Short communication

Novel nanofiber-based triple-layer proton exchange membranes for fuel cell applications

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ARTICLE INFO

ABSTRACT

New types of triple-layer membranes were fabricated using multi-step impregnation of Nafion in electrospun webs based on bead-free nanofibers of sulfonated poly(ether sulfone) (SPES). The results showed that the fabricated nanofiber-filled membrane owing to its reduced methanol permeability as well as sufficient proton conductivity and membrane selectivity can be used as a promising proton exchange membrane for direct methanol fuel cell (DMFC) applications. The single cell DMFC performance results revealed that the SPES nanofiber-based triple-layer membranes have higher electrochemical performance than commercial Nafion membranes.

1. Introduction

Proton exchange membranes (PEMs) are considered as one of the most important parts of fuel cells due to their ability to transport proton rapidly through themselves and also their fuel barrier characteristics [1]. The applicability of perfluorosulfonated membranes such as Nafion is now limitted in the case of direct methanol fuel cells (DMFCs) owing to their high permeation rate of methanol. Up to now, different methods have been proposed for fabrication of high-performance and low methanol permeable PEMs. Synthesis, structural modification and blending of existing PEMs, as well as organic/inorganic composite membranes preparation are among the most successful approaches for enhancement in DMFC performance using new-designed PEMs [2–8].

Among the non-fluorinated polymers, aromatic poly(ether sulfone) (PES) has been considered as a proper candidate for advanced technology applications due to its unique properties such as good chemical, thermal, hydrolysis and oxidative stability as well as its high mechanical strength and chain flexibility [8]. The low proton conductivity of PES can be improved using sulfonation process. Recently, membranes containing ion-exchanges nanofibers have been introduced as new type of high-performance PEMs. Electrospinning is one of the most common methods for fabrication of nanofibers with unique characteristics such as high specific surface area and good mechanical properties [9–11].

Electrospinning and solution properties of Nafion/poly(acrylic acid), Nafion-poly(vinyl alcohol), and Nafion-poly(ethylene oxide) have been lately reported [12,13]. Pintauro and coworkers [14] also reported proton conduction capability of electrospun sulfonated poly(arylene ether sulfone) (sPAES) based membranes for fuel cell applications. On the other hand, in the case of membranes based on Nafion-filled electrospun nanofibrous poly(vinylidene fluoride), Manthiram and coworkers [15] reported that single cell DMFC performance of these membranes is better than Nafion115 owing to reduced methanol crossover through the membrane. However, they used a system based on non-conducting nanofibrous webs and ion conducting matrices. To the best our knowledge, only a recent report investigated the composite membranes based on proton

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conducting electrospun web and ionomeric matrices for hydrogen fuel cell applications [16]. However, they used a same polymer for nanofiber fabrication and impregnation process.

Up to now, our research group fabricated several types of composite membranes as PEM [1,7,8] and also we fabricated several nanofibrous three-dimensional scaffolds for tissue engineering applications [9–11]. In this study, we aimed to combine the capabilities of these two concepts to reach high-performance membranes for DMFC applications. Therefore, for the first time sulfonated poly(ether sulfone) (SPES) nanofibers have been prepared via electrospinning technique and a new class of triple-layer polyelectrolyte membranes based on Nafion-filled nanofibrous webs has been fabricated and investigated for DMFC applications. To the best of our knowledge, this type of electrospun ion conductive nanofiber-based multilayer membranes has not been reported so far.

2. Experimental

2.1. Preparation of Nafion-filled triple-layer membranes

The sulfonation process of PES (Ultrason E6020P, BASF) was performed by the procedure reported in our previous study [8]. Briefly, PES was dissolved in concentrated sulfuric acid, and chlorosulfonic acid (Merck) was added dropwise to the resultant solution under vigorous stirring at 5 °C. Then, the mixture was precipitated in deionized water (Milli-Q) and the polymer was recovered by filtration.

