morphology of the dried films were carried out using a scanning electron microscope (SEM), Cambridge S 360.

Film formation

The nafion-based films were prepared through three different ways:[7,8]

Solution casting

The films were formed by pipetting 26.6 mL of 5% Nafion suspension (d = 1.4 g/cm^3) into a Teflon mold and subsequent evaporation to dryness in an oven under vacuum. The casted films were peeled off from the mold by immersing in distilled water. Solution-derived films were brittle with poor mechanical properties and easily cracked.

Solution casting with solvent

Totally, 9.7 mL DMSO was added to 32.3 mL of 5% Nafion suspension (d = 1.4 g/cm^3). To concentrate the mixture, solution was heated up at 80°C, then at 150°C, respectively. The viscous solution was poured into a Teflon mold and heated up in an oven under vacuum for 2.5 h to dryness. The casted thick films with $\sim$ 170 μm thickness were peeled off from Teflon mold by immersing in distilled water.

Annealing the film

The prepared films using solution casting with solvent were annealed by heating in an oven under vacuum at 170°C for 4 h.

Measurement of ion-exchange capacity

The ion-exchange capacity (IEC) of samples was measured by titration method. Nafion based films in acidic forms were placed in 0.1M NaCl solution for 24 h to convert the membrane from acidic to sodium salt form. The protons released due to the exchange reaction with Na$^+$ ions were titrated against 0.02M standardized NaOH solution, using phenol red indicator solution.[9] The volume of applied sodium hydroxide solution was used to calculate the mole numbers of H$^+$ in solution according to the following equation:

$$IEC \text{ (meq/g)} = \frac{(V \times N)_{NaOH}}{\text{Weight (Polymer)}} \quad (1)$$

$$\text{Equivalent weight (EW)} = 1/IEC \times 1000 \quad (2)$$

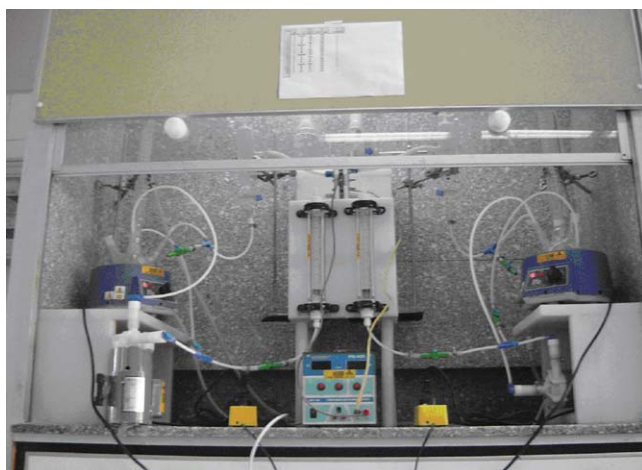where V is volume and N is normality of sodium hydroxide solution.

Figure 4 A photograph of the Chlor-Alkali set-up. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Swelling of films

Swelling percentage of different films was evaluated on weighing manner. First, the Nafion-based films were immersed in a 0.5M NaCl for producing sodium salt form, then in deionized water for 48 h at 25°C. The films were picked up and dried at room temperature, then weighed to obtain the wet weight of the films. The films were dried in a vacuum oven at 80°C and weighed to obtain the dried weight of the films. Swelling percentage was calculated according to the following equation:[10]

$$\text{Swelling (\%)} = \left(\frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}}\right) \times 100 \qquad (3)$$

where, W_{wet} and W_{dry} are the wet and dry weights of the samples, respectively.

Density of films

Hydrostatic method was used to evaluate the density of films. The Nafion-based films were washed in water then surface dried and weighed to obtain the average weight of the samples. The initial weight (W_o) is obtained by weighing a glass beaker, full of water, which has a metallic wire in the middle. Dried and wet Nafion samples were hanged to metallic wire in beaker and weighed (W). Density of samples was calculated according to the following relationship:

$$d_n = \frac{m}{(W - W_o)/d_w} + d_a \qquad (4)$$

where d_n, d_w, and d_a are densities of films, water (0.9982 g/cm^3) and air (0.00129 g/cm^3) at 20°C and 760 mmHg, respectively.

