

# Proton-conducting membranes based on poly(2,5-benzimidazole) (ABPBI) and phosphoric acid prepared by direct acid casting

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## Abstract

We report the preparation of phosphoric acid doped poly(2,5-benzimidazole) (ABPBI) membranes for PEMFC by simultaneously doping and casting from a poly(2,5-benzimidazole)/phosphoric acid/methanesulfonic acid (MSA) solution. The evaporation of MSA yields a very homogeneous membrane having a better controlled composition, avoiding the use of solvent-intensive procedures. Membranes have been prepared with contents of up to 3.0H<sub>3</sub>PO<sub>4</sub> molecules per ABPBI repeating unit. These membranes achieve a maximum conductivity of  $1.5 \times 10^{-2} \text{ S cm}^{-1}$  at temperatures as high as 180 °C in dry conditions. These ABPBI membranes are more conveniently prepared than those conventionally formed and doped in separate steps while featuring comparable conductivities (ABPBI  $\times$  2.7H<sub>3</sub>PO<sub>4</sub> prepared by the soaking method showed a conductivity of  $2.5 \times 10^{-2} \text{ S cm}^{-1}$  at 180 °C in dry conditions).

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## 1. Introduction

The polymer membrane most widely used in polymer electrolyte membranes fuel cells (PEMFC) is the perfluoro-sulfonated membrane Nafion®. This membrane becomes a good electrolyte upon impregnation with water, and therefore needs to be hydrated to keep its good proton conductivity, and if the membrane dehydrates, the performance of the cell decays sharply. Furthermore, traces of CO frequently present in the hydrogen fuel used in PEMFC, poisons the platinum catalyst, decreasing significantly the power of the cell, even at CO concentrations as low as 10–20 ppm [1]. The design of cells based on materials which could work at temperatures of about 150–200 °C is therefore of the utmost importance for the practical development of PEMFC. At those temperatures CO poisoning would not represent a serious problem and the cell would tolerate a much higher concentration of CO in the fuel [1]. But Nafion® and other perfluorinated membranes used, do not allow to work at

these moderately high temperatures because they dehydrate and their conductivity is practically lost.

To solve this problem many different types of alternative high-temperature polymer electrolyte membranes have been studied [2–4]. One of the most promising is acid-doped polybenzimidazole (PBI). Acid-doped PBI has a very good proton conductivity and thermal stability at temperatures up to 200 °C [5–8]. PBI has been used in PEMFC fuelled by H<sub>2</sub> [1,9–12], alcohols [13–15], or propane [16] among others. PBI has been also blended with other polymers as sulfonated polysulfones and doped with phosphoric acid in order to improve its conductivity [17]. Yet, despite extensive work on PBI membranes, there are other members of the benzimidazole family, such as the simpler poly(2,5-benzimidazole) (ABPBI), which are very much worth of attention and study. We have reported recently the use of ABPBI as electrolyte in H<sub>2</sub>/O<sub>2</sub> PEMFC [10] or supercapacitors [18]. ABPBI is indeed the simplest among benzimidazole type polymers since it can be prepared easily from a single, inexpensive and commercial monomer (3,4-diaminobenzoic acid (DABA)) by condensation in polyphosphoric acid (PPA) [8,10,19,20]. Furthermore,

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impregnation of ABPBI with a given phosphoric acid solution leads to higher acid uptake in comparison with commercial PBI [10,19].

Litt and coworkers [8,21] have reported that direct acid casting of PBI/H<sub>3</sub>PO<sub>4</sub>, and also ABPBI/H<sub>3</sub>PO<sub>4</sub>, from trifluoroacetic acid (TFA) solutions improves the conductivity on PBI/H<sub>3</sub>PO<sub>4</sub> membranes and also allows a better control of the acid content in the resulting membrane. Based on these reports we decided to develop a similar procedure for the preparation of phosphoric acid-doped ABPBI membranes by a simultaneous casting and doping method. We will refer to this method as direct acid casting (DAC) as introduced by Litt and Savinell for PBI [8,21]. Here, we report and compare two methods for obtaining phosphoric acid doped ABPBI membranes (i) the previous methanesulfonic acid (MSA) casting of ABPBI membranes followed by phosphoric acid bath doping, and (ii) direct MSA casting of ABPBI/phosphoric membranes in a single step. Membranes of similar composition, prepared following these two different procedures have been compared mainly in terms of proton conductivity.

