



## Recycling and regeneration of used perfluorosulfonic membranes for polymer electrolyte fuel cells

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### Abstract

This paper describes a method for the recycling and regeneration of used perfluorosulfonic Nafion® (Dupont) membranes by dissolution and recasting. The dissolution of the used Nafion® membranes from polymer electrolyte fuel cells is realized using dimethyl sulfoxide as a solvent under atmospheric pressure and 190 °C. A mechanically robust membrane can be reproduced by a recast process of the dissolved Nafion® solution at 170 °C. The recycled membrane has shown a good crystalline structure and high mechanical strength. Membrane properties, including water uptake, exchange capacity and resistance are similar to that of the as-received Nafion® 115 membrane. Fuel cells prepared by the recycled membrane demonstrate a comparable performance to that of the fresh fuel cell.

### 1. Introduction

As a perfluorosulfonic proton conductor, Nafion® (Dupont) membrane is widely used in various electrochemical processes such as fuel cells [1, 2], chloro-alkali electrolysis [3, 4] and photoelectrochemical systems [5] because of its good thermal, chemical and mechanical stabilities. As more and more polymer membranes are used in these applications, there will be a vast amount of used or failed membrane materials waiting to be reprocessed. This is particularly so if the polymer electrolyte fuel cells are to be commercialized in the transportation and portable electronics applications. As with used batteries, the disposal of these membranes could cause an enormous environmental problem because of the mechanically stable polytetrafluoroethylene backbone in the membrane. Moreover, if the economic factor for producing membranes is taken into account, it will make good sense to develop a sustainable technology to recycle and reuse the 'old' membranes. To this end, we report a membrane regeneration technique and demonstrate that the reproduced membrane can be used as effectively as the fresh counterpart.

The recycling strategy involves the processes of membrane dissolution and recasting. Perfluorosulfonic membrane is typically insoluble at room temperature in alcohol and water. The dissolution of this membrane can be realized by immersing in a mixture of ethanol and water at high temperature and high pressure [6]. It has also been reported that the mechanical strength of the recast film from this solution can be improved by

introducing a strong polar and high boiling point solvent, such as dimethyl sulfoxide (DMSO), during the recast process [7]. In this work, we report a dissolution process operated at atmospheric pressure. The polymer solution obtained using DMSO was subsequently recast to form a new membrane at high temperature. Surface analytical techniques including X-ray diffraction, electrochemical impedance spectroscopy and cell polarization measurements were conducted to characterize the properties and performance of the recast membrane.

### 2. Experimental details

#### 2.1. Materials

Fresh Nafion® 115 membranes and 5% Nafion® solutions (both in H<sup>+</sup> form) were obtained from Electro-Chem, USA. The used membranes were collected from membrane electrode assemblies (MEAs) after performance testing at 80 °C and atmospheric pressure, with hydrogen feeding to the anode and oxygen to the cathode. The duration of the performance tests for different MEAs varied from several days to one month. The detailed procedure for electrode and membrane pretreatment has been reported in previously [8] and the MEA was formed by hot pressing at 135 °C and 90 atm for 90 s. All the other reagents were reagent grade and used as received. High purity water was obtained by

circulating deionized water through a milli-Q water purification system.

## 2.2. Dissolution of the used Nafion<sup>®</sup> membranes

The used membrane electrode assemblies were placed in a beaker containing isopropanol and boiled for 20 min. Because of the significant difference in swelling between the Nafion<sup>®</sup> 115 membrane and electrodes, the electrodes would be delaminated from the membrane. After the removal of the remaining trace amount of catalysts using a mechanical means, these membranes were then put in a 3–5% H<sub>2</sub>O<sub>2</sub> solution and boiled for 1 h until colourless membranes were obtained. Following that the membranes were converted to the Na<sup>+</sup> form by soaking in 0.5 M NaOH overnight for the purpose of preventing the membrane materials from degradation during the high temperature dissolution. These Na<sup>+</sup> form membranes were then placed in the solution of DMSO and refluxed at 190 °C under N<sub>2</sub> until all the membranes were totally dissolved to form a ~2 wt% Nafion<sup>®</sup> solution. The purpose of adding N<sub>2</sub> is to prevent the membranes and DMSO from being oxidized at high temperature.

