



Short communication

# New proton conducting polymer blends and their fuel cell performance

N. Gourdoupi<sup>a</sup>, J.K. Kallitsis<sup>a,b</sup>, S. Neophytides<sup>b,\*</sup>

<sup>a</sup> Department of Chemistry, University of Patras, University Campus, GR-26500 Rio-Patras, Greece

<sup>b</sup> Institute of Chemical Engineering and High Temperature Chemical Processes, ICE/HT-FORTH, P.O. Box 1414, 26500 Patras, Greece

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## ABSTRACT

Novel polymer blends based on aromatic polyethers with pyridine units have been prepared for their use as electrolytes after being doped with phosphoric acid for high temperature PEM fuel cells. They exhibit very good film-forming properties, mechanical integrity, high modulus up to 230 °C, high glass transition temperatures (up to 260 °C) and high thermal stability up to 400 °C. In addition to the above required properties, these novel materials show high oxidative stability and acid doping ability, enabling proton conductivity in the range of  $10^{-2}$  S cm<sup>-1</sup> at 130 °C. The preparation and fuel cell testing of membrane electrode assemblies, demonstrated very promising performance, and an initial study has shown the positive effect of humidity on the measured conductivity.

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## 1. Introduction

Hydrogen and fuel cells address all of the major energy and environmental challenges and have the flexibility to adapt to the diverse energy sources that will be available in the future. Among the several types of fuel cells, PEM fuel cells (PEMFC) have the highest potential for market penetration addressing automotive, stationary and mobile applications [1]. Membranes commonly used in PEMFC technology are perfluorinated polymers containing sulfonic acid groups on side chains e.g. Nafion [2] and sulfonated aromatic polyethers [3–5] which are considered to be the alternative solution to the high cost perfluorinated polymers. High temperature PEM fuel cells possess certain advantages, such as increased catalytic activity, reduced poisoning effect of the catalyst by fuel steam impurities e.g. CO, easier thermal management, no need of humidification, compared to conventional low temperature PEM fuel cells [6].

The core part of a PEM fuel cell is the membrane electrode assembly (MEA), where the membrane is a polymer electrolyte material with certain properties. The polymer membranes should exhibit high proton conductivity after doping with a strong acid e.g. phosphoric acid and good mechanical, thermal and oxidative stability. Polybenzimidazole [7–9] (PBI) is the state of the art high temperature polymer electrolyte, combining high thermal stability with increased proton conductivity although it possesses moderate

mechanical properties and low oxidative stability. There is a significant research effort towards the development of some novel polymeric materials which can be used alternatively to PBI. Such materials are specially designed aromatic polyethers that show high mechanical, thermal and chemical stability with incorporated polar groups, and can interact with and retain high amounts of phosphoric acid [10–17].

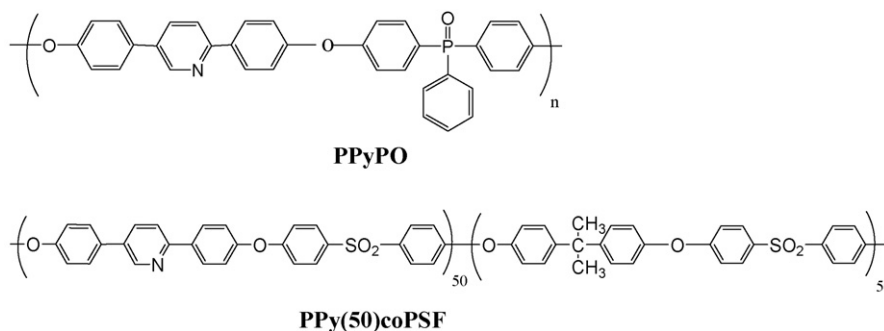
Our present approach concerns the development of polymer blends comprised of pyridine based polymers and copolymers. All studied blends were found miscible with good mechanical and film-forming properties and with high ionic conductivity after doping with phosphoric acid.

## 2. Experimental

### 2.1. Materials and instrumentation

Polymer PPyPO (Scheme 1) and copolymer PPy(50)coPSF (Scheme 1) were prepared according to the synthetic procedure reported in the literature [14,15]. DMA measurements were performed using a solid-state analyzer RSA II, Rheometrics Scientific Ltd., at 10 Hz. Thermogravimetric analysis was performed at a DuPont 951 TGA accessory. *I*-*V* plots were acquired using a system of a galvanostat/potentiostat EG&G model 263A for a 25 cm<sup>2</sup> active area single cell. AC impedance measurements were carried out using EG&G potentiostat model 763 in cooperation with a frequency response detector EG&G model 1025. The ionic resistance of the membrane is measured at the high frequency intercept of the Nyquist plot with the real *Z*-axis.

