J Appl Electrochem (2008) 38:543–550
DOI 10.1007/s10800-007-9471-5

ORIGINAL PAPER

# PEO–PPO–PEO triblock copolymer/Nafion blend as membrane material for intermediate temperature DMFCs

**Jin Hu · Vincenzo Baglio · Vincenzo Tricoli · Antonino S. Aricò · Vincenzo Antonucci**

Received: 20 July 2007 / Revised: 6 December 2007 / Accepted: 12 December 2007 / Published online: 22 December 2007

**Abstract** This paper describes homogeneous triblock copolymer/Nafion blend membranes, which facilitate proton conduction in direct methanol fuel cells (DMFCs) at intermediate temperatures. The interaction between the two polymer components is investigated by FT-IR spectroscopy. The blend membranes show higher proton conductivity than recast Nafion under partially anhydrous conditions. Protons can be transported with the assistance of ether chain under such conditions at elevated temperature. In addition, the membranes exhibit more favourable methanol permeability and selectivity. This kind of blend membrane shows somewhat better performance in DMFC compared to bare recast Nafion at intermediate temperature (≥120 °C). This work is a first attempt in our group to design membrane materials with enhanced proton conductivity under conditions typical of intermediate temperature DMFCs.

**Keywords** Direct methanol fuel cell · Blend membrane · Recast Nafion · PEO–PPO–PEO triblock copolymer · Intermediate temperature

## 1 Introduction

Direct methanol fuel cell (DMFC) devices presently suffer from methanol crossover across polymer electrolyte membranes (crossover affects fuel efficiency as well as performance of the cathode) and poor methanol electro-oxidation kinetics at low temperature at Pt-based anode catalysts [1]. Other disadvantages are the cost of materials (namely the noble metal catalysts and the perfluorosulfonic membrane) and the cost of production for various components of the device.

Most of the shortcomings associated with low-temperature DMFC technology can be partly solved or avoided by developing membranes capable of operation at temperatures above 100 °C [2–6]. The ensuing advantages include the following: (1) The kinetics of both electrode reactions are enhanced, which is of special importance for the direct oxidation of methanol in DMFC [2, 3]. (2) The CO tolerance of Pt is dramatically enhanced, for example, from 10 to 20 ppm of CO at 80 °C, up to 30,000 ppm at 200 °C [7]. High working temperatures reduce catalyst poisoning, thus increasing the oxidation kinetics and even allowing platinum to be replaced by a non-noble metal [4]. (3) The required cooling system is simple and practically possible due to the increased temperature gradient between the fuel cell stack and the coolant [8]. Thus the overall system efficiency is significantly improved. Consequently, the availability of proton conducting membranes retaining satisfactory conduction properties at intermediate temperature (100–200 °C) could permit the realization of efficient methanol fuel cells which is of special interest for electric car applications.

Current DMFC technology is based on perfluorosulfonic acid (PFSA) polymer membranes (e.g., Nafion) [1, 9, 10]. Nafion exhibits generally good chemical stability and proton conductivity at high relative humidity and low temperature. Besides its high cost, a major drawback of Nafion is the low conductivity under low humidity condition, which bears poor fuel cell performance at elevated temperatures (above 100 °C). Considerable effort has been

---

J. Hu · V. Tricoli (✉)
Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali, Università di Pisa, 56126 Pisa, Italy
e-mail: v.tricoli@ing.unipi.it

V. Baglio · A. S. Aricò · V. Antonucci
CNR-ITAE Institute, 98126 Messina, Italy

made to modify Nafion membranes in order to improve performance under high-temperature operation. These approaches include impregnating the membranes with hygroscopic oxide nanoparticles and solid inorganic proton conductors [11–16]. However, these strategies often lead to worsening of the mechanical properties of the composite membranes. Since the poor proton conductivity of Nafion at high temperature is due to water loss, an alternative approach suitable for intermediate temperature DMFC operation could be blending Nafion with unsoluble and nonvolatile polymers, which can act as proton solvents similar to water. It is well known that polyethylene oxide (PEO) is the basis for many nonaqueous solvent-free solid electrolytes currently under study, especially for the lithium ion battery. In fact, PEO can dissolve even high concentration of a wide variety of alkali metal salts to form polymer/electrolyte blends (not to be confused with polyelectrolytes where either the cation or the anion is covalently fixed to the polymer repeat unit) [17–20]. PEO acts like the solvent for Li-ion transportation in the solvent-free polymer/electrolyte blend.

The concept of PEO as a “solid solvent” where $Li^+$ transport can occur has also suggested PEO as a non-aqueous solid solvent for $H^+$ ion transport. The ethylene oxide group is a strong electron donor and should in principle be capable of interaction with protons. Unfortunately, PEO is soluble in water, which makes it unsuitable for DMFC application. Some liquid amphiphilic triblock copolymers of the kind $EO_n$–$PO_m$–$EO_n$ are involatile and insoluble in water and methanol/water solutions, due to the hydrophobic PPO segment. Moreover, these triblock copolymers are sufficiently stable below 160 °C and can be blended with Nafion, which makes them potentially interesting for DMFCs. To demonstrate the feasibility of this concept, we have prepared and characterized triblock PEO–PPO–PEO/Nafion blend membranes. We utilized commercially available Pluronic® PE10100 as the triblock copolymer. The electrochemical performance of a DMFC based on these blend membranes at intermediate temperature (up to 140 °C) has been investigated.