Percentage of crystallinity

The degree of Crystallinity (χ_C) of the films was also determined from DSC thermograms using the following equation:

$$\chi_C = \frac{\Delta H_f}{\Delta H_f^o (1 - \varphi)} \times 100 \qquad (5)$$

where, $1 - \varphi$ is the weight fraction of polymer and ΔH_f^o is the theoretical enthalpy value for a 100% crystalline polymer.

Cell performance test

The electrochemical cell performance of the membranes was evaluated in a CA set-up designed for electrolysis of aqueous solution of NaCl at 90°C and anolyte with acidity of pH > 2. A laboratory filter-press type electrolyzer (ElectroCell AB, Sweden) with 10 cm^2 projected electrode area, using a standard chlorine evolution anode (DSA Cl$_2$) and a H$_2$ evolution Ni cathode was employed. The anolyte and catholyte were prepared by dissolving appropriate amount of Analar grade of NaCl and NaOH in 1-L double-distilled water each; and recirculated in separate hydraulic circuits by magnetic pumps throughout the elecectrolysis experiment. The electrolyte flow rate was measured with two calibrated Rotameters for brine and caustic solutions. The complete experimental set-up was located under a laboratory hood for safe ventilation. A photograph of this CA set-up was shown in Figure 4, while the hydraulic circuit used was drawn in Figure 5. Galvanostatic operation was applied to the electrolyzer using a digital DC power supply. The cell voltage and current densities were measured using two multimeters.
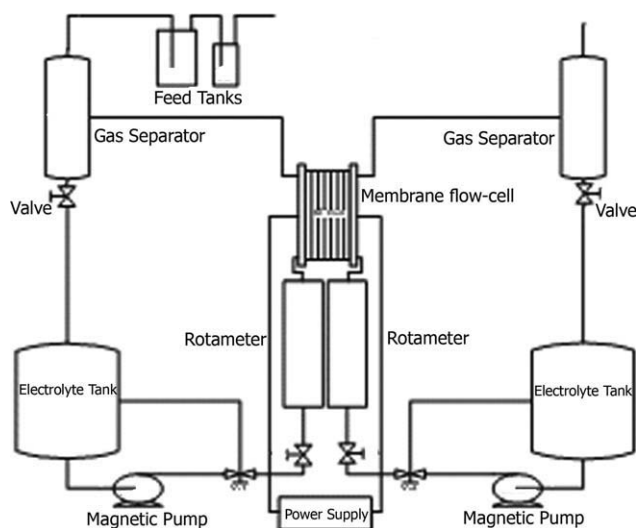

Figure 5 The process flow diagram of the CA cell performance test.

TABLE I
Ion Exchange Capacity (IEC), Equivalent Weight (EW), and Water Sorption of Nafion-Based Films

Polymer film	Thickness (μm)	IEC (meq/g)	EW (g/meq)	Swelling (%)
a	168	0.894	1118.5	–*
b	169	0.892	1121.6	13.95
c	167	0.899	1112.3	14.01
d	178	0.910	1098.9	16.0

a, solution cast; b, solution cast with solvent; c, annealed; d, Nafion-11.

* Not measured due to the film brittleness.

RESULTS AND DISCUSSION

Physical properties

The ion exchange capacity (IEC), equivalent weight (EW) and water sorption of the perfluorosulfonated films are depicted in Table I. The IEC of the films strictly depends on the content of sulfonic acid group incorporated into the polymer structure.[11] The IEC is an indicative of the ion exchange sites available for ion conduction. The results showed that the ion exchange capacities of Nafion 117 and solution cast films are comparable. The slight reduction in ion exchange capacities of the prepared films in comparison with that of the commercial film is probably due to the loss of some ionic sites during solution casting. Therefore, solution casting by a suitable manner has no significant effect on ion exchange capacity or equivalent weights of the films.

