



Preparation of KOH-doped PVA/PSSA Solid Polymer Electrolyte for DMFC: The Influence of TiO₂ and PVP on Performance of Membranes

A. H. P. de Oliveira^{1,2}, M. L. F. Nascimento², H. P. de Oliveira^{1*}

¹ Instituto de Pesquisa em Ciência dos Materiais, Universidade Federal do Vale do São Francisco, 48902-300 Juazeiro, Bahia, Brazil

² Departamento de Engenharia Química, Escola Politécnica, Universidade Federal da Bahia, 40210-630 Salvador, Bahia, Brazil

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Abstract

The development of low cost alkaline anion solid exchange membranes requires high ionic conductivity, low liquid uptake, strong mechanical properties and chemical stability. PVA/PSSA blends cross-linked with glutaraldehyde and decorated with titanium dioxide nanoparticles introduce advantages relative to the pristine membrane of PVA and

PVA/PVP membranes due to their improved electrical response and low methanol uptake/ swelling ratio allowing their use in alkaline direct methanol fuel cells.

Keywords: Alkaline Fuel Cell, Conductivity, Direct Methanol Fuel Cell, Methanol Fuel Cells, Polymer Electrolyte Membrane

1 Introduction

The production of efficient energy storage devices depends on development of electrolytes with improved electrical transport and chemical stability [1–11]. Solid electrolytes have been considered as potential substitutes of liquid electrolytes due to the improved mechanical strength [12].

In particular, alkaline anion solid exchange membranes (AASEM) introduce important advantages on conventional proton exchange membranes (PEM) such as improvement in water management, fast kinetics of oxygen reduction reactions and reduced alcohol crossover [13]. The required high purity of fuel and oxidant feeds represents other important limitation circumvented by AAEMs.

On the other side, the requirement for low methanol crossover introduces a critical limitation for commercial perfluoro-sulfonate ionomer membranes, such as Nafion (a standard membrane for PEM applications). Methanol permeation appears as a strong impediment for large-scale applications, due to the loss of fuel and typical reduction in the electrochemical performance of device [2, 7, 14, 15].

Basic requirement for production of cost-effective AAEMs are suitable ionic conductivity and reduced methanol uptake under operation conditions [7, 16–19]. Poly (vinyl alcohol)

(PVA), a semi-crystalline and non-fluorinated polyhydroxy polymer, introduces interesting properties in fuel cell applications [20–22].

Based on these promising properties, different strategies have been developed in order to optimize the use of PVA-based devices. Particularly, ionic transport in alkaline-doped PVA (PVA-KOH) is favored by inter-penetrating networks obtained with incorporation of stabilizer/plasticizer agents with cross-linking modification of polymeric matrix [13].

In this direction, the literature reports the use of PVA in blends with sulfonic acid groups-based polymers (*viz.* polystyrene sulfonic acid-PSSA) and poly (styrene sulfonic acid-co-maleic acid) (PSSA-MA) cross-linked with