## 2. Experimental

### 2.1. Polymer synthesis

ABPBI monomer 3,4-diaminobenzoic acid 97% and methanesulfonic acid 99% were obtained from Across Organics and used without further purification. Polyphosphoric acid 85% P<sub>2</sub>O<sub>5</sub>, and phosphoric acid 85% were purchased from Panreac.

ABPBI was synthesized in polyphosphoric acid from the DABA monomer at 200 °C for 5 h (see Fig. 1). Excess PPA was eliminated washing with water, NaOH 10%, and water again until neutrality of the washing water. Detail studies of this polymerization as well as different analyses of the materials obtained have been reported earlier [10,19,22]. A Canon-Fenske 300 viscosimeter was used for the measurement of viscosities of polymer solutions in 96% H<sub>2</sub>SO<sub>4</sub>. Typical inherent viscosities about 2.3–2.4 dl g<sup>-1</sup> were high enough to allow the casting of membranes from 20 to 150 μm. Higher inherent viscosities can be obtained by purifying the monomer and/or adding P<sub>2</sub>O<sub>5</sub> to the reaction mixture [8,21] but these viscosities allowed the preparation of membranes with acceptable mechanical properties.

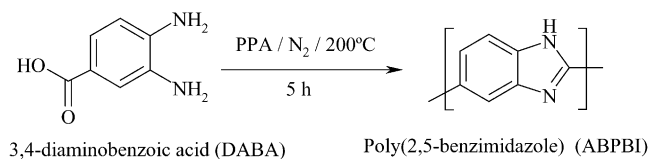


Fig. 1. Synthesis of ABPBI from DABA in PPA.

### 2.2. ABPBI membranes casting and subsequent doping in phosphoric acid bath

The first method studied for the preparation of phosphoric acid doped ABPBI membranes was based on the previous casting of an ABPBI membrane from a polymer solution in methanesulfonic acid, followed by the doping of these membranes in a concentrated phosphoric acid bath. The complete procedure has been described earlier by us [10,19]. The H<sub>3</sub>PO<sub>4</sub> uptake of the membrane was determined by elemental analyses (C, N, H and S), using a Carlo Erba Instruments EA1108 Elemental Analyzer. No S was detected in any sample, indicating that MSA is easily and completely eliminated in the doping step. The residue different from C, H and N, was attributed to PO<sub>4</sub><sup>3-</sup>.

This procedure allows the fabrication of membranes containing up to slightly more than 70% of acid in the membrane, yielding membranes with mechanical stability good enough to be used in PEMFC. Thermal stability up to 150–200 °C and their increased capacity for phosphoric acid uptake mentioned above [10] make of these ABPBI membranes very good candidates for their application as polymer electrolytes in PEMFC.

### 2.3. ABPBI acid doped membranes prepared by simultaneous casting and doping (direct acid casting)

Following the first procedure (bath soaking), we can control very well the acid uptake knowing the phosphoric acid bath concentration, but in order to control even better the composition of the doped ABPBI membranes, we have developed a second procedure, based on the simultaneous casting of both components (the polymer and the phosphoric acid) from a MSA solution. This procedure yields a membrane of a very well defined composition as shown below. This new procedure is described here in detail, and is compared to the first one (bath soaking), and TFA DAC reported by Savinell and coworkers [8].

For the preparation of the direct acid cast membranes, we prepared different solutions of ABPBI in MSA/phosphoric acid as summarized in Table 1. The resulting solution was homogeneously dispersed on a glass plate and heated into a ventilated hood in order to eliminate the MSA. Once the MSA evaporation had finished, the membrane was allowed

Table 1  
Solutions used for the preparation of ABPBI × xH<sub>3</sub>PO<sub>4</sub> membranes by simultaneous casting and doping (direct acid casting)

Membrane	Composition	ABPBI (mg)	H <sub>3</sub> PO <sub>4</sub> 85% (mg)	MSA (ml)	Evaporation (days)
#1	ABPBI × 3.0H <sub>3</sub> PO <sub>4</sub>	200	596	6	1
#2	ABPBI × 3.0H <sub>3</sub> PO <sub>4</sub>	400	1192	6	5
#3	ABPBI × 2.0H <sub>3</sub> PO <sub>4</sub>	200	397	3	1
#4	ABPBI × 1.0H <sub>3</sub> PO <sub>4</sub>	200	199	3	3