## 2 Experimental

### 2.1 Membrane preparation

Nafion was purchased from Aldrich as a 20 wt% solution in a mixture of low molecular weight alcohol and water. Triblock copolymer Pluronic® PE10100 (MW = 3500, $HO(CH_2CH_2O)_3(CHCH_3CH_2O)_{54}(CH_2CH_2O)_3OH$) was purchased from BASF Ltd. All chemical reagents were used without further purification. Initially, a 10 wt% PE10100/*N,N*-dimethyformamide (Aldrich) solution was prepared. Then, five volumes of the Nafion solution were mixed with five volumes of denatured ethanol (Alfa Aesar), three volumes of *N,N*-dimethyformamide and the desired amount of the PE10100/DMF solution. The resulting clear solution was poured in a Teflon dish with a glass bottom and placed in a vacuum oven at 80 °C until complete evaporation of the solvents. The resulting product (blend membrane) was then treated in 5 wt% $H_2O_2$ solution (Aldrich) and in 1 M $H_2SO_4$ solution at 80 °C for half an hour, respectively. Finally, the membranes were heated in boiling deionized water for half an hour. The 5 wt% PE10100/Nafion blend membrane was named PE5 and the 10 wt% blend membrane was named PE10. We also prepared PE20 blend membranes for Infrared Spectroscopy investigation only and bare recast Nafion membranes for comparison in all the experiments. The thickness of the obtained membranes was always 65–70 μm.

### 2.2 Characterization

The morphology of the sample was investigated by a scanning electron microscope (JEOL, model JSM 5600 LV) fitted with an EDX analyzer (Oxford, model 6587). FT-IR spectra were collected on a Perkin Elmer Spectrum One FT-IR Spectrometer using the attenuated total reflection (ATR) technique since the membrane is too thick for transmission measurements. The half-hydrated sample was prepared by vacuuming the sample at ambient temperature for half an hour. The anhydrous sample was prepared by vacuuming the sample at 70 °C for one night.

### 2.3 Proton conductivity measurements

Proton conductivity values of the membranes were obtained from the impedance data, which were collected on a Solatron 1255/1287 FRA/Electrochemical workstation in the frequency range of 1–$10^6$ Hz with an applied voltage of 10 mV. The test cell had a “sandwich” structure with the membrane clamped and sealed between two stainless steel electrodes (diameter 6 mm). The impedance measurements were performed at 100% relative humidity (RH) and also under fully anhydrous condition from ambient temperature to 80 °C. With regard to conductivity determinations under anhydrous condition, it should be noted that the membrane was first dehydrated for 2 h in a vacuum oven at 80 °C. The oven was allowed to cool to ambient temperature while maintaining vacuum. Finally, the membrane was immediately transferred and sealed into the electrochemical impedance cell for measurements.

### 2.4 Methanol permeability determination

The permeability experiments were carried out using a glass diffusion cell. A detailed description of the experimental set-up and procedure can be found elsewhere [21]. The methanol concentrations were measured by a capillary gas chromatograph (Fison, model 8000) fitted with a flame ionization detector. 1-butanol was used as the internal standard.

### 2.5 Membrane and electrodes assemblies (MEAs) fabrication

Pt–Ru (1:1 in atom) black and Pt black powder (purchased from Alfa Aesar) were used as the anode and cathode catalyst for the MEA, respectively. Platinum loading was 2 ± 0.1 mg $cm^{-2}$ for both anode and cathode. The electrode was prepared by pasting the catalyst slurry on a Teflonized gas diffusion layer for high temperature operation (purchased from E-TEK) and drying overnight at atmospheric conditions. The catalyst slurry was prepared by directly mixing the catalyst powder with the as-received 5 wt% Nafion solution (Aldrich) in an ultrasonic bath at 60 °C thereby forming a suspension. The latter was concentrated upon solvent evaporation until a thick paste was obtained. MEAs were fabricated by hot-pressing the anode and cathode onto opposite sides of a membrane at 130 °C and 50 kg $cm^{-2}$ for 1.5 min.

### 2.6 DMFC tests

Single cell tests were carried out in a 5 $cm^2$ single DMFC (GlobeTech, Inc.) connected to a HP 6060B electronic load. A 2 M methanol solution was fed into the anode of the cell at a flow rate of 2.5 mL $min^{-1}$ whereas oxygen was fed to the cathode at a flow rate of 300 mL $min^{-1}$ after passing through a humidification bottle maintained at 100 °C. Different operating temperatures for the cell were in the range of 90–140 °C. The anode back-pressure was varied between 1 and 3.5 atm as the temperature was increased from 90 to 140 °C; the cathode compartment back-pressure was maintained constant at 3.5 atm. The cell resistance was determined at various temperatures by the current interrupter method during cell operation at 0.5 A $cm^{-2}$. Prior to recording polarization curves, deionized water was fluxed through both the anode and the cathode compartments of the DMFC for 12 h. Then the DMFC was operated at 90 °C for 5 h at fixed output voltage of 200 mV. Finally, the polarization curve was recorded several times. Usually, after four or five runs (during which the fuel cell performance somewhat improves) the polarization curve always becomes highly reproducible with no appreciable variations during subsequent runs. Also, no significant deviation was generally observed for polarization curves obtained with different MEAs provided that electrodes from the same batchs were used. To ensure consistent comparison of the PE5, PE10 and Nafion membranes in DMFC, the various MEAs were fabricated from the same anode and cathode sheets in all cases.