SPES samples with a definite degree of sulfonation were used for nanofiber fabrication. Solutions for electrospinning were prepared by dissolving polymer in a certain amount (25 wt%) of N,N-dimethylformamide (Merck). A syringe pump was used to feed the solution through an extension tube ended in a blunted 21-gauge needle. To collect the nanofibers, a cylindrical stainless steel collector was located in 15 cm distance from the needle and high voltage potential was also applied between the needle and the collector. The polymer solution was forced to leave the needle and be collected as nanofibers on the rotating cylinder.

The porous SPES nanofibrous membranes were impregnated with defined amount of Nafion solution (5 wt%, DuPont) for 24 h in a multi-step process. Briefly, bottom layer was casted on a glass plate at 70 °C and then nanofibrous web mounted on the casted membrane and filled with Nafion solution. After a good pore-filling, an excess amount of Nafion solution was used to form a uniform top layer. The impregnated membranes were then annealed at 120 °C for 12 h, swollen in sulfuric acid (0.5 M) for 1 h and washed exhaustively with deionized water.

2.2. Characterization methods

For the morphological evaluations, the specimens were gold coated using a sputter coater and then scanned by a scanning electron microscope (SEM, Philips XL30, Netherlands). Also, dried membranes were dipped and fractured in liquid nitrogen and coated with gold for cross-sectional studies.

Proton conductivity measurements were performed via 4-point probe conductivity cell. The cell was set into a humidity chamber at 95% RH. Methanol permeability measurements were carried out in a two-compartment glass diffusion cell using a gas chromatograph as previously described in details [7,8].

Membrane electrode assemblies (MEAs) were prepared via the catalyst painting technique similar to our previous reports [7,8]. Pt and Pt/Ru-black (Johnson–Matthey) in the loading weights of 4 mg cm^{-2} were used as the catalysts for the cathode and anode, respectively. Prepared MEAs were performed in the DMFC single

cell which is described in details before [7,8]. Methanol was fed to the anode side at 20 psi back pressure for 1 h and air was introduced to the cathode side with a gradual increase in pressure up to 20 psi. All single cell tests were conducted three times, and the results are presented as the mean values.

For methanol crossover measurements, humidified nitrogen was fed to cathode side at 70 °C, and the fuel cell was performed until a limiting current occurs. This limiting current obtained at the open circuit condition indicates the oxidation current of methanol crossover from anode to cathode [7,17]. The methanol crossover current density, I_C, can be calculated by applying the following equation between the methanol crossover current at open and anode mass transport limiting current density: $I_C = I_{C,OC} (1 - (I/I_L))$, wherein $I_{C,OC}$, I and I_L are methanol crossover current density at open circuit, operating current density and anode mass transport limiting current density, all in mA cm^{-2} [18,19].

3. Results and discussion

SEM micrographs of SPES nanofibers as well as cross-sectional area of the triple-layer membrane (TLM) have been shown in Fig. 1. Image analysis of nanofibers (Fig. 1(a)) revealed that SPES nanofibers had an average diameter of 170 ± 48 nm. A layered morphology including a nanofiber containing layer sandwiched between two Nafion layers was clearly demonstrated in Fig. 1(b-1). Higher magnification micrographs of interface between Nafion layer and SPES fiber-Nafion layer confirmed designed composite structures (Fig. 1(b-2)). Absence of considerable fiber pull out or crack indicates good interfacial surfaces between SPES nanofibers and Nafion matrix (Fig. 1(b-3)).

In this study, proton conductivity behavior is investigated at several temperatures as one of the most important features of a PEM for fuel cell applications. As a matter of fact, SPES with a low degree of sulfonation (about 15 mol%) was used in the current research due to its higher dimensional stability even at elevated temperatures.

Conductivity measurements were carried out in a range of temperature from 25 °C to 80 °C. Fig. 2(a) illustrates the conductivity-temperature relationship of the TLM in comparison with that of Nafion112 and Nafion117. The conductivity of TLM is competitive with both commercial Nafion membranes.

