Journal of Power Sources 242 (2013) 23–27

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Electro-casting of proton exchange membranes from a heterogeneous solution

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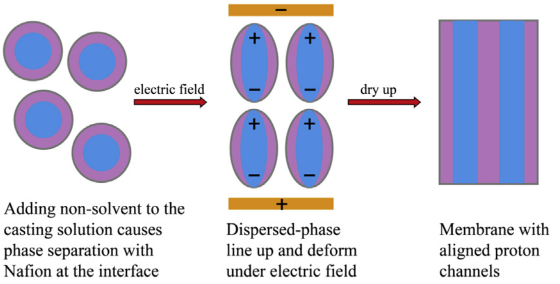
HIGHLIGHTS

- Non-solvent CCl4 leads to phase separation of the casting solution of Nafion.
- Electric field treatment to the solution leads to improved proton conductivity.
- Proton channels of the PEM are oriented in the trans-plane direction.
- The PEMs are mechanically robust despite of phase separation in casting solution.
- It is suggested that the non-solvent induced phase separation is a deciding factor.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 March 2013
Received in revised form
4 May 2013
Accepted 8 May 2013
Available online 23 May 2013

Keywords:
Proton exchange membranes
Nafion
Orientate
Phase-separated
Self-organization
Electric field

ABSTRACT

A novel solution casting method of membrane preparation is explored to improve the conductivity of proton exchange membranes (PEMs). A high voltage alternative electric field is applied to a heterogeneous Nafion solution while evaporating the solvents, leaving aligned proton channels in the solidified membrane, and SAXS and WAXS have been given as direct evidences. Therefore, the trans-plane conductivity of the PEM is increased. A Non-solvent of low polarity carbon tetrachloride (CCl_4) causes phase separation in the casting solution, which facilitates the Nafion ionomer to respond to the applied electric field. Despite the severe phase separation in the casting solution, the resultant electro-casting membrane shows a higher mechanical strength than that of the normal recast Nafion membrane.

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are considered to be a very promising alternative power source for a wide spectrum of applications. The PEM in such fuel cells is often a performance-limiting component. Perfluorosulfonic acid membranes with the trade name Nafion are the most commonly used electrolyte in PEM fuel cells. Although the Nafion has become the PEM of choice since the late-1960's and is still among the best available, it is not satisfactory in conductance property, which can lead to problems, such as ohmic losses at high current density, resistance to water transport from cathode to anode, or proton

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http://dx.doi.org/10.1016/j.jpowsour.2013.05.024

conductance deterioration at high temperature or low humidity [1]. Therefore, numerous efforts have been made to improve the conductivity performance of Nafion membranes. Generally, the increase in ion exchange capacity (IEC) of PEMs can significantly elevate the conductivity, however, high IEC is usually achieved at the sacrifices of other properties of the PEMs, such as the mechanical stability and solvent resistance [2].

One attractive approach of improving the conductivity of PEMs is to construct straight proton conducting channels, since under such condition the utilization of sulfonate groups can be improved, and therefore high conductivity can still be expected even with a relatively low IEC. To this end, electric field treatment has been suggested as a method for achieving oriented proton channels in PEMs [3]. Molecular-dynamics simulations have been used to study the morphological changes induced in ionomer by imposition of a strong electric field, and it has been observed that upon removal of the electric field, the structures aligned along the direction of the applied field persist and have a lower calculated free energy than the original isotropic morphology [4].

Some researchers have used the electric field to construct oriented proton channels in PEMs. Three orders of magnitude enhancement of conductivity was obtained by Gasa et al. [5] and Wei and Yate [6] who have applied an electric field to hybrid polymers that blend non-conductive matrix polymers with conductive sulfonated poly (ether ketone ketone) or Nafion solid particles. However, the conductive component is the dispersed phase with low volume fractions slightly lower than the percolation threshold. This can cause great improvement in conductivity after the electric field is applied, but the value of the conductivity remains relatively low even after being improved. What is more, by dispersing a conductive component into a non-conductive matrix, the conductivity of the hybrid membranes is limited, which can never be higher than that of the conductive component by itself. On the other hand, the electric field treatment will be less effective given the conductive phase is the major component of PEMs. Therefore, a hybrid PEM containing a minority conductive dispersed phase is not a good system where to construct oriented proton channels.