## 3 Results and discussion

### 3.1 SEM characterization

Figure 1 shows a typical SEM image at cross-section of a PEO–PPO–PEO/Nafion membrane. It can be seen that the blend membrane appears quite homogeneous with no observable voids or defects. Moreover, results of EDX analysis evidenced uniform oxygen atom distribution through the membrane cross-section, which further supports homogeneity of the triblock copolymer/Nafion blends.

### 3.2 FT-IR spectra

Infrared spectra of the recast Nafion at anhydrous and fully hydrated states are compared in Fig. 2. The assignments of the characteristic peaks for recast Nafion at anhydrous state are given at Table 1. Vibrational bands associated with the $-SO_3H$ and $-SO_3^-$ groups can give information about coordination behavior and transport mechanism of protons in Nafion. Bands at 1410 and 851 $cm^{-1}$ have been assigned as S=O and S–OH stretching bands of the $-SO_3H$ group (marked by arrow). It can be observed clearly that at fully hydrated state, these two peaks disappear. This is due to ion

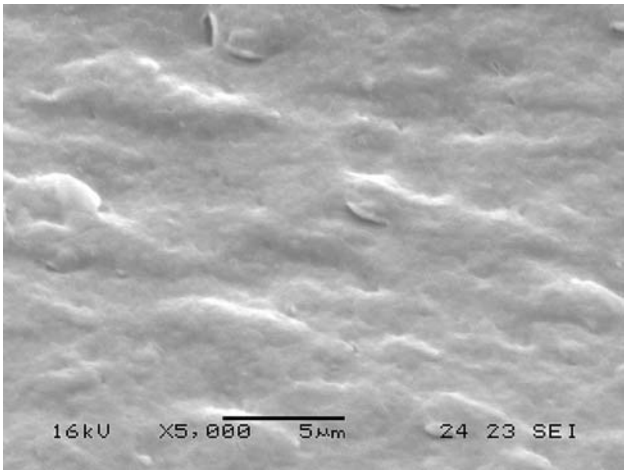

**Fig. 1** SEM image of the PE10 membrane cross section

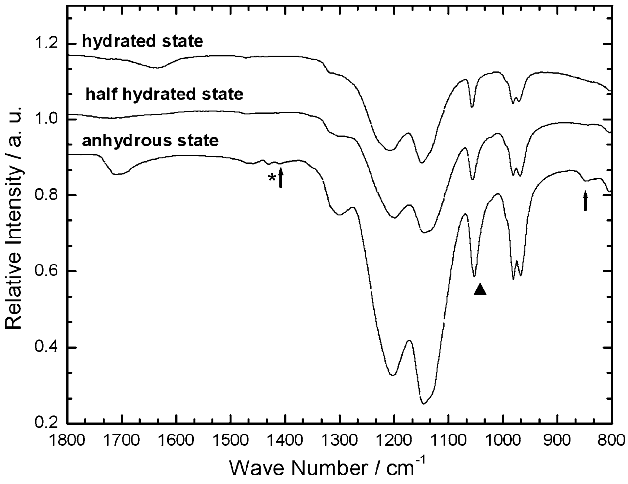

**Fig. 2** FT-IR spectra of the recast Nafion at anhydrous, half-hydrated and fully hydrated states

**Table 1** Assignments of the characteristic peaks of the FT-IR spectrum for recast Nafion at anhydrous state

| Peak position/cm$^{-1}$ | Group assignment [Ref.] |
|---|---|
| 1709 | Bending band of $H_2O$ [22, 23] |
| 1410 | S=O stretch band of –$SO_3H$ [22, 23] |
| 1302 | C–F stretching band [22] |
| 1200 | F–C–F asymmetric stretching [24] |
| 1144 | F–C–F symmetric stretching [24] |
| 1052 | –$SO_3^-$ symmetric stretching [22, 24, 25] |
| 981 | C–F stretching –$CF_2$–$CF(CF_3)$– group [22–24] |
| 967 | C̄ŌC symmetric stretching [24] |
| 851 | S–OH stretching band of –$SO_3H$ [22, 23] |