From Arrhenius plots of conductivity, it could be found that conductivity of all membranes exhibits positive dependency with temperature, which disclosed that proton conduction is a thermally activated process. Furthermore, activation energies for proton conduction were calculated from Arrhenius equation and were shown in Fig. 2(b). As both of Grotthuss and vehicle mechanisms has been accepted for proton conduction through Nafion membranes, lower activation energies of the TLM compared to pristine Nafion117 and Nafion112 could be considered as capability of ionomeric nanofibers to enhance proton conduction characteristics.

The methanol permeability of the TLM, Nafion112, and Nafion117 are 1.35×10^{-6}, 3.22×10^{-6}, and 2.00×10^{-6} cm^2 s^{-1}, respectively. The methanol permeability reduction occurs from the longer and tortuous diffusive pathway in the presence of nanofibers at the middle layer.

The selectivity parameter, which is defined as the ratio of proton conductivity to methanol diffusion coefficient, is often used to evaluate the potential performance of DMFC membranes [1]. Room temperature selectivity values of the TLM is about 63,760 S s cm^{-3} compared to 28,300 and 40,500 S s cm^{-3} for Nafion112 and Nafion117, respectively. An improvement in the membrane selectivity has been achieved due to the incorporation of SPES nanofiber-filled layer into the Nafion.

The main goal of multilayer membrane fabrication is its reduced methanol permeability. Methanol permeation obstructs oxygen
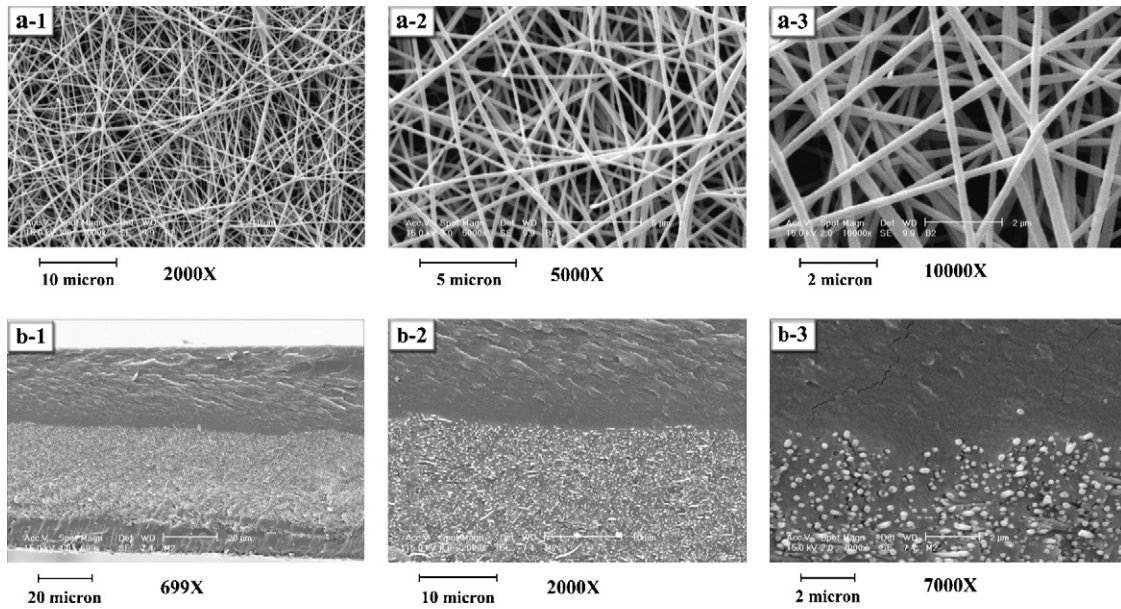
Fig. 1. SEM micrographs of SPES electrospun nanofibers (a) and cross-sectional area (b) of the TLM at different magnifications.

reduction reaction at the cathode side and consequently results in a significant reduction in the open circuit potential. Methanol crossover also leads to poisoning at the cathode electrode and low efficiency of fuel consumption due to the methanol loss [17]. Effects of methanol crossover on performance of the TLM at operational condition were investigated using methanol crossover current density which is calculated from the methanol crossover current density at open circuit, operating current density and anode

mass transport limiting current density. The results of methanol crossover measurements have been plotted in Fig. 3 for 1 and 5 M methanol concentrations.