\* Corresponding author. Tel.: +30 2610965265; fax: +30 2610965223.  
E-mail address: [neoph@iceht.forth.gr](mailto:neoph@iceht.forth.gr) (S. Neophytides).



**Scheme 1.** Chemical structures of PPyPO and PPy(50)coPSF.

## 2.2. Membrane preparation

Both polymer PPyPO and copolymer PPy(50)coPSF were dissolved in dimethylacetamide at room temperature using concentrations of 3 wt.%. The two solutions were mixed and stirred at room temperature for 3 h. The solution was filtrated through glass-wool and poured in glass dish of 100 mm diameter. The solvent was slowly evaporated in an oven at 80 °C for 24 h and the membrane was washed with water and dried at 170 °C for 48 h under vacuum.

## 2.3. Treatment with H<sub>2</sub>O<sub>2</sub> (Fenton test)

Membrane strips were immersed in a 3 wt.% H<sub>2</sub>O<sub>2</sub> aqueous solution containing 4 ppm FeCl<sub>2</sub> at 80 °C for 72 h. After the treatment, possible changes in thermal and mechanical properties were examined by means of dynamic mechanical analysis and thermogravimetric analysis.

## 2.4. Electrodes and MEA preparation

A slurry of 70 wt.% carbon powder and 30 wt.% PTFE was applied onto carbon cloth. The resulting hydrophobic layer was dried and sintered at 350 °C for 30 min. A mixture of 50 wt.% Pt from a Pt/C (28.6 wt.% Pt loading on carbon) catalyst powder and 50 wt.% polymer PPyPO from a 3 wt.% polymer solution in dimethylacetamide, was well mixed and applied onto the supporting layer of the carbon cloth. The electrodes were initially dried at 80 °C for 20 h and for 1 h at 190 °C under vacuum. The platinum loading in the catalyst layer of the anode and the cathode was 1 mg cm<sup>-2</sup> per each side.

For the preparation of MEA, a membrane of PPyPO/PPy(50)coPSF 50/50 blend was immersed into 85% phosphoric acid at 90 °C for 1 h. The membrane surface was wiped well with a filtration paper and the phosphoric acid doping level was between 140 and 160 wt.% (720–820 mol%). The doping level is defined as the weight percent of the acid per gram of the blend. The membrane electrode assembly was mounted into a 25 cm<sup>2</sup> active area single cell.

## 3. Results and discussion

### 3.1. Polymer membrane preparation and characterization

The polymer electrolytes based on aromatic polyethers bearing pyridine units in the main chain, have been proposed in our previous studies [11,14–17] as an alternative to polybenzimidazole for high temperature fuel cell operation. As an extension, we report here on the preparation of blends comprised of copolymer PPy(50)coPSF and PPyPO, whose structures are given in Scheme 1.

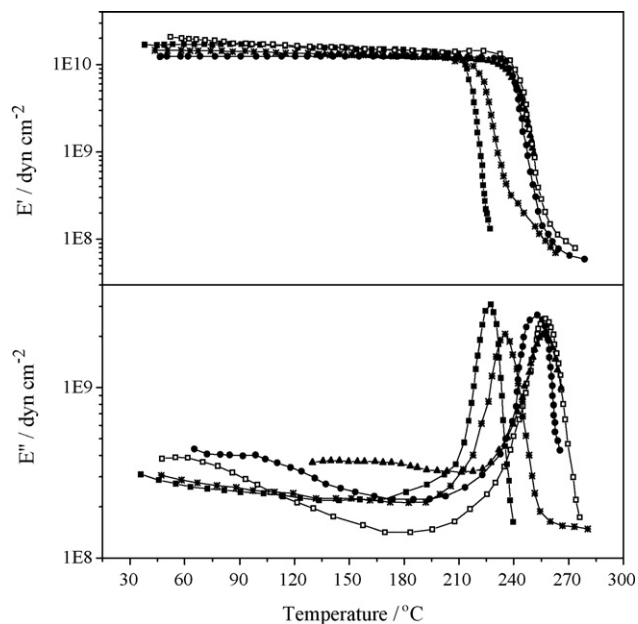
Copolymer PPy(50)coPSF presents high *T<sub>g</sub>* value, high thermal and oxidative stability but moderate ability to be doped with