The water sorption (swelling percentage) of the films was evaluated at room temperature. The water sorption is directly proportional to ion conductivity of the membrane and conductivity is an indication of ion concentration and its mobility.[2]

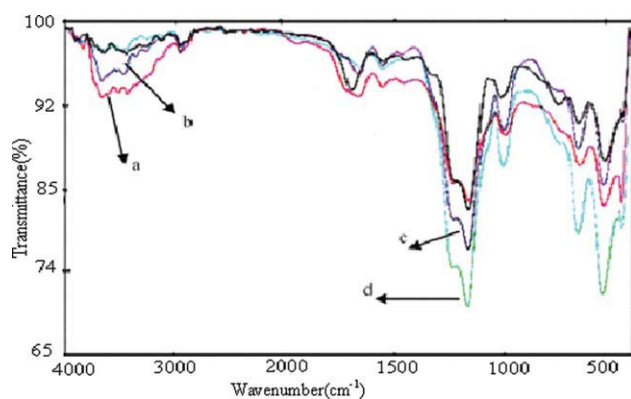The maximum water sorption of the prepared films was 14%, which is slightly lower than that of

Figure 6 ATR spectra of the cast films and Nafion-117 membrane. (a) Solution cast, (b) Solution cast with solvent, (c) Annealed, (d) Nafion-117. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
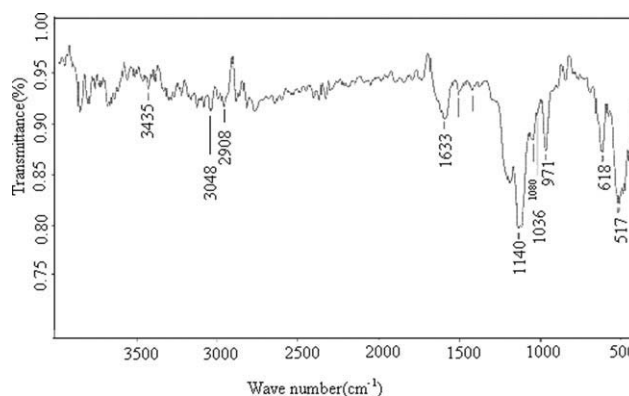
Figure 7 A typical FT-IR spectrum of the cast films.

commercial Nafion 117 film (16%). This revealed that the water sorption of solution casted with solvent and annealed films were comparable with that of the commercial Nafion 117 film.

Chemical structure

To assess the chemical structure of the cast films, ATR and FTIR spectra of the samples are taken and shown in Figures of 6 and 7, and the data are collected in Table II. The characteristic absorption bands of sulfonic acid groups around 1036 cm^{-1} and 1080 cm^{-1} confirmed the symmetric and asymmetric sulfonated bands, respectively. The SO$_2$ vibration of sulfonic acid group was observed at around 1140 cm^{-1}. The band at 971 cm^{-1} was attributed to pendant ether group. The absorption bands at 517 cm^{-1} and 618 cm^{-1} are characteristics bands of Nafion backbone.[2] Comparison of the ATR spectra shows the similarity of the absorption bands of different samples and revealed that the chemical structure of the recast Nafion films were remained intact. These results confirm that (re)casting of the operated films has no detectable effect on the chemical structure of them. Xu et al.[6] also reported similar results.

Mechanical properties

Tensile measurement

The stress-strain curves obtained for the films are represented in Figure 8. According to these graphs,

TABLE II
ATR and FTIR Data

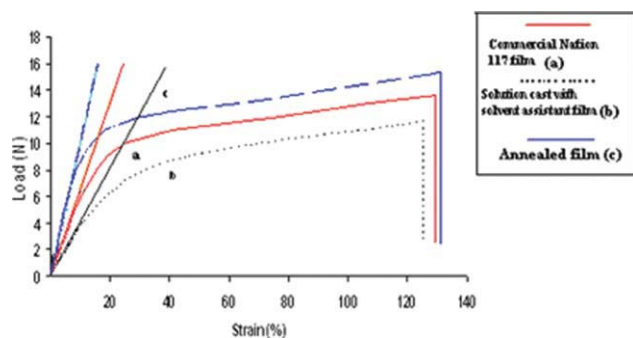| Polymer	Wave number (cm^{-1})
Cast films	517, 618 (CF$_2$—CF$_2$)
	971 (C—O—C)
	1036 (sulfonic acid, sym.)
	1080 (sulfonic acid, assym.)
	1140 (SO$_2$ vibration)

Figure 8 Comparison of stress-strain behavior of commercial Nafion-117 and the cast membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the mechanical properties of the cast membranes were almost similar to the commercial Nafion membrane. All of the samples showed elastomeric behavior with high elongation at break. However, the annealed film has a higher modulus in comparison with the solution cast film probably due to a short range ordering and a higher degree of crystallinity.[12] Therefore, good mechanical properties are achieved by annealing process, which cause prevention of less void formation, crack development, leading to a lower internal stress and an increase in the modulus.