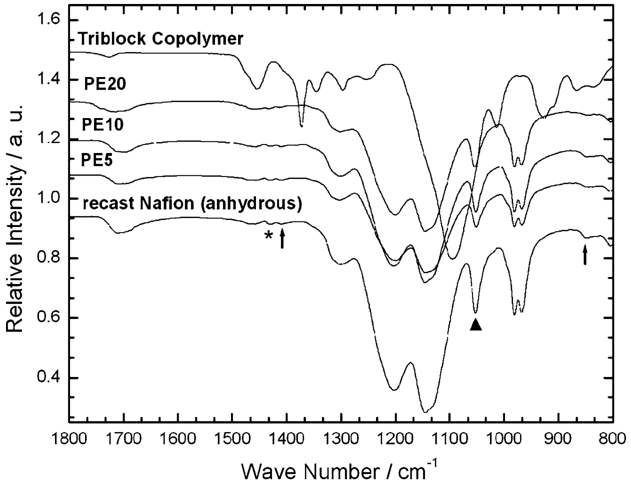

**Fig. 3** FT-IR spectra of the triblock copolymer, recast Nafion, PE5, PE10 and PE20 blend membranes in anhydrous condition

dissociation of –$SO_3H$ group with the proton getting hydrogen bonded to water. The symmetric stretching band of –$SO_3^-$ is observed at 1052 cm$^{-1}$ (marked by ▲). This band was considered in studies of ion pairing in polymer electrolytes between metal ions (namely $Li^+$) and the triflate ($CF_3SO_3^-$) ion [25]. It was observed in that study that ion pairing produces an upshift of the $v_s(SO_3^-)$ band. In the present investigation this band upshifts from 1052 to 1056 cm$^{-1}$ at fully hydrated state (Fig. 2), which is further evidence of hydrogen bond to water molecules. Unfortunately, the antisymmetric stretching vibrations of the –$SO_3^-$ group are masked by the strong C–F stretching bands at 1300 cm$^{-1}$. A peak (marked by star) should be noted at 1430 cm$^{-1}$ for the anhydrous membrane. Assignment of this peak is still not clear since no direct information can be found in the literature. However this peak disappears when Nafion is hydrated.

In order to eliminate the influence of water, we investigated the interaction between the triblock copolymer and Nafion at anhydrous state. Figure 3 shows the FT-IR spectra of our blend membranes along with bare Nafion at anhydrous state. The weak peak noted at 1410 cm$^{-1}$ for anhydrous Nafion can still be observed in the spectra of PE5 and PE10. However, it appears considerably attenuated and almost disappears in the spectrum of PE20. Moreover, the peak at 851 cm$^{-1}$ is totally absent in the spectrum of PE20. Furthermore, the –$SO_3^-$ peak at 1052 cm$^{-1}$ for anhydrous Nafion upshifts to 1054 cm$^{-1}$ for PE20. Meanwhile, the peak at 1430 cm$^{-1}$ becomes weaker in the spectra of PE5 and PE10 and almost disappears in PE20. The variations of the sulfonic group peaks in these membranes at different states are summarized in Table 2. These variations indicate existence of molecular interaction between the Nafion and the triblock copolymer. This interaction is likely of hydrogen bond type since variations of the vibrational bands related to the sulfonic group in the blend membranes are the same as in the Nafion/water system. On the other hand, since the oxygen atom in ether group is strong electron donor, hydrogen bond formation with $H^+$ ions should not come as a surprise.

### 3.3 Proton conductivity

Figure 4a and b show proton conductivity of the recast Nafion and blend membranes at hydrated and anhydrous states, respectively. At fully the hydrated condition (Fig. 4a), proton conductivity of PE5 and PE10 is close to the value of the recast Nafion at ambient temperature. However, the proton conductivity versus temperature increases more rapidly for recast Nafion as compared to the blend membranes. At anhydrous state, proton conductivity of the blend membranes is generally notably better than that of the recast Nafion except at the highest temperature (Fig. 4b). Both at hydrated and anhydrous states, the

**Table 2** Variations of the FT-IR peaks related to the sulfonic group for Nafion and PE20 at anhydrous and hydrated states

| Group | Anhydrous Nafion | Hydrated Nafion | Anhydrous PE20 | Hydrated PE20 |
|---|---|---|---|---|
| S=O stretching band of –$SO_3H$ | 1410 $cm^{-1}$ | Disappear | Very weak | Disappear |
| Symmetric stretching of –$SO_3^-$ | 1052 $cm^{-1}$ | 1056 $cm^{-1}$ | 1054 $cm^{-1}$ | 1056 $cm^{-1}$ |
| S–OH stretching band of –$SO_3H$ | 851 $cm^{-1}$ | Disappear | Disappear | Disappear |