Fuel efficiency, η_{Fuel}, was calculated using methanol crossover results via following equation: $\eta_{Fuel} = I/(I + I_C)$ [17–19]. Thermodynamic efficiency, η_{Therm}, is defined as the ratio of Gibbs free energy change per mole of methanol, Δg, to enthalpy change per mole of methanol, Δh. The voltage efficiency of fuel cell, η_{Volt}, is determined
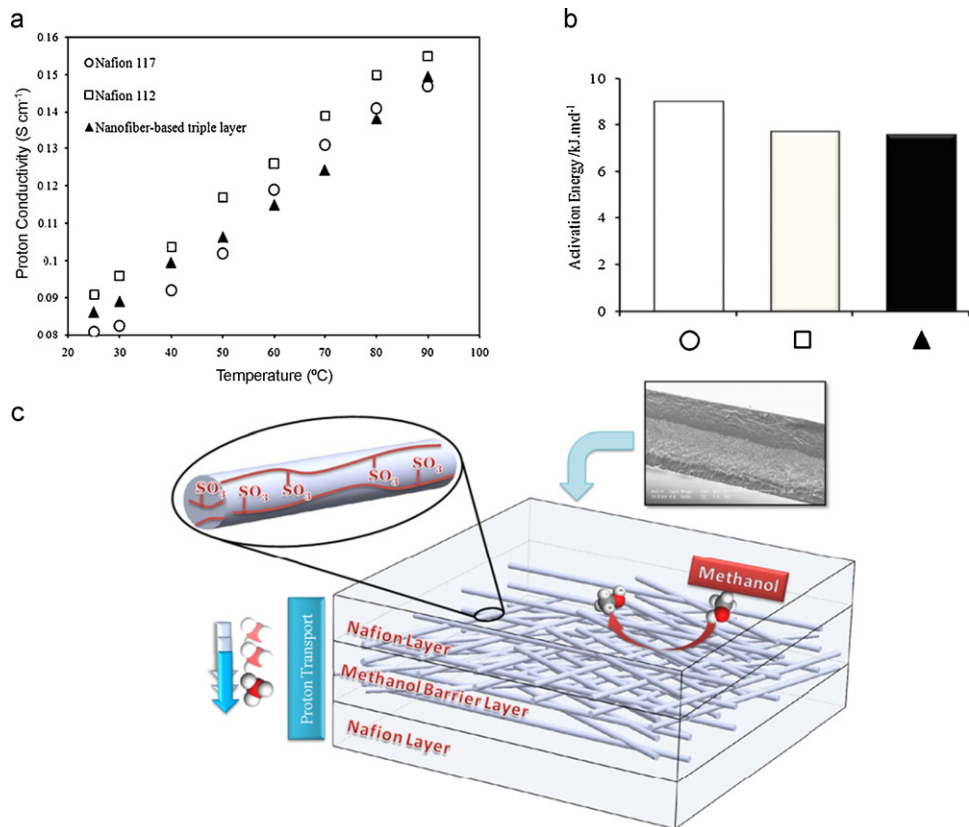