phosphoric acid. The blend formation with PPyPO aims to the enhancement of acid uptake. In other words, these blends were prepared with the view of combining the high proton conductivity of PPyPO with the high mechanical integrity of copolymer PPy(50)coPSF after doping with H<sub>3</sub>PO<sub>4</sub>. For this reason blends rich in PPyPO were prepared in the following compositions PPyPO/PPy(50)coPSF 50/50, 70/30, 80/20.

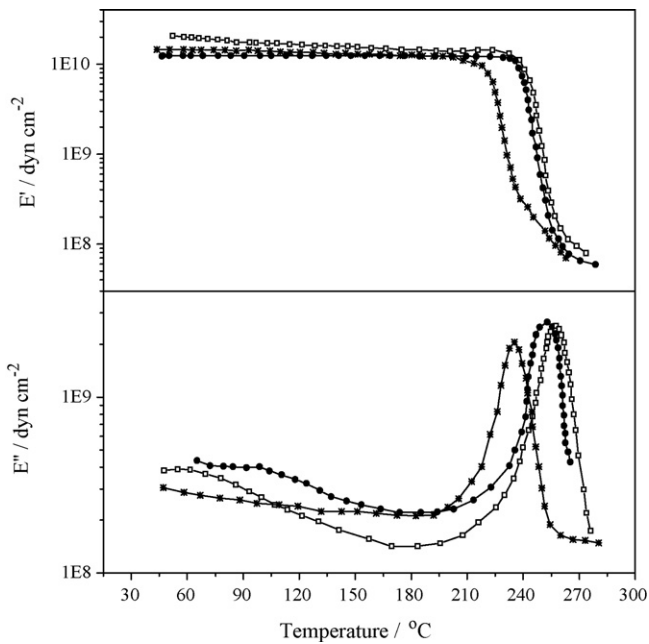
The miscibility behavior of the blends was examined by means of dynamic mechanical analysis using the single glass transition criterion. As shown in Fig. 1, a single *T<sub>g</sub>* is observed for all studied blends at temperatures between the pure polymers *T<sub>g</sub>*s denoting the miscibility of this polymer pair.

The blend membranes were tested with respect to their oxidative stability using the Fenton test. In all cases the blend membranes retain their mechanical integrity and their high thermal stability as shown in Figs. 2 and 3 after the treatment with H<sub>2</sub>O<sub>2</sub>. It should be noticed that after the Fenton's treatment the blend membranes retained their integrity with no detectable weight loss while these specimens were used for dynamic mechanical analysis and tested up to 280 °C without any stability problems.

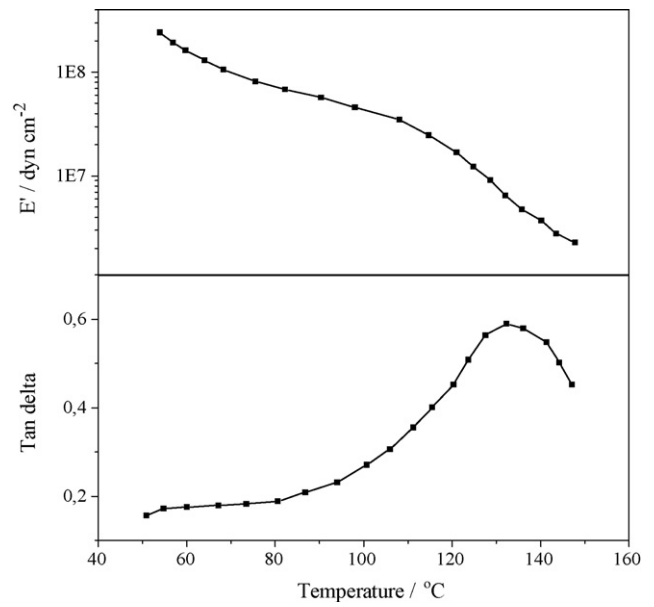
In order to prove the combination of high doping ability of PPyPO with high mechanical integrity of PPy(50)coPSF, the blend PPyPO/PPy(50)coPSF 50/50 was doped with phosphoric acid at a percentage of 250 wt.% and its mechanical properties were mea-



**Fig. 1.** Temperature dependence of storage (*E'*) and loss (*E''*) modulus of blends PPyPO/PPy(50)coPSF, 50/50 (\*), 70/30 (●), 80/20 (□), PPyPO (▲) and copolymer PPy(50)coPSF (■).