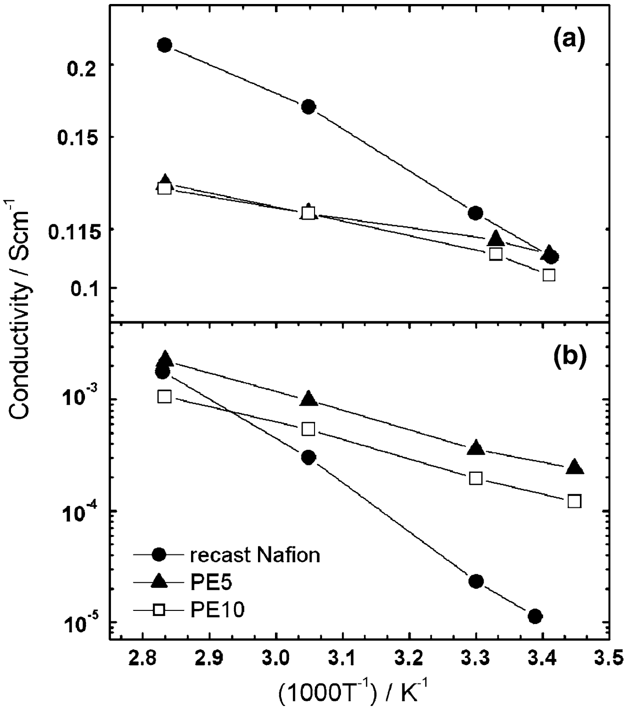

**Fig. 4** Arrhenius plots of proton conductivity as a function of temperature for recast Nafion and triblock copolymer/Nafion blend membranes at fully hydrated (**a**) and anhydrous (**b**) conditions

conductivity versus temperature curves of these membranes obey the Arrhenius law. In Table 3 proton conductivity along with respective activation energy $E_p$ is reported for all the investigated membranes under fully hydrated conditions as well as in the anhydrous state. Generally $E_p$ is significantly lower for the blend membranes with respect to Nafion both under wet and anhydrous conditions. The fact that proton conduction is more weakly activated process for the blend membranes particularly at anhydrous state may be significant evidence of proton solvent characteristic of the PEO group present in the blend. The proton conductivity mechanism will be discussed further below, in connection with the results of DMFC tests.

### 3.4 Methanol permeability and selectivity

Figure 5 plots methanol permeability at room temperature (20 °C) as a function of Pluronic copolymer content in the blend membranes. The permeability values are also reported in Table 3. The presence of the triblock copolymer depresses significantly membrane permeability as compared with bare recast Nafion. As shown in a previous work, sorbed water plays a major role in transport of methanol molecules through Nafion membranes [21]. Water sorption into Nafion is driven by hydration of the ionizable sulfonic groups. The above FT-IR investigation has shown that the PEO segment of the triblock copolymer can actually behave similarly to a proton solvent in our blend membranes. We may tentatively speculate that PEO solvates sulfonic groups to some extent thereby depressing the amount of sorbed water. The lower water content would, in turn, determine the lower methanol permeability values observed for the blend membranes. As recognized and discussed in previous work [21, 26] of special relevance to the DMFC is the relative selectivity of the polymer electrolyte membrane defined as the ratio between proton conductivity and methanol permeability. Generally, higher membrane selectivity bears more favourable trade-off between methanol cross-over and internal ohmic resistance of the DMFC. Also shown in Fig. 5 is the selectivity of the blend membranes at ambient temperature as a function of the copolymer content. The blend membranes show better selectivity as compared to bare recast Nafion thereby bringing further promise of improved DMFC performance.

**Table 3** Proton conductivity, methanol permeability and selectivity at ambient temperature of recast Nafion and triblock copolymer blend membranes

| Membrane | Conductivity (wet) 20 °C/$\Omega^{-1}cm^{-1}$ | Methanol permeability 20 °C/$10^{-6}$ $cm^2s^{-1}$ | Selectivity 20 °C/$10^4$ $\Omega^{-1}cm^{-3}s$ | $E_p$ (wet)/kJ $mol^{-1}$ | $E_p$ (dry)/kJ $mol^{-1}$ |
|---|---|---|---|---|---|
| Recast Nafion | 0.11 | 1.81 | 6.08 | 10.9 | 84.8 |
| PE5 | 0.111 | 1.31 | 8.47 | 2.7 | 33.7 |
| PE10 | 0.104 | 1.08 | 9.63 | 4.1 | 33.5 |

Also reported is the activation energy $E_p$ for proton conduction in wet and anhydrous state

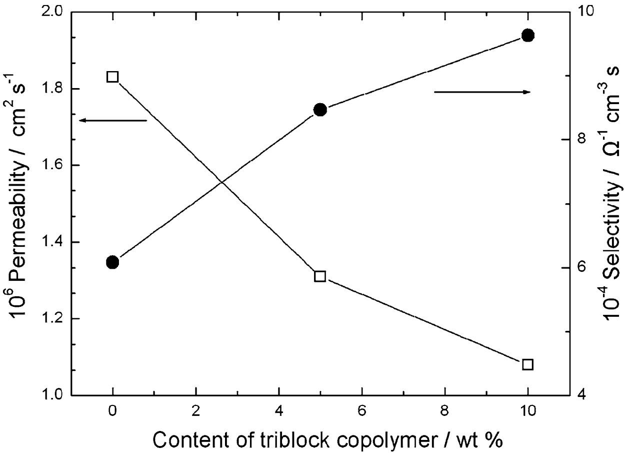

**Fig. 5** Methanol permeability and selectivity of the blend membranes at room temperature as a function of triblock copolymer content