## 2.3. Preparation of recast membrane

The DMSO solution containing the Nafion ionomer was put in a Petri dish and heated at 150 °C under N<sub>2</sub>. After drying off most of the DMSO solvent, a 2 h heat treatment at 170 °C was conducted. The recast Nafion<sup>®</sup> membrane was then detached from the Petri dish using high purity water. A standard procedure was subsequently employed for the final treatment of the membrane [9]. For comparison, a fresh recast membrane was made at room temperature using commercial 5% Nafion<sup>®</sup> solution. To evaluate the properties of recast membranes, their thickness should be maintained at the same level as the commercial Nafion<sup>®</sup> 115 membrane (127 μm). The actual thickness of recast membrane from DMSO solution at 190 °C and recast membrane from 5% solution at room temperature were determined at 120 and 137 μm, respectively.

## 2.4. Membrane characterization

Powder X-ray diffraction (XRD) patterns for the prepared membranes were obtained on a Philips powder diffraction system (model PW1830) using a CuK<sub>α</sub>-source operating at 40 keV and at a scan rate of 0.025 degree s<sup>-1</sup>.

An Instron (model 5567) tensile tester was used for the measurement of the tensile strength of the membranes. For this purpose, the membranes were cut into a rectangular shape with a width of 5 mm.

Water uptake of the prepared membranes was determined by measuring the weight difference between the dried and fully hydrated membrane.

The membrane resistance and performance evaluations were realized using a 5 cm<sup>2</sup> FCT-2000 fuel cell test

station (ElectroChem, USA) and Autolab Potentiostat (Eco Chemie, Netherlands) with a built in frequency response analyser. For the purpose of cell performance testing, a MEA unit was prepared by hot pressing the membrane with two commercial E-TEK electrodes (0.4 mg cm<sup>-2</sup> Pt loadings and 1.0 mg cm<sup>-2</sup> Nafion<sup>®</sup> impregnation) at 135 °C and 90 atm for 90 s [8].

The equivalent weight (EW) of the membrane was determined using the following protocol [10]. The tested membrane was soaked in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution for 1 h to completely convert it into the H<sup>+</sup> form. After rinsing several times with high purity water, it was placed in a beaker with 20 ml 1 M NaCl solution and soaked for another 24 h to fully exchange sodium ions for the protons in the membrane. The exchanged protons were titrated with NaOH solution using phenolphthalein as the indicator. The experiments were repeated three times and the average values of the EW were reported. The membrane EW was calculated by normalizing the weight of Nafion<sup>®</sup> in the sample by the moles of proton found from titration as follows:

$$EW = \frac{W_g}{C_{\text{NaOH}} \cdot V_{\text{NaOH}}}$$

where  $W_g$  is the dry weight of membrane,  $C_{\text{NaOH}}$  is the molar concentration of NaOH solution and  $V_{\text{NaOH}}$  is the titration volume of NaOH.

## 3. Results and discussion

The X-ray diffraction patterns of the fresh and recycled membranes are shown in Figure 1. The result for the recast membrane from 5% solution at room tempera-

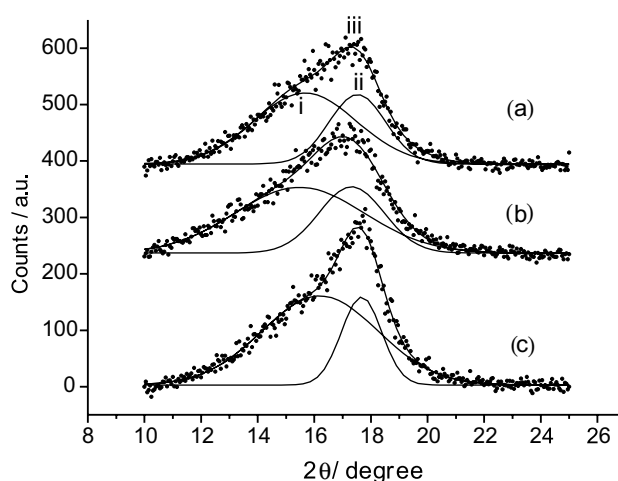


Fig. 1. X-ray diffraction patterns of different membranes in protonic form and dry state: (a) as-received Nafion<sup>®</sup> 115 membrane; (b) recast membrane from DMSO solution at 190 °C; (c) recast membrane from 5% solution at room temperature. Measured data shown by dotted line. Curve i and ii are the deconvoluted profiles, representing the amorphous and crystalline components, respectively. Curve iii is the convolution of curves i and ii.