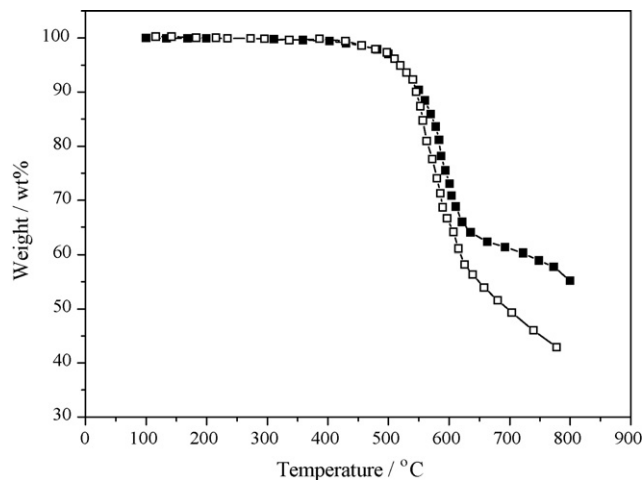
**Fig. 2.** Temperature dependence of the storage ( $E'$ ) and loss ( $E''$ ) modulus of PPyPO/PPy(50)coPSF 50/50 (\*), 70/30 (●) and 80/20 (□), blends after treatment with  $H_2O_2$  (Fenton test).



**Fig. 4.** Temperature dependence of the storage ( $E'$ ) modulus and tandelta of PPyPO/PPy(50)coPSF 50/50 blend doped with phosphoric acid at a doping level of 250 wt.%.

sured as shown in Fig. 4. A decrease of the storage modulus ( $E'$ ) of the doped membrane is observed, however the measured value is similar to the respective values given for PBI  $H_3PO_4$  imbibed membranes [18,19]. The  $T_g$  of the pristine blend is located at 230 °C (Fig. 1) while the corresponding value of the doped blend is ca. 140 °C which is within the temperature window of its fuel cell operation.

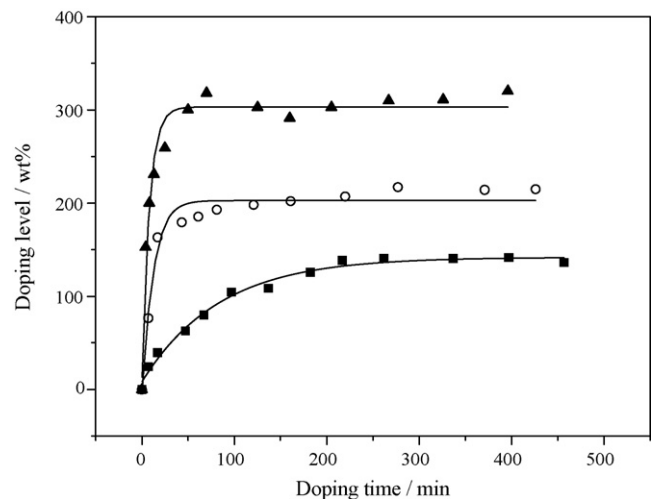
The membranes were doped with phosphoric acid at different temperatures and for different doping times, depending on the membrane composition. An example of the doping behavior of the PPyPO/PPy(50)coPSF at a 50/50 blend composition membrane is shown in Fig. 5. As the doping temperature increases the phosphoric acid doping level also increases reaching plateau at shorter doping times. Thus by selecting the proper doping conditions the membranes can be doped with the preferred doping level avoiding any mechanical stability problem which can arise from undesired high acid uptake.