Table 2  
Elemental analysis of ABPBI  $\times$   $x\text{H}_3\text{PO}_4$  simultaneously cast and doped

	#2, ABPBI $\times$ 3.0H <sub>3</sub> PO <sub>4</sub>		#3, ABPBI $\times$ 2.0 H <sub>3</sub> PO <sub>4</sub>		#4, ABPBI $\times$ 0H <sub>3</sub> PO	
	EA experimental	EA calculated	EA experimental	EA calculated	EA experimental	EA calculated
C (%)	21.39	20.49	20.56	26.92	34.27	39.25
H (%)	3.12	3.17	3.68	3.21	3.26	3.27
N (%)	7.10	6.83	6.28	7.69	10.39	13.08
S (%)	<0.1	0	4.87	0	5.60	0
Residue (PO <sub>4</sub> <sup>3-</sup> )	68.39	69.51	65.04	62.18	46.48	44.40
H <sub>3</sub> PO <sub>4</sub> (%)	70.5	71.7	Not calculated	62.8	Not calculated	45.8

to hydrate absorbing water from the atmosphere. This facilitated its peeling off from the plate. The membranes obtained in this way present a more homogeneous aspect than the acid bath soaked ones (first method), and are almost transparent. Finally, the membrane was dried again at 100 °C. The membrane composition was determined by elemental analyses as detailed above (see Table 2).

#### 2.4. X-ray diffraction and AC conductivity measurements

The X-ray diffraction pattern of the DAC membrane was collected with a rotating anode Rigaku Rotaflex Ru-200B diffractometer ( $\lambda = 1.5418 \text{ \AA}$ , Cu K $\alpha$ )  $2\theta$  between 5 and 60° (0.02° step, 4° min<sup>-1</sup>).

Four probe ac conductivity measurements, as a function of temperature were made in air (open sample holder) at a fixed frequency of 500 Hz – 2 kHz measuring almost pure resistive behavior as describe before [10,19,23]. Membranes were first heated at 180 °C in order to eliminate all the water. By means of thermogravimetric analyses we were able to detect the elimination of absorbed water around 100 °C [10]. Conductivity measurements at different temperatures were performed while cooling the sample down to room temperature.

### 3. Results

#### 3.1. Elemental analysis (EA) of the direct acid cast membranes

Two membranes of ABPBI  $\times$  3.0H<sub>3</sub>PO<sub>4</sub> where analyzed by EA, showing that no Sulfur (MSA) was left (limit of detection 0.1%). The experimental composition is very close to the one calculated for the expected formula (Table 2).

On the other hand, when ABPBI  $\times$  2H<sub>3</sub>PO<sub>4</sub> and ABPBI  $\times$  1H<sub>3</sub>PO<sub>4</sub> cast membranes were analyzed, their sulfur analyses showed some residual MSA in the membrane, even after heating overnight. The EA shows that for lower phosphoric acid concentrations, more MSA remains in the membrane. This is consistent with the MSA initially protonating the benzimidazole groups of the polymer being displaced by phosphoric acid. As more phosphoric acid is added, more easily displaces MSA, which gets eliminated by heating.

In conclusion, this DAC procedure allows for the preparation of very homogeneous membranes, having good mechanical stability even for high acid loadings, but the phosphoric acid contents need to be very high if we want to eliminate all the MSA. In this work, we have characterized an ABPBI  $\times$  3.0H<sub>3</sub>PO<sub>4</sub> membrane prepared by direct acid casting.

#### 3.2. X-ray diffraction of direct acid cast ABPBI $\times$ 3.0H<sub>3</sub>PO<sub>4</sub>

XRD of direct acid cast ABPBI  $\times$  3.0H<sub>3</sub>PO<sub>4</sub> (Fig. 2) shows a higher crystallinity for this membrane, compared to samples conventionally doped in an acid bath. In the latter membranes there is only a single broad peak at about 25° [10], corresponding to the spacing between two parallel benzimidazole chains, but in Fig. 2 (direct acid cast ABPBI  $\times$  3.0H<sub>3</sub>PO<sub>4</sub>) we can see some overlapped peaks at about 25°, and a new broad diffraction peaks about 7–8°. This peak does not correspond to any spacing of the known crystal structure of pure semi-crystalline ABPBI [24]. Wainright et al. [8] have reported that heating PBI/phosphoric acid membranes prepared by bath doping, increase their crystallinity and continue to crystallize by further heating. The same is