Table 1. Deconvolution of XRD profiles for three membranes

	Nafion <sup>®</sup> 115 membrane		Recast membrane from DMSO solution at 190 °C		Recast membrane from 5% solution at room temperature	
	Peak i	Peak ii	Peak i	Peak ii	Peak i	Peak ii
Peak position (2θ/degree)	15.7	17.5	15.4	17.4	16.2	17.6
Peak area	587	288	652	351	810	277
FMHM (2θ/degree)	4.30	2.29	5.34	2.75	4.83	1.65
Average crystal size/nm	–	1.8	–	1.5	–	2.5

ture is also presented for comparison. The diffraction peak at about  $2\theta = 18^\circ$  is related to the hexagonal structure of Nafion<sup>®</sup>, and it overlaps with the X-ray scattering from the amorphous region of the membrane at lower Bragg angles. The detailed peak profile analysis using the multi-peaks fitting (Table 1) reveals an increase in the ratio between the crystalline peak and the amorphous scattering for the membrane prepared from DMSO solution and as-received Nafion<sup>®</sup> 115, compared with the recast membrane made of 5% Nafion<sup>®</sup> solution [11, 12]. Surprisingly, the crystalline peak is sharper for the recast membrane from 5% solution, indicating a larger crystal size. The differences in the crystalline structure contribute to different mechanical and physical properties. The higher crystalline component in the recycled membrane might be explained by the high processing temperature and the existence of DMSO. It is proposed that the membrane reconstructed at low temperature could behave like an amorphous material [13]. There is no long-range order among the lamellar crystallites, resulting in a lower mechanical strength. When a high processing temperature is applied, molecules reequilibrate and a long-range order develops. Thus, some degrees of crystallinity can be observed. Furthermore, because of the presence of residual solvent with high boiling point acting as a plasticizer, the higher crystalline component for the membrane recast from DMSO solution can be obtained and thus a higher

mechanical strength achieved. It can also be observed from Figure 1 that the XRD patterns are similar for the as-received membrane and the regenerated membrane.

Consistent result can be obtained from the tensile strength measurement of the membranes as shown in Figure 2. The membrane prepared at 190 °C with DMSO shows a higher mechanical strength and breaks at a higher load than the performance of the membrane recast from 5% Nafion<sup>®</sup> solution at room temperature. However, neither recast membrane reached the strength of as-received Nafion<sup>®</sup> 115.

Listed in Table 2 is the comparison of water uptake between the recycled membrane and the as-received Nafion<sup>®</sup> 115 membrane. Similar water contents can be achieved for both membranes. The water uptake is closely related to the proton conductivity. As in any other conducting medium, the magnitude of the proton conductivity is determined by the product of proton concentration and proton mobility. The proton concentration (or the exchange capacity) measures the total amount of ionic sites which provide proton exchange ability. With less water in the membrane, some of the sites might be isolated within a fluorocarbon matrix and the sulfonates are inaccessible to the available protons and cannot contribute to the exchange capacity. For a fully hydrated Nafion<sup>®</sup> membrane, this exchange capacity is similar to that in 1 M aqueous sulfuric acid solution. As a measure of the membrane exchange capacity, the equivalent weight (EW) of this recast membrane and as-received Nafion<sup>®</sup> 115 membrane is presented in Table 3. The measured value for Nafion<sup>®</sup>

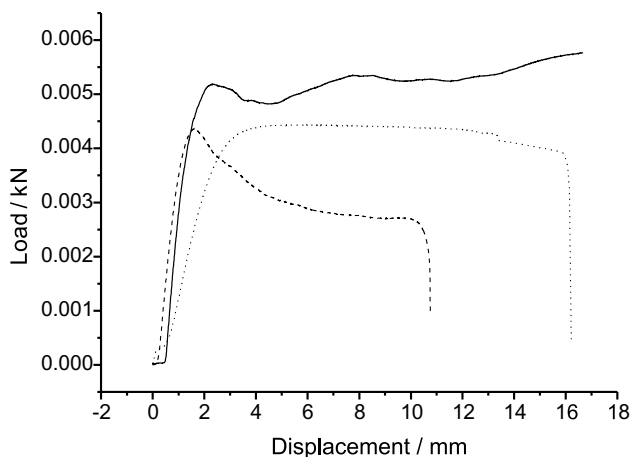


Fig. 2. Tensile strength measurements for the three membranes. (—) As-received Nafion<sup>®</sup> 115 membrane; (---) recast membrane from 5% solution at room temperature; (···) recast membrane from DMSO solution at 190 °C. Operating conditions: crosshead speed 2.50 mm min<sup>-1</sup>, temperature 23 °C, humidity 50%.