In this communication, a method of electric field treatment has been established to synthesize a PEM with oriented proton channels using only Nafion as the ionomer. Besides the Nafion ionomer and solvent DMF, the casting solution also contains a low polarity non-solvent CCl_4 which induces intense phase separation in the casting solution. Conductivity and mechanical strength of the PEM have been measured. Crystallinity of the PEM is obtained from the X-ray diffraction (XRD) spectrum.

2. Experiment

2.1. Membrane preparation

Commercial Nafion solution (5 wt %, DE520) was purchased from Aldrich. The received Nafion solution was heated in a vacuum oven at 333 K to obtain dry Nafion resin, which was then redissolved in DMF to get a 10 wt % solution. CCl_4 was mixed with the solution under agitation to obtain an opaque 3.8 wt % Nafion casting solution. A membrane was obtained by casting the opaque solution under an alternative electric field (4500 V cm^{-1}, 0.1 Hz) on a glass plate at 353 K for 12 h, and then at 373 K for 4 h. The membrane prepared using the described method is denoted as M1 and another membrane prepared following exactly the same procedure but without applying the electric field is denoted as M2. A conventional recast Nafion membrane obtained from a 10 wt % Nafion/DMF solution was also prepared under identical conditions, which will be referred to as M3. The membranes were peeled off from the glass plates in deionized water, then protonated by immersing in 1 mol dm^{-3} sulfuric acid solution at room temperature for 24 h and rinsed thoroughly with deionized water. The thickness of the membranes in dry state is approximately 70 μm.

2.2. Characterization

The proton conductivities in the in-plane and trans-plane directions of the PEMs are measured following the method described in our previous works [7,8].

The small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) measurements were conducted using an X-ray diffractometer (Rigaku D/Max-2500V-PC, Rigaku) with a Cu Kα source ($\lambda = 1.54$ Å) at 40 kV, 200 mA. The samples of membrane were immersed in deionized water for a week before testing to ensure full hydration. The same instrument was also used to obtain XRD data, from which the crystallinity of membrane was obtained by first identifying the crystalline (at $2\theta = 14.5°$) and amorphous (at $2\theta = 16.5°$ and 39.7°) peaks, and then calculating the ratio of the crystalline peak area to the sum of the three peak areas [9].

A sealed cell of the heterogeneous solution was put under an alternative electric field (4500 V cm^{-1}, 0.1 Hz) of trans-plane direction at room temperature without evaporation. The resistance of the solution in the in-plane direction varied with time, which was monitored by a frequency response analyzer (FRA, PARSTAT® 2273, Princeton Applied Research Inc.).

The composition of the dispersed phase and continuous phase in the heterogeneous solution is separately analyzed by a gas chromatograph-mass spectrometer (GC-MS, QP5000, Shimadzu Co.). Samples taken from casting solutions were diluted with an appropriate amount of DMSO and injected directly into the GC.

The mechanical strength of the membranes is measured using an electronic universal testing machine (WD-10D, Changchun Second Tester Factory). The sample preparation and measurement procedures are carried out in accordance with the Chinese Standard GB-13022-91.

3. Results and discussion

3.1. Conductivity

M1 has priority over M2 in the trans-plane conductivity from 293 to 333 K (Fig. 1a). However, the conductivities in orthogonal directions should be inversely proportional for PEMs with oriented proton channels, which has been observed by Majewski et al. [10]. To further certify the orientation of proton channels in the M1, in-plane conductivity of the PEMs has been measured and shown in Fig. 1b that the M2 takes priority over the M1 in the in-plane conductivity from 293 to 353 K. Such phenomena of inverse proportion indicate that the proton channels in the M1 sample have been oriented in the trans-plane direction by the electric field. Compared with random proton channels, the oriented proton channels can shorten the proton transport distance through PEMs and improve the utilization of the sulfonate groups in ionomer. As a result, the resistance of PEMs can be decreased with a constant thickness and IEC of the PEMs, and high mechanical strength and solvent resistance could be expected.

In addition, the higher conductivity of M1 and M2 over that of M3 implies that without the electric field treatment the non-solvent by itself can also contribute to the conductivity improvement, which makes another story [11].

3.2. Crystallinity and mechanical analysis

As properties of the PEMs are strongly affected by their microphase separated morphology, works have been done with the aim