Fig. 2. Proton conductivity at different temperatures (a); activation energy values (b) for the TLM, Nafion112, and Nafion117, respectively, and schematically representation of designed TLM (c).
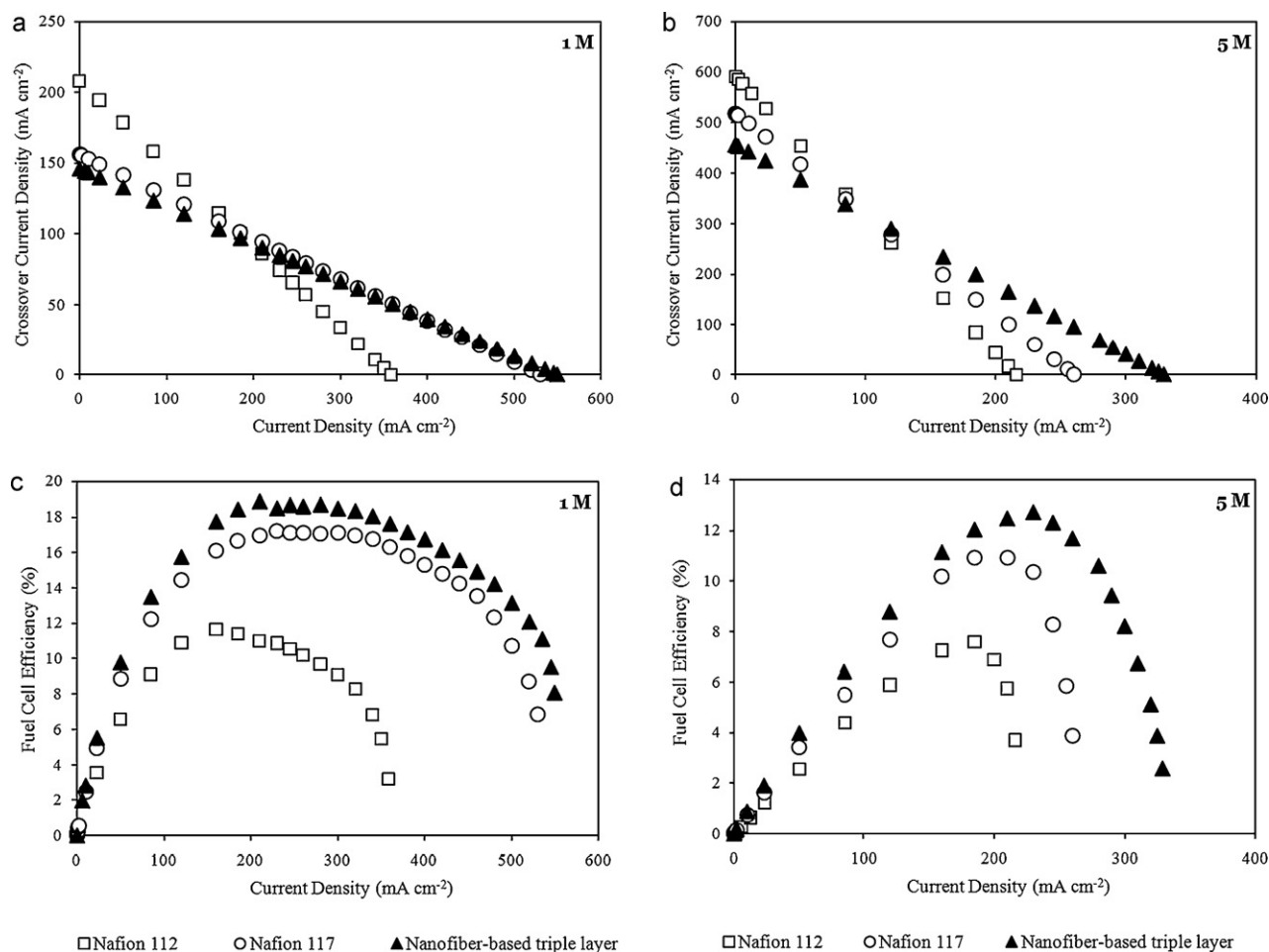
Fig. 3. Methanol crossover of TLM compared to Nafion112 and Nafion117 membrane at 1 M (a), and 5 M methanol concentrations (b). A collation between real fuel cell efficiency of membranes at 1 M (c) and 5 M (d) methanol concentrations at 70 °C.

as ratio of the real operating voltage, V_{Cell}, to theoretical maximum voltage, V_{Th}, of fuel cell. Accordingly, real efficiency of fuel cell, η_{Real}, is obtained the combination of fuel efficiency, thermodynamic efficiency, and voltage efficiency [17]: $\eta_{Real} = \eta_{Fuel} \cdot \eta_{Therm} \cdot \eta_{Volt}$.