Thermal properties

The thermal behavior of Nafion-based films, prepared from solution casting and treated as described above, was studied by DSC technique in 50–360°C region. DSC thermograms of solution cast films are given in Figure 9. According to these thermograms within the temperature range studied, two endothermic peaks are observed at nearly 180°C and 250°C, which are assigned to matrix glass transition (T_{gm}) and ionic cluster glass transition (T_{gc}) of the Nafion polymer. Similar thermograms were also reported by other workers, which are consistent with those shown in this study.[13,14] The extracted data from DSC thermograms are also summarized in Table III while the percentage of crystallinity was calculated according to Equation 5. The value of $\Delta H^{\circ}_{transition}$ is an identical constant for all the samples. As seen, the percentage of crystallinity is almost similar for prepared and commercial Nafion membranes. However, the annealed film showed a slightly higher crystallinity because the morphology of the heat-treated copolymer was slightly changed into a local order phase. The solution cast film with solvent has a lower crystallinity with respect to the annealed sample.

Morphology study

The scanning electron spectroscopy (SEM) technique was employed to study the morphology of the films. The SEM micrographs of the commercial Nafion-117
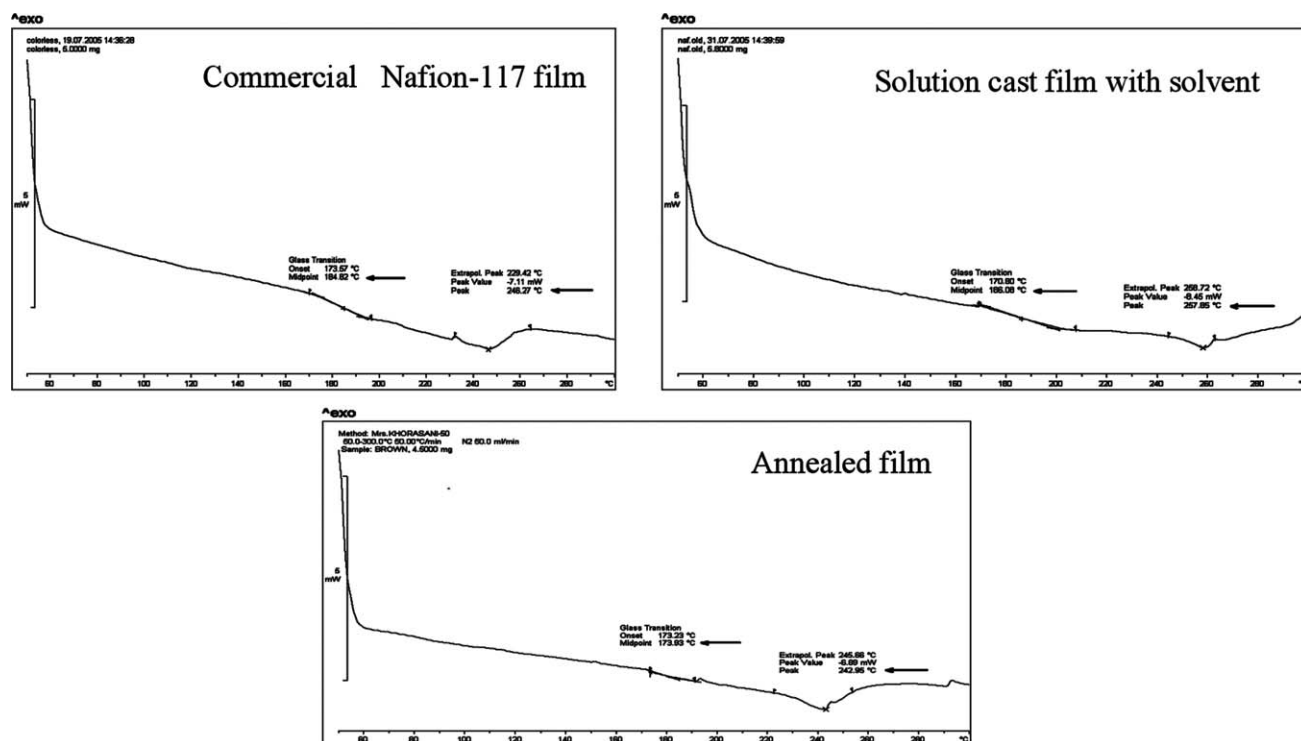

Figure 9 DSC thermograms of solution derived films.