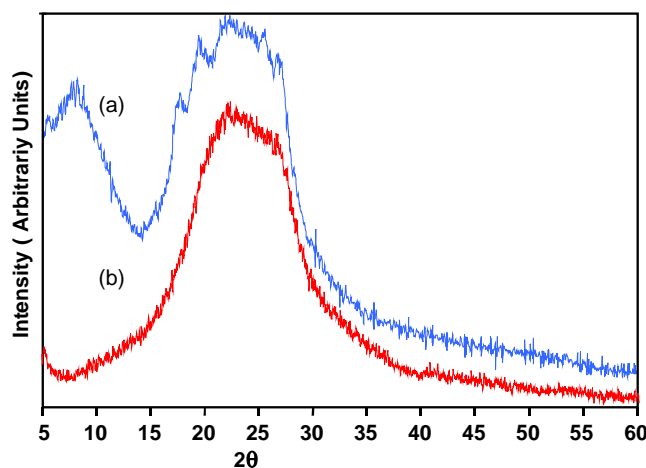


Fig. 2. XRD pattern of (a) ABPBI  $\times$  3.0H<sub>3</sub>PO<sub>4</sub> simultaneously cast and doped (membrane #1) and (b) ABPBI  $\times$  3.0H<sub>3</sub>PO<sub>4</sub> prepared by MSA casting and phosphoric acid bath doping.

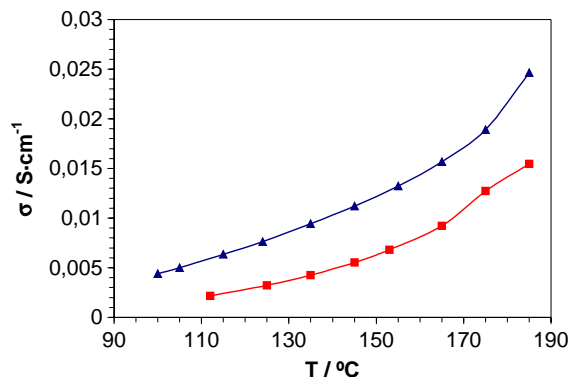


Fig. 3. Conductivity of ABPBI  $\times$  3.0H<sub>3</sub>PO<sub>4</sub> anhydrous, prepared by direct acid casting from a ABPBI/H<sub>3</sub>PO<sub>4</sub>/MSA solution (■); and ABPBI  $\times$  2.7H<sub>3</sub>PO<sub>4</sub> anhydrous, prepared by doping in a phosphoric acid bath (▲).

observed for undoped ABPBI MSA cast membranes [19]. As TFA cast PBI/H<sub>3</sub>PO<sub>4</sub> membranes are more crystalline and have higher conductivity than bath doped PBI membranes, an increase of conductivity or at least the same conductivity would be expected for MSA DAC ABPBI/H<sub>3</sub>PO<sub>4</sub> membranes described here.

### 3.3. Conductivity

Figs. 3 and 4 show the conductivity of ABPBI  $\times$  3.0H<sub>3</sub>PO<sub>4</sub> prepared by direct acid casting, and ABPBI  $\times$  2.7H<sub>3</sub>PO<sub>4</sub> prepared by phosphoric acid bath immersion of pre-cast membranes, respectively. Despite its lower acid content, the bath-doped membrane presents a higher conductivity, almost double than the direct cast membrane (ABPBI  $\times$  3.0H<sub>3</sub>PO<sub>4</sub> direct cast,  $1.5 \times 10^{-2}$  S cm<sup>-1</sup>; and ABPBI  $\times$  2.7H<sub>3</sub>PO<sub>4</sub> acid bath cast,  $2.5 \times 10^{-2}$  S cm<sup>-1</sup> at 185 °C). Results were repeated for the DAC membrane without significant changes in the conductivity of the DAC ABPBI  $\times$  3.0H<sub>3</sub>PO<sub>4</sub> membrane.