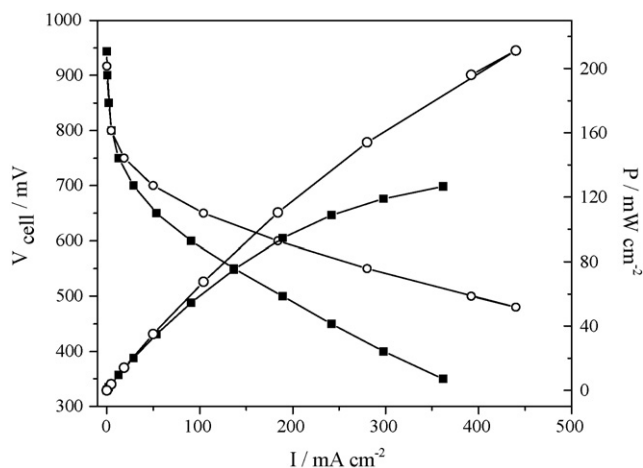
**Fig. 3.** TGA experiment of PPyPO/PPy(50)coPSF 50/50 before (■) and after (□) treatment with  $H_2O_2$  (Fenton test).

### 3.2. MEA fuel cell testing

The MEA is prepared by the use of phosphoric acid imbibed PPyPO/PPy(50)coPSF 50/50 blend. The performance of the MEA is depicted in Fig. 6. The  $I$ - $V$  plots were recorded at 130 and 140 °C under  $H_2$  and  $O_2$  feeds at ambient pressure. The data evidently show the potential use of phosphoric acid imbibed pyridine containing aromatic polyethers as high temperature polymer electrolytes in high temperature PEM fuel cells. The doping level of the membrane was not higher than 160 wt.%, thus strongly indicating that adequate proton conductivity values can be achieved with lower doping values as compared to the corresponding PBI membranes. The cell performance is very promising and comparable to the state of the art PBI MEAs [7,20,21].



**Fig. 5.** Time dependence of doping level for different doping times for the PPyPO/PPy(50)coPSF 50/50 blend at 50 °C (■), 80 °C (○) and 100 °C (▲).

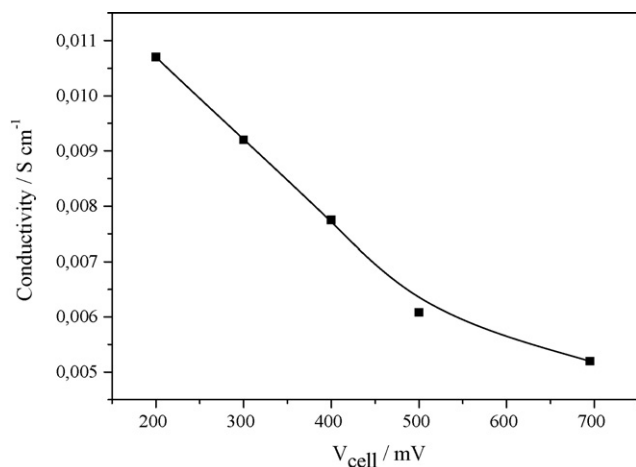


**Fig. 6.** *I*–*V* curves of PPy(50)coPSF/PPy(50) based MEA at 130 °C (■) and 140 °C (○). Doping level: 160 wt.%, membrane thickness: 85 μm, active area: 25 cm<sup>2</sup>, Pt loading: 1 mg cm<sup>-2</sup>.

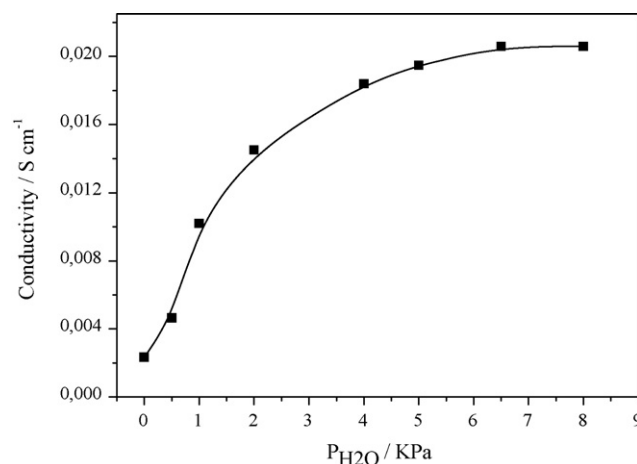
### 3.3. Conductivity measurements

Conductivity has been measured in situ in a single fuel cell reactor by means of AC impedance spectroscopy. Fig. 7 depicts the dependence of the membrane conductivity under fuel cell conditions for different cell voltages. It is clearly shown that polymer electrolyte's conductivity is improved significantly with decreasing cell voltage or equivalently increasing cell current. As it is further shown, this can be attributed to the formation of H<sub>2</sub>O at the cathode and the simultaneous hydration of the electrolyte membrane. Fig. 8 shows the effect of water's vapor partial pressure on the proton conductivity of the membrane. An increase of even an order of magnitude is observed, when moving from dry to hydrated conditions. At water partial pressures above 4 kPa a steady value has been reached. The fact that the conductivity values depicted in Figs. 7 and 8 vary within the same range strongly indicates that the variation under fuel cell operation is due to the promotional effect of the produced water vapors at the cathode.