TABLE III
DSC Data and Percentage of Crystallinity

Sample	$T_{g,m}$ (°c)	$T_{g,c}$ (°c)	W (g)	$\Delta H_{\text{Transition}}$	Crystallinity (%)
b	186.1	257.9	5.8	−8.45	$656/\Delta H^o_{\text{fusion}}$
c	173.9	242.9	4.5	−6.89	$689/\Delta H^o_{\text{fusion}}$
d	184.8	246.3	5.0	−7.11	$640/\Delta H^o_{\text{fusion}}$

and those of the cast films are depicted in Figure 10. As seen, the surface structure of the commercial sample is smooth and homogenous, but the cast films contain some micro pores, which are produced during solution casting. The solution cast film has the largest amount of micro pores leading to a brittle structure. However, the solution cast with solvent and the annealed films contain lower amount of micro pores, which led to much better mechanical properties, compared with that of the solution cast film.

Cell performance test

Cell voltage can be used as a criterion for evaluation of cell performance due to different cell components or different process parameters.[15–18] This is the most important process parameter proportional to the power consumption of a CA plant. The lower the cell voltage, the lower is the energy consumption. There are different ways to measure or predict cell voltage. These ways are experimental measurement, prediction by statistical methods,[16] analytical formulations,[16] and nonparameter regression methods like artificial neural networks (ANNs)[17] and support
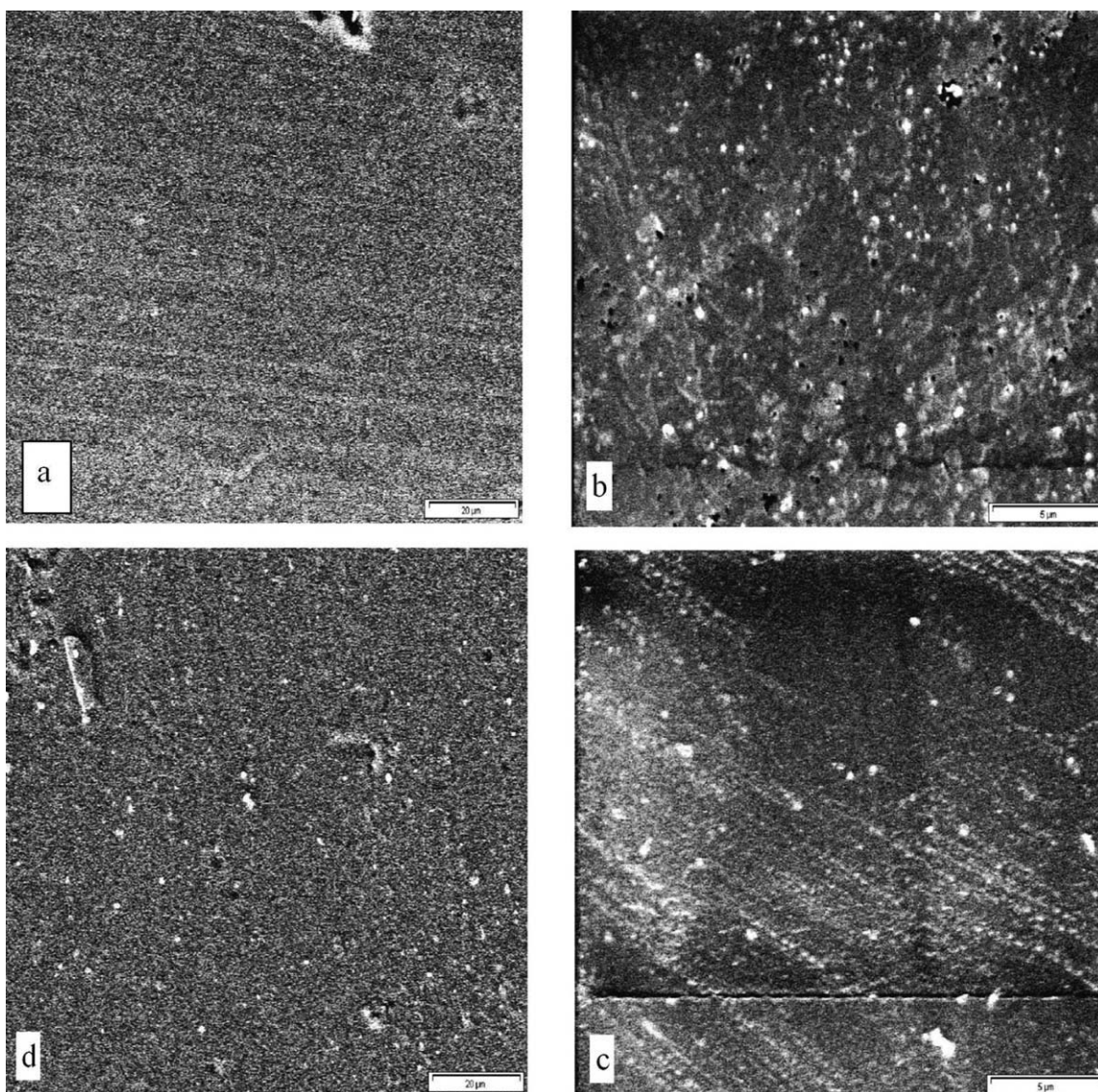