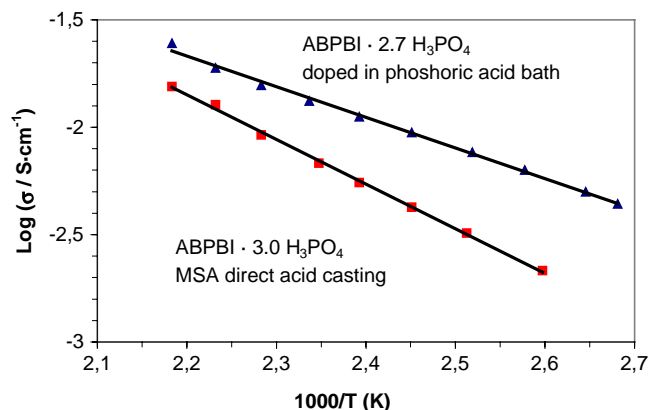


Fig. 4. Conductivity of ABPBI  $\times$  3.0H<sub>3</sub>PO<sub>4</sub> anhydrous, prepared by direct acid casting from a ABPBI/H<sub>3</sub>PO<sub>4</sub>/MSA solution (■); and ABPBI  $\times$  2.7H<sub>3</sub>PO<sub>4</sub> anhydrous, prepared by doping in a phosphoric acid bath (▲). Arrhenius plot.

As expected, the new direct acid cast membranes have a conductivity high enough to be used in PEMFC with good performance, but its conductivity is not as high as the “conventional” bath-doped membranes. Coming back to the EA, if we compare the calculated value with the experimental value of acid percent, the experimental value is a little bit lower (but still higher than the acid percent of the bath cast membrane which have the higher conductivity). This could be due to a small dehydration of the acid, yielding H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, but this difference in the EA is not big enough to confirm this dehydration. The dehydration of the phosphoric acid leads to the formation of species of lower conductivity, which would agree with the lower conductivity of the direct cast membrane. On the other hand, DAC membranes are allowed to absorb humidity in order to detach the membrane from the glass plate much easier, so the equilibrium of phosphoric acid and humidity could be reached again.

The activation energies ( $E_a$ ) can be calculated from the Arrhenius plot (Fig. 4). For the ABPBI  $\times$  3.0H<sub>3</sub>PO<sub>4</sub> (direct acid cast)  $E_a = 39.8$  kJ mol<sup>-1</sup>, higher than the 27.4 kJ mol<sup>-1</sup> calculated for the ABPBI  $\times$  2.7H<sub>3</sub>PO<sub>4</sub> (acid bath doped). We have reported earlier that when the acid percent is increased in a series of identical membranes the  $E_a$  decreases [10] and therefore in the present case the larger  $E_a$  for the DAC membrane, with a larger phosphoric acid molar ratio must be due to the intrinsic differences in the structure of the DAC and acid-bath membranes. MSA cast and bath doped ABPBI membranes have the same conductivity and activation energy as TFA cast membranes prepared by Ma and Savinell [25] having exactly the same ABPBI  $\times$  3.0H<sub>3</sub>PO<sub>4</sub> composition. On the other hand, the DAC ABPBI membranes have a much higher activation energy for this composition. Thus, as lower relative humidity leads to less conductive species due to the phosphoric acid–water equilibria [6], DAC membranes must dehydrate during the casting procedure and do not reach completely the initial equilibrium during the short time allowed to detach from the plate by rehydration followed by drying again at 100 °C.

## 4. Conclusions

A new procedure for the preparation of phosphoric acid doped ABPBI has been developed. In this method, ABPBI and H<sub>3</sub>PO<sub>4</sub> 85% are dissolved together in MSA at room temperature. The phosphoric acid doped ABPBI membranes are directly cast from this solution and formed by heating the solution dispersed over a glass plate. Membranes can be prepared having only 3.0H<sub>3</sub>PO<sub>4</sub> molecules per ABPBI repeating units, whereas lower phosphoric acid molar ratios lead to traces of MSA remaining in the membrane.

The direct acid cast membranes prepared in that way present somewhat lower conductivities (and larger activation energies) than the conventional acid bath doped membranes, probably due to the dehydration of the phosphoric acid during MSA evaporation at 150–200 °C. This crystallinity,

based on previous reports compared here, should involve a higher conductivity, but dehydration during the casting process leads to a lower conductivity. Yet, the conductivity values of  $1.5 \times 10^{-2} \text{ S cm}^{-1}$  at  $180^\circ\text{C}$  found for direct acid cast ABPBI  $\times 3.0\text{H}_3\text{PO}_4$  membranes are good enough for PEMFC applications. Furthermore, in addition to the advantage of their simplified fabrication procedure, these DAC membranes are even more homogeneous than those prepared by casting and soaking in acid baths, have a higher crystallinity, and its composition is more easily controlled than our first bath doping process. If the step in the preparation that reduces the conductivity is found, that would be a very interesting procedure for ABPBI membranes preparation.