The water effect on conductivity has been discussed by other research groups, and mainly for the PBI/H<sub>3</sub>PO<sub>4</sub> system. Wainright et al., mention that for doping level 160 wt.%, an increase of relative humidity from 2 to 25% at 130 °C, leads to a conductivity increase from  $5 \times 10^{-3}$  to  $2 \times 10^{-2}$  S cm<sup>-1</sup> [8]. He et al., reported that an increase of relative humidity from 5.6 to 20% at 140 °C, slightly

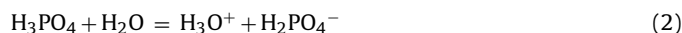


**Fig. 7.** Voltage dependence of ionic conductivity of PPy(50)coPSF/PPy(50) based MEA at 140 °C. Doping level: 140 wt.%.



**Fig. 8.** Effect of water partial pressure on PPy(50)coPSF/PPy(50) MEA's ionic conductivity at 130 °C. Doping level: 140 wt.%. Anode: Ar/H<sub>2</sub>O, cathode: Ar.

increases the conductivity from 0.03 to 0.04 S cm<sup>-1</sup> while at 200 °C an increase from 1 to 5% leads to a conductivity increase from 0.04 to 0.07 S cm<sup>-1</sup> [22]. The water absorbance by the H<sub>3</sub>PO<sub>4</sub> imbedded polymeric membranes has been recently shown by Daletou et al. by means of thermogravimetric experiments [23]. The water uptake has been attributed to the hydration of pyrophosphoric acid according to reaction (1) and to the hydration of the H<sub>3</sub>PO<sub>4</sub> according to the equilibrium reaction (2).



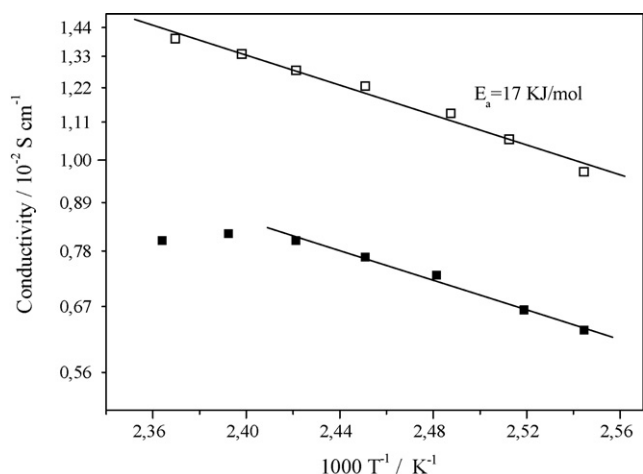
The hydration of the acid induces its ionic dissociation rendering water molecule as a flexible proton carrier.

The presence of water molecules can be considered as the main proton pathway either acting as a vehicle (vehicle mechanism, H<sub>3</sub>O<sup>+</sup>) or facilitating proton hopping between aligned hydronium and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (Grotthuss mechanism). This can be realized by considering the higher flexibility of water molecule to rotate and be aligned with other molecules so that the proton hopping can take place. This is also corroborated by the fact that hydrogen bonds between acid molecules are linear and strong (2.2 Å) while between H<sub>2</sub>O and H<sub>3</sub>PO<sub>4</sub>, are non-linear and less strong (2.39 Å) [9,24].

The aforementioned considerations can also adequately explain the non-linearity observed in the Arrhenius plot where the logarithm of the conductivity under open circuit and polarization conditions is plotted against temperature (Fig. 9). Under open circuit (dry) conditions log  $\sigma$  deviates from linearity with respect to  $1/T$  at temperatures >140 °C. This behavior and the resulting lower conductivity can be attributed either to the dehydration of the H<sub>3</sub>PO<sub>4</sub> or the formation of pyrophosphoric acid which is formed under dry conditions [9]. In the case of fuel cell operating conditions (polarization) the water formation at the cathode facilitates the hydration of the MEA thus similarly resulting in the improvement of conductivity and more interestingly the linearity of the plot in Fig. 9 is maintained at temperatures even higher than 140 °C. Similar behavior has been observed for other high temperature systems such as PBI/H<sub>3</sub>PO<sub>4</sub> and ABPBI/H<sub>3</sub>PO<sub>4</sub> [8,9,25,26].