As shown in Fig. 3, with increasing methanol concentration from 1 to 5 M in the case of Nafion112 and Nafion117 membranes, cell efficiency is remarkably decreased from 11.6% to 7.6% and from 17.23% to 10.9%, respectively, and also current density at the maximum efficiency was decreased as well. However, higher cell efficiency of 18.8% and 12.7% is provided using triple-layer membrane at 1 and 5 M methanol feed.

The fuel cell performance tests for manufactured membranes were done in an air-methanol single cell. The performance test was carried out using two different methanol concentrations of 1 M and 5 M at 70 °C. The open circuit voltages (OCVs) for the TLM, Nafion112, and Nafion117 membranes were measured to be 0.734, 0.583, and 0.686 V for 1 M methanol, and 0.613, 0.522, and 0.572 V for 5 M methanol, respectively. OCV is directly related to the methanol crossover and increases when the methanol permeation is reduced [7]. The higher OCV clearly indicates that the incorporated nanofiber-based layer into the Nafion structure (Fig. 2(c)) suppresses the methanol crossover, which is consistent with the methanol permeability results.

As shown in Fig. 4, the maximum power density of the TLM at the methanol concentration of 1 M reached 94.84 mW cm^{-1} compared to 42.69 mW cm^{-1} for Nafion112 and 86.73 mW cm^{-1} for Nafion117. At a 5 M methanol concentration, the maximum power

density of the TLM was measured to be as high as 60.29 mW cm^{-1}, whereas the highest power density output of the reference Nafion112 and Nafion117 membranes at the same methanol concentration was obtained to be 29.31 mW cm^{-1} and 47.04 mW cm^{-1}, respectively. The remarkable improvement in membrane selectivity of the TLMs compared to the neat Nafion was also reflected by their superiority in fuel cell performance.

The thickness of TLM is about 76 μm in comparison with 53 and 180 μm for Nafion112 and Nafion117, respectively. The layers' thickness is about 10, 36, and 30 μm for upper layer, middle layer, and bottom layer, respectively. The Nafion layer is better for catalyst preparation and designed as two layers, thinner and thicker, as layers close to anode and cathode electrodes. It is known that the membrane resistance of Nafion112 is lower than that of Nafion117, due to its reduced thickness, but the power production using Nafion112-based MEA is lower than that of Nafion117 owing to its high methanol crossover. In this paper we consider the methanol crossover as one of the most important characteristics of DMFC's membrane. Although three types of membranes have same methanol crossover value at 200 mA cm^{-2}, by the way the reduction slopes for them are far from each other. This means that overall behavior is more important than single point consideration. According to suppressed methanol permeation through the fabricated TLM; its fuel cell performance is better than commercial Nafion membranes.