## 3.5 DMFC performance

Figure 6 compares ohmic resistance at different operating temperatures for the DMFC equipped with the various MEAs prepared with the blend membranes and recast Nafion. The cell resistances of these membranes show similar variation behavior: decreasing in the range of 90 °C to 110 °C and increasing above 110 °C. An analogous behavior was also observed in our previous work with other Nafion-based membranes [27]. This phenomenon is because of the opposite effect of temperature on intrinsic conductivity and on the level of hydration of the membrane. In fact, the intrinsic proton conductivity of Nafion increases as temperature increases. However, water retention decreases dramatically at 100 °C (or higher, if the operating pressure is above 1 atm, as in the present case), which, in turn, produces strong reduction in conductivity of the membrane. Regarding the cell resistance for the MEA equipped with recast Nafion, it is lower than that of the blend membranes below 110 °C, which can be attributed to the higher proton conductivity of Nafion in the hydrated state. Above 110 °C, the cell resistance of these blend membranes is lower than that of the recast Nafion at each test temperature. Since the triblock copolymer contains hydrophobic PPO segments as well as a hydrophylic PEO segment which likely solvates the sulfonic groups present in Nafion, water retention of blend membranes should be worse than that of bare Nafion. Thus, the enhanced conductivity of the blend membranes under partially anhydrous conditions above 110 °C seems to be ascribable to the role of PEO segments as solid solvent in which proton transport can occur, to some extent, even in the absence of water. Such behaviour indicates that the triblock copolymer has a positive effect on the proton conductivity at intermediate temperatures in the DMFC. Representative DMFC polarization and power density curves for recast Nafion, PE5 and PE10 based MEAs operating at 100 °C are compared in Fig. 7. At 100 °C, the open circuit voltage (OCV) of PE5 and PE10 (0.77 V and 0.78 V) are significantly higher than that of the recast Nafion (0.69 V). In addition, the output voltage at low current density (<0.2 A $cm^{-2}$) of these two blend membranes are higher than that of the recast Nafion. This can be attributed to the better barrier properties of the blend membranes with respect to methanol. The polarization curves of PE5 and recast Nafion almost overlap each other when the current density is lower than 0.9 A $cm^{-2}$. But at high current density, PE5 exhibits better performance than the recast Nafion. For PE5, a maximum power density of 320 mW $cm^{-2}$ was obtained at current density of 1.05 A $cm^{-2}$,

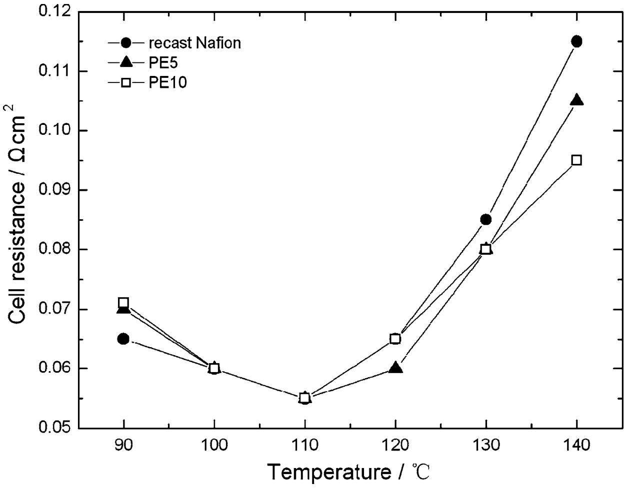

**Fig. 6** Variation of cell resistance values as a function of the operating temperature for DMFC employing the PE5 and PE10 blend membranes compared to recast Nafion

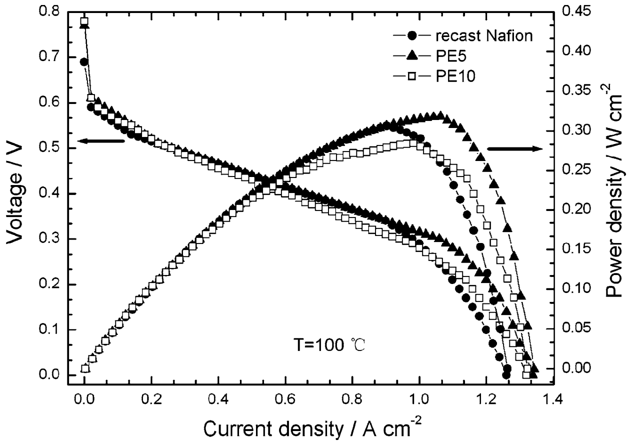

**Fig. 7** Polarization and power density curves of DMFC operated 100 °C for various MEAs equipped with PE5 and PE10 blend membranes compared to recast Nafion