Activation energy ( $E_a$ ) values reported in bibliography for PBI/H<sub>3</sub>PO<sub>4</sub> vary most probably due to the variation of parameters such as doping level, humidity and temperature region. A small change to any of these parameters leads to different  $E_a$  values. Bouchet and Siebert [26] report  $E_a$  values between 70 and 80 kJ mol<sup>-1</sup> for doping region 20–300 mol%. They claim that for this doping region, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> are the dominant species and the proton moves between imidazole groups through a phosphoric anion





**Fig. 9.** Temperature dependence of ionic conductivity of PPyPO/PPy(50)coPSF 50/50 MEA under open circuit (■) and under voltage  $-400$  mV (□) for temperature range  $150$ – $120$  °C. Doping level:  $140$  wt.%.

that is positioned in between (Grotthuss mechanism). Pu et al. [27] present the same  $E_a$  values ( $75$ – $80$  kJ mol<sup>-1</sup>) for similar doping levels ( $180$ – $380$  mol%), but they claim that proton transport takes place with both Grotthuss and vehicle mechanism. Moreover, comparing  $E_a$  values with and without relative humidity, a decrease is observed in the presence of humidity. The explanation given suggests that H<sub>2</sub>O molecules act as additional proton solvents and contribute to their movement either through diffusion or through fast proton exchange via hydrogen bonding increasing conductivity and decreasing  $E_a$  [27]. Taking into account that changes in hydration may affect the activation energy of the H<sub>3</sub>PO<sub>4</sub> imbedded membrane, the slope of the log  $\sigma$  vs.  $1/T$  of Fig. 9 is assumed to represent the apparent activation of the proton conductivity through the membrane. This is estimated to be  $17$  kJ mol<sup>-1</sup> under fuel cell operating conditions being very close to pure phosphoric acid proton conduction activation energy ( $14$  kJ mol<sup>-1</sup>). This means that a possible quasi-liquid like proton conduction mechanism may take place. This aspect is supported by He et al. [22], who measured  $E_a$   $8$ – $11$  kJ mol<sup>-1</sup> for doping levels  $200$ – $570$  mol% for temperatures  $140$ – $200$  °C assuming this value close to pure H<sub>3</sub>PO<sub>4</sub>. Ma et al. [9] and He et al. [22] report reduction of  $E_a$  with increasing doping level but they claim quite different values for similar doping levels.

The fact that a low activation energy value was observed even with a membrane doped with relatively low amount of phosphoric acid ( $140$  wt.%), shows that the imbedded amount of phosphoric acid might have a less significant contribution to the conduction mechanism compared to the polymer matrix itself. Moreover, as has been reported in Ref. [23], water molecule can play the role of proton carrier since it can be more flexible because of its smaller size in comparison to the positive H<sub>4</sub>PO<sub>4</sub><sup>+</sup>. Proton conduction can be attributed to the reorientation of water molecules which can be a prerequisite for the proton transport between hydronium and water molecule either through hopping or tunneling in accordance to the Grotthuss mechanism [24].

## 4. Conclusions

New high temperature polymer electrolytes have been prepared composed of polymer blends of pyridine containing aromatic polyethers. The phosphoric acid imbedded blends exhibit very good mechanical properties, high thermal and oxidative stability and high ionic conductivities. The preparation of membrane electrode assemblies and the fuel cell tests demonstrated the feasibility of this type of electrolyte to be used in high temperature PEM fuel cells.