Table 2. Comparison of water content between the Nafion<sup>®</sup> 115 membrane and the recast membrane from DMSO solution

Membrane identification	Dry weight /g	Wet weight /g	Water content /%
Nafion <sup>®</sup> 115	0.545	0.768	41
Recast membrane	0.343	0.460	41

Table 3. Comparison of equivalent weight between the Nafion<sup>®</sup> 115 membrane and the recast membrane from DMSO solution

Membrane identification	Equivalent weight/g mol <sup>-1</sup> of SO <sub>3</sub> <sup>-</sup>	
	Theoretical	Measured
Nafion <sup>®</sup> 115	1100	1120
Recast membrane	–	1160

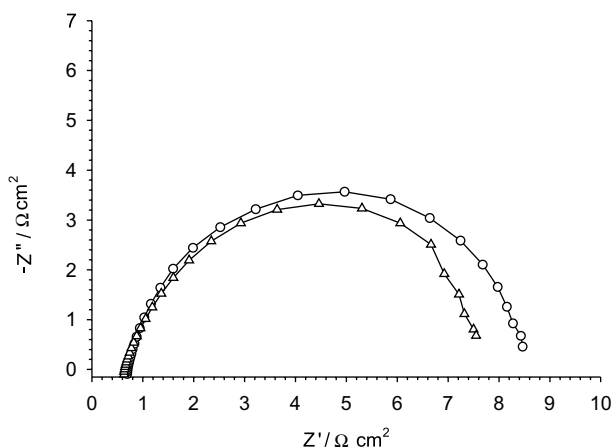


Fig. 3. Electrochemical impedance spectra for the two membranes measured at open circuit: (○) Nafion<sup>®</sup> and 115 and (△) recast. Operating condition: cell temperature 50 °C, humidifier temperature 75 °C, atmospheric pressure, O<sub>2</sub> and H<sub>2</sub> flow rate at 100 ml min<sup>-1</sup>.

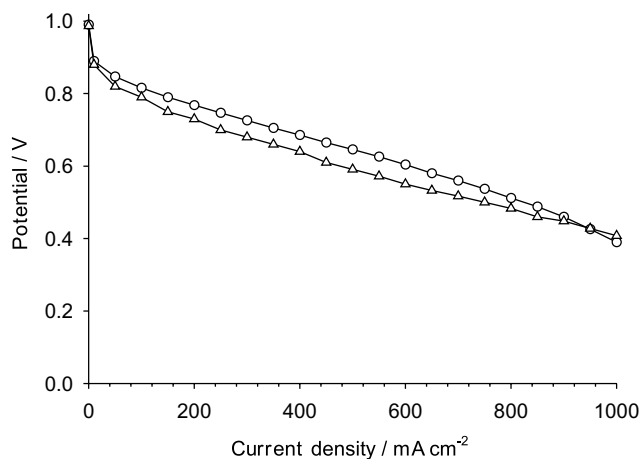


Fig. 4. Cell polarization curves for two membrane systems: (○) Nafion<sup>®</sup> and 115 and (△) recast. Operating conditions: cell temperature 50 °C, humidifier temperature 75 °C, atmospheric pressure, O<sub>2</sub> and H<sub>2</sub> flow rate at 100 ml min<sup>-1</sup>.

115 is in agreement with the theoretical value, [14] indicating the validity of this method. It can also be observed that the value for the recast membrane is only slightly higher than that of the Nafion<sup>®</sup> 115 membrane, suggesting that the amount of sulfonate groups destroyed during the high temperature process is insignificant. The similar EW can also be verified from the measurement of membrane resistance by electrochemical impedance spectroscopy as shown in Figure 3, where both membranes show similar resistance.

The fuel cell polarization behaviour obtained with these membranes (Figure 4) show that the recycled membrane-based fuel cell performance is only 10% less than the fresh membrane fuel cell. The analyses described above indicate that the membrane recycling strategy proposed in this work is a viable option for reuse of perfluorosulfonic polymer membranes in the fuel cell industry.

#### 4. Conclusions

Recycling of used Nafion<sup>®</sup> membranes was realized by dissolving them in DMSO and subsequent recasting at a high temperature. With enhanced mechanical strength, the membrane obtained has similar structure as the as-received membrane and comparable performance can be obtained in terms of water uptake, exchange capacity, membrane resistance and cell performance between the fresh and recycled membranes.

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