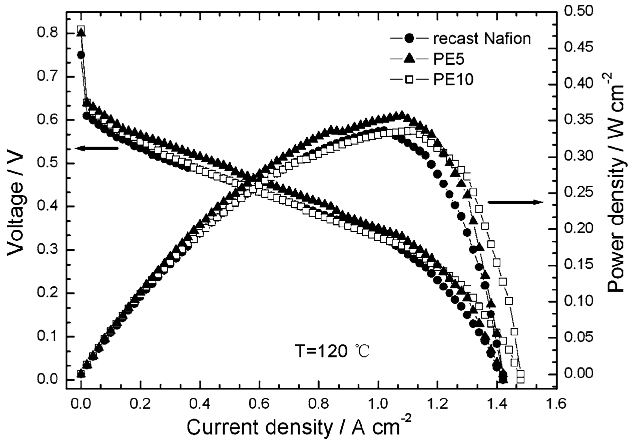

**Fig. 8** Polarization and power density curves of DMFC operated 120 °C for various MEAs equipped with PE5 and PE10 blend membranes compared to recast Nafion

higher than that of the PE10 blend membrane (280 mW cm$^{-2}$) and recast Nafion (300 mW cm$^{-2}$). When the operating temperature reaches 120 °C (Fig. 8), the polarization curves of recast Nafion and PE10 blend membrane almost overlap each other at low current density (below 1.1 A cm$^{-2}$). The single cell performance of PE5 is better than the other two membranes. The polarization curve of PE5 is about 25 mV higher than that of recast Nafion. A maximum power density of 360 mW cm$^{-2}$ can be obtained at current density of 1.06 A cm$^{-2}$. Meanwhile, the OCV for the blend membranes is still higher than for recast Nafion. However, when the operation temperature reaches 140 °C, the single cell performance for PE10 is better than for the other two membranes (Fig. 9). A maximum power density of 382 mW cm$^{-2}$ can be obtained at current density of 1.12 A cm$^{-2}$. It should be mentioned that not only the output voltage at low current density but also the maximal current density of PE10 is higher than that of the recast Nafion. This indicates that both improved methanol permeability and proton conductivity are responsible for the better single cell performance of PE10. The variation of the maximum power density as a function of temperature for the MEAs equipped with different blend membranes compared to recast Nafion is shown in Fig. 10. The maximum power density both for recast Nafion and PE5 stops increasing after the operating temperature reaches 130 °C. This can be attributed to the water loss and subsequently low proton conductivity at high temperature. Limited by the power of the heating plate, it was difficult setting the operation temperature of the cell above 140 °C. However, trends observed in Fig. 10 clearly indicate that significant further enhancement can be achieved at operation beyond 140 °C for the PE10 membrane as compared to PE5 and bare Nafion. Thus, PEO–PPO–PEO triblock copolymer/Nafion blend membranes have promise for intermediate temperature DMFC application. The above results of proton conductivity (both under hydrate and anhydrous condition), DMFC internal resistance and DMFC performance demonstrate that the triblock copolymer does have a positive effect on the proton transport in the copolymer/Nafion blend membranes under dehydrated conditions at high temperature. These, along with results from FT-IR analysis, suggest that the PEO segments of the triblock copolymer may behave, similarly to water, as a solid solvent for the acidic sulfonic group of the Nafion matrix, thereby inducing ion dissociation of the same. Accordingly, migration of the resulting H$^+$ ions can occur assisted by transient hydrogen bonds to the ether chain even in the absence of water. Both in the hydrated and anhydrous states, the conductivity versus temperature curves of Nafion and blend membranes obey the Arrhenius law, unlike the PEO/Li-salt polymer system. This implies that the

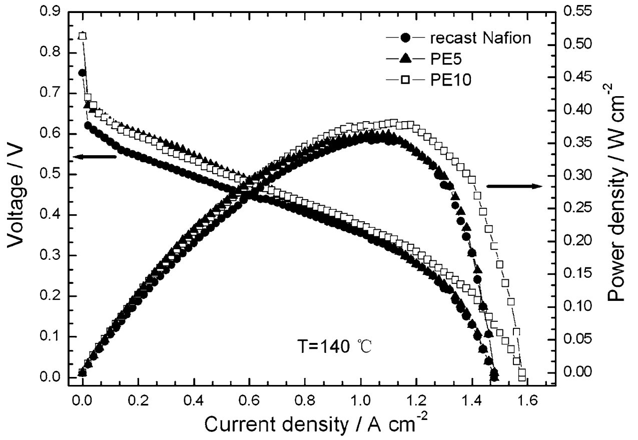

**Fig. 9** Polarization and power density curves of DMFC operated 140 °C for various MEAs equipped with PE5 and PE10 blend membranes compared to recast Nafion

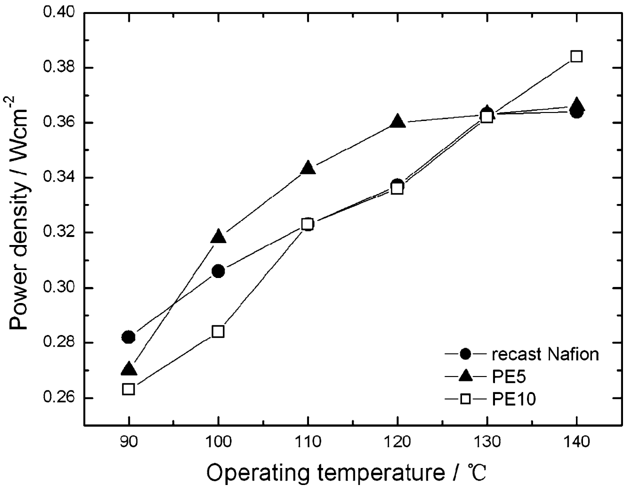

**Fig. 10** Variation of maximal power density values as a function of the operating temperature for DMFC employing the PE5 and PE10 blend membranes compared to recast Nafion

proton conduction mechanism of the blend membranes is similar to that of the Nafion/water system instead of the PEO/Li-salt polymer electrolyte. A more definite and unambiguous understanding of the proton transfer mechanism in the triblock copolymer blend membrane needs further investigation. Although membrane stability was not specifically investigated, no sign of membrane degradation was noticed upon aging in water at ambient conditions for 2–3 weeks. Furthermore, the membranes appeared stable under DMFC operating conditions up to at least 140 °C with similar results over operating periods of 5–7 days. An ad hoc investigation is necessary to assess long term stability of these membranes in DMFCs.