## Acknowledgements

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## References

- [1] B.C. Steele, A. Heinzel, *Nature* 414 (2001) 345–352.
- [2] K.A. Mauritz, R.B. Moore, *Chem. Rev.* 104 (2004) 4535–4585.
- [3] K.D. Kreuer, *J. Membr. Sci.* 185 (2001) 29–39.
- [4] B.R. Einsla, Y.S. Kim, M.A. Hickner, Y.-T. Hong, M.L. Hill, B.S. Pivovar, J.E. McGrath, *J. Membr. Sci.* 255 (1–2) (2005) 141–148.
- [5] F. Wang, M. Hickner, Q. Ji, W. Harison, J. Mechem, T.A. Zawodzinski, J.E. McGrath, *Macromol. Symp.* 175 (2001) 387–396.
- [6] Q.F. Li, R.H. He, J.Q. Jensen, N.J. Jensen, N.J. Bjerrum, *Chem. Mater.* 15 (2003) 4896–4915.
- [7] J.T. Wang, R.F. Savinell, J. Wainright, M. Litt, H. Yu, *Electrochim. Acta* 41 (2) (1996) 193–197.
- [8] J.S. Wainright, J.T. Wang, D. Weng, R.F. Savinell, M. Litt, *J. Electrochem. Soc.* 142 (7) (1995) L121–L123.
- [9] Y.-L. Ma, J.S. Wainright, M.H. Litt, R.F. Savinell, *J. Electrochem. Soc.* 151 (1) (2004) A8–A16.
- [10] F. Wang, M. Hickner, Y.S. Kim, T.A. Zawodzinski, J.E. McGrath, *J. Membr. Sci.* 197 (2002) 231–242.
- [11] E.K. Pefkianakis, V. Deimede, M.K. Daletou, N. Gourdoupi, J.K. Kallitsis, *Macromol. Rapid Commun.* 26 (2005) 1724–1728.
- [12] V. Deimede, G.A. Voyatzis, J.K. Kallitsis, L. Qingfeng, N.J. Bjerrum, *Macromolecules* 33 (2000) 7609–7617.
- [13] C. Hasiotis, L. Qingfeng, V. Deimede, J.K. Kallitsis, C.G. Kontoyannis, N.G. Bjerrum, *J. Electrochem. Soc.* 148 (2001) A513–A519.
- [14] N. Gourdoupi, A.K. Andreopoulos, V. Deimede, J.K. Kallitsis, *Chem. Mater.* 15 (2003) 5044–5050.
- [15] M.K. Daletou, N. Gourdoupi, J.K. Kallitsis, *J. Membr. Sci.* 252 (2005) 115–122.
- [16] M. Geomezi, V. Deimede, N. Gourdoupi, N. Triantafyllopoulos, S. Neophytides, J.K. Kallitsis, *Macromolecules* 41 (23) (2008) 9051–9056.
- [17] N. Gourdoupi, K. Papadimitriou, S. Neophytides, J.K. Kallitsis, *Fuel Cells* 8 (3–4) (2008) 200–208.
- [18] R. He, Q. Li, A. Bach, J.O. Jensen, N.J. Bjerrum, *J. Membr. Sci.* 277 (2006) 38–45.
- [19] Q. Li, J.O. Jensen, R.F. Savinell, N.J. Bjerrum, *Prog. Polym. Sci.* 34 (2009) 449–497.
- [20] Y. Oono, A. Sounai, M. Hori, *J. Power Sources* 189 (2) (2009) 943–949.
- [21] C. Pan, Q. Li, J.O. Jensen, R. He, L.N. Cleemann, M.S. Nilsson, N.J. Bjerrum, Q. Zeng, *J. Power Sources* 172 (1) (2007) 278–286.
- [22] R. He, Q. Li, G. Xiao, N.J. Bjerrum, *J. Membr. Sci.* 226 (2003) 169–184.
- [23] M.K. Daletou, J.K. Kallitsis, G. Voyatzis, S.G. Neophytides, *J. Membr. Sci.* 326 (2009) 76–83.
- [24] J.O'M. Bockris, A.K.N. Reddy, M. Gamboa-Aldeco, *Modern Electrochemistry* 2A, 2nd ed., Kluwer Academic/Plenum Publishers, New York, 2000, p. 1455.
- [25] L. Xiao, H. Zhang, T. Jana, E. Scanlon, R. Chen, E.-W. Choe, L.S. Ramanathan, S. Yu, B.C. Benicewicz, *Fuel Cells* 2 (2005) 287–295.
- [26] R. Bouchet, E. Siebert, *Solid State Ionics* 118 (1999) 287–299.
- [27] H. Pu, W.H. Meyer, G. Wegner, *J. Polym. Sci. B: Polym. Phys.* 40 (2002) 663–669.