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### References

- [1] Q. Li, R. He, J.-A. Gao, J.O. Jensen, N.J. Bjerrum, *J. Electrochem. Soc.* 150 (2003) A1608.
- [2] O. Savadogo, *J. New Mater. Electrochem. Syst.* 1 (1998) 47.
- [3] J. Rozière, D.J. Jones, *Annu. Rev. Mater. Res.* 33 (2003) 503.
- [4] P. Jannasch, *Curr. Opin. Colloid Interface Sci.* 8 (2003) 96.
- [5] J.S. Wainright, J.T. Wang, D. Weng, R.F. Savinell, M. Litt, *J. Electrochem. Soc.* 142 (1995) L121.
- [6] Y.-L. Ma, J.S. Wainright, M.H. Litt, R.F. Savinell, *J. Electrochem. Soc.* 151 (2004) A8.
- [7] S.R. Samms, S. Wasmus, R.F. Savinell, Thermal stability of proton conducting acid doped polybenzimidazole in simulated fuel cell environments, *J. Electrochem. Soc.* 143 (1996) 1225–1232.
- [8] J.S. Wainright, M.H. Litt, R.F. Savinell, High temperature membranes, in: *Fuel Cell Handbook*, 2003.
- [9] J.T. Wang, R.F. Savinell, J.S. Wainright, M. Litt, H. Yu, *Electrochim. Acta* 41 (1996) 193.
- [10] J.A. Asensio, S. Borrós, P. Gómez-Romero, *J. Electrochem. Soc.* 151 (2003) A304.
- [11] O. Savadogo, B. Xing, *J. New Mater. Electrochem. Syst.* 3 (2000) 345.
- [12] Q. Li, H.A. Hjuler, N.J. Bjerrum, *J. Appl. Electrochem.* 31 (2001) 773.
- [13] J.T. Wang, J.S. Wainright, R.F. Savinell, M. Litt, *J. Appl. Electrochem.* 26 (1996) 751.
- [14] J.T. Wang, S. Wasmus, R.F. Savinell, *J. Electrochem. Soc.* 142 (1995) 4218.
- [15] Q. Li, H.A. Hjuler, C. Hasiotis, J.K. Kallitsis, C.G. Kontoyannis, N.J. Bjerrum, *Electrochem. Solid State Lett.* 5 (2002) A125.
- [16] O. Savadogo, F.J. Rodriguez Varela, *J. New Mater. Electrochem. Syst.* 4 (2001) 93.
- [17] C. Hasiotis, Q. Li, V. Deimede, J.K. Kallitsis, C.G. Kontoyannis, N.J. Bjerrum, *J. Electrochem. Soc.* 148 (2001) A513.
- [18] P. Gómez-Romero, M. Chojak, K. Cuentas-Gallegos, J.A. Asensio, P.J. Kulesza, N. Casañ-Pastor, M. Lira-Cantú, *Electrochem. Commun.* 5 (2003) 149.
- [19] J.A. Asensio, Ph.D. thesis, Institut Químic de Sarrià, Universitat Ramon Lull, Barcelona, 2003.
- [20] J.A. Asensio, S. Borrós, P. Gómez-Romero, *Electrochem. Commun.* 5 (2003) 967.
- [21] M. Litt, R. Ameri, Y. Wang, R. Savinell, J. Wainwright, *Mater. Res. Soc. Symp. Proc.* 548 (1999) 313.
- [22] J.A. Asensio, S. Borrós, P. Gómez-Romero, *J. Polym. Sci. Part A: Polym. Chem.* 40 (2002) 3703.
- [23] B.D. Cahan, J.S. Wainright, *J. Electrochem. Soc.* 140 (1993) L185.
- [24] S.J. Krause, T. Haddock, G.E. Price, P.G. Lenhart, J.F. O'Brien, T.E. Helminiak, W.W. Adams, *J. Polym. Sci. Part B: Polym. Phys.* 24 (1986) 1991.
- [25] Y.-L. Ma, R.F. Savinell, unpublished data.