## 4 Conclusion

Homogeneous PEO–PPO–PEO triblock copolymer/Nafion blend membranes were prepared by evaporation-casting the solvent from clear solutions of Nafion and the triblock copolymer. FT-IR spectroscopy shows that interactions of the hydrogen bond type subsist between the triblock copolymer and the acid sulfonic groups of the Nafion matrix. These blend membranes exhibit higher proton conductivity than bare recast Nafion in the anhydrous state. In addition, they show better methanol barrier properties and transport selectivity. Above 110 °C, the internal ohmic resistance of a DMFC equipped with these blend membranes is lower than for recast Nafion membrane at each test temperature. Furthermore, the blend membranes enable improved DMFC performance as compared to the recast Nafion at temperature above 120 °C. These facts prove that the utilized triblock copolymer does enhance proton transfer in the Nafion matrix under low humidity conditions at elevated temperature. Proton migration can occur under such conditions assisted by transient hydrogen bonds to the ether chain of the block copolymer. This work demonstrates a new concept to facilitate proton conduction in blend membranes under conditions typical of DMFCs operated at intermediate temperature and brings promise of further development.

**Acknowledgements** We are grateful to Dr. A. Lampertico of BTC S.p.A., Milan for kindly provinding us with the Pluronic products and to Mr. P. Narducci of the University of Pisa for valuable help with SEM and EDX.

## References

1. Aricò AS, Srinivasan S, Antonucci V (2001) Fuel Cells 1:133
2. Li QF, He RH, Jensen JO, Bjerrum NJ (2003) Chem Mater 15:4896
3. Alberti G, Casciola M, Palombari R (2000) J Memb Sci 172:233
4. Adjemian KT, Lee SJ, Srinivasan S, Benziger J, Bocarsly AB (2002) J Electrochem Soc 149:256
5. Honma I, Nakajima H, Nishikawa O, Sugimoto T, Nomura S (2003) Solid State Ionics 162/163:237
6. Costamagna P, Yang C, Bocarsly AB, Srinivasan S (2002) Electrochim Acta 47:1023
7. Li Q, He R, Gao J, Jensen JO, Bjerrum NJ (2003) J Electrochem Soc 150:A1599
8. Li Q, Hasiotis HA, Hasiotis C, Kallitsis JK, Kontoyannis CG, Bjerrum N (2002) Electrochem Solid-State Lett 5:A125
9. Kerres JA (2001) J Memb Sci 185:3
10. Mauritz KA, Moore RB (2004) Chem Rev 104:4535
11. Watanabe M, Uchida H, Seki Y, Emori M, Stonehart P (1996) J Electrochem Soc 143:3847
12. Antonucci PL, Aricò AS, Cretì P, Ramunni E, Antonucci V (1999) Solid State Ionics 125:431
13. Tricoli V, Nannetti F (2003) Electrochim Acta 48:2625
14. Alberti G, Casciola M (1997) Solid State Ionics 97:177
15. Baglio V, Aricò AS, Di Blasi A, Antonucci V, Antonucci PL, Licoccia S, Traversa E, Serraino Fiory F (2005) Electrochim Acta 50:1241
16. Giordano N, Staiti P, Hocevar S, Aricò AS (1996) Electrochim Acta 41:397
17. Fenton DE, Parker JM, Wright PV (1973) Polymer 14:589
18. Lightfoot P, Mehta MA, Bruce PG (1993) Science 262:883
19. Lee HS, Yang XQ, McBreen J, Xu ZS, Skotheim TA, Okamoto Y (1994) J Electrochem Soc 141:886
20. Meyer WH (1998) Adv Mater 10:439
21. Tricoli V (1998) J Electrochem Soc 145:3798
22. Ludvigsson M, Lindgren J, Tegenfeldt J (2000) Electrochim Acta 45:2267
23. Buzzoni R, Bordiga S, Ricchiardi G, Spoto G, Zecchina A (1995) J Phys Chem 99:11937
24. Liang Z, Chen W, Liu J, Wang S, Zhou Z, Li W et al (2004) J Memb Sci 233:39
25. Bernson A, Lindgren J (1993) Solid State Ionics 60:37
26. Tricoli V, Carretta N, Bartolozzi M (2000) J Electrochem Soc 147:1286
27. Baglio V, Aricò AS, Di Blasi A, Antonucci PL, Nannetti F, Tricoli V, Antonucci V (2005) J Appl Electrochem 35:207