By considering the transport and electrochemical properties of TLMs, this novel type of membranes can be suitable for high-performance direct methanol fuel cells. Our findings suggested that
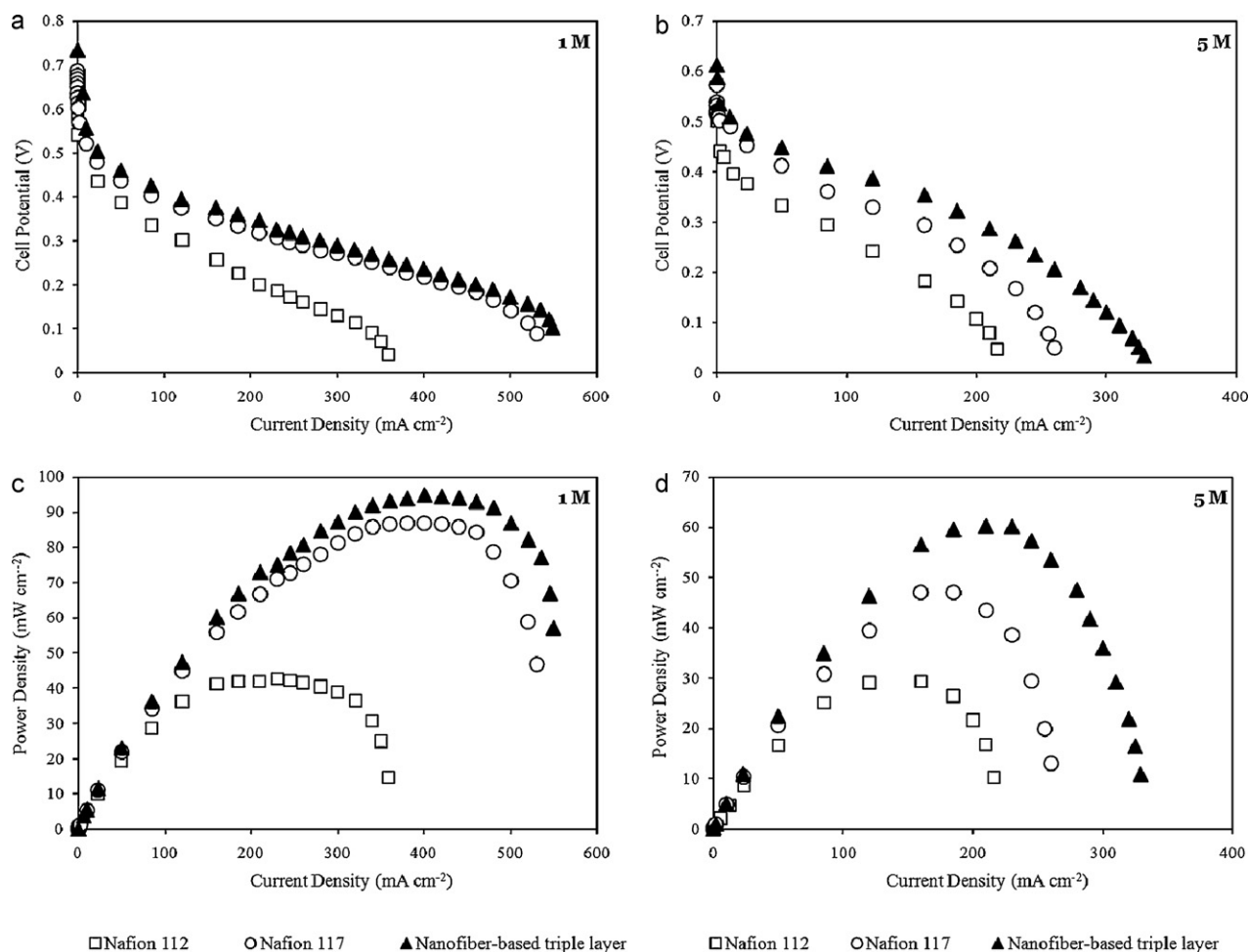
Fig. 4. Polarization curves (a and c) and power outputs (b and d) of Nafion/SPES nanofiber/Nafion, Nafion112, and Nafion117 using 1 M (a and b), and 5 M (b and d) methanol concentrations at 70 °C.

the fabricated nanofiber-based membranes hold suitable characteristics for direct methanol fuel cell applications.

4. Conclusion

Nanofibrous webs based on sulfonated poly(ether sulfone) (SPES) were fabricated and Nafion-filled triple-layer membrane (TLM) was prepared. The proton conductivity of the SPES based membranes was in the same range as Nafion112 and Nafion117 with lower activation energy. Presence of SPES nanofibers significantly reduced methanol permeability. The open circuit potentials for TLMs are higher than Nafion112 and Nafion117 membranes. The results revealed that the multilayer membranes based on the Nafion-impregnated sulfonated nanofibers can be considered as a novel type of polyelectrolyte membrane for direct methanol fuel cell applications.

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