Figure 10 The SEM micrograph of nafion-117 and solution cast films: (a) Commercial Nafion-117 film; (b) Solution cast film; (c) Solution cast with Solvent; (d) Annealed film.
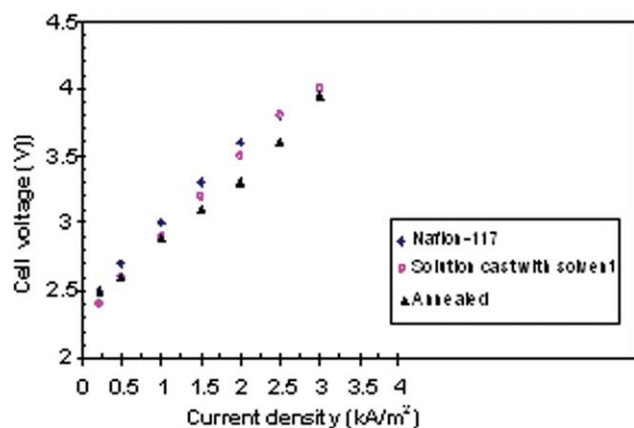
Figure 11 Cell voltage versus current density for different Na type Nafion membranes in a standard CA cell at 90°C, pH > 2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

vector machine (SVM).[18] In this study, we used the experimental method for measurement of overall cell voltage as a function of current density for performance comparison of different membranes.

Figure 11 shows a plot of the measured overall cell voltage against current density obtained for all Nafion membrane samples in a CA set-up according to the procedure described in experimental section. The cell voltage for a commercial Nafion 117 was also depicted for comparison. Because of poor mechanical properties and brittleness, the cell performance test for solution cast film was not carried out. Within the experimental range studied, a linear correlation between cell voltage and current density was observed for all membranes tested. Similar results are obtained for commercial membranes in our earlier studies.[16–18] The lowest cell voltage at a constant current density corresponds to the annealed Nafion film showing a better cell performance.

CONCLUSIONS

A series of tough, ductile and bright membranes with a controlled thickness of 150–180 μm, containing a pendant perfluorosulfonic sodium type end group has been obtained by solution casting and annealing techniques for Chlor-Alkali application. The new prepared films are similar to the commer-cially available Nafion-117 membrane modified with Na^+ ion in terms of chemical structure, morphology, mechanical, and thermal properties. The mechanical properties of the annealed membrane were similar to the commercial Nafion membrane. However, the former has a higher modulus compared with the solution cast one. DSC studies also revealed no significant difference between the thermal behaviors of the samples, despite the initial sources of the resin used for membrane forming. Some micro pores were observed in the cast films during solution casting resulting in poorer mechanical properties. These high-quality solution-cast PFSI membranes were then evaluated in Chlor-Alkali set up and a comparable cell performance characteristic was obtained. Such PFSS type films may be used as the anodic layer of the composite membrane in a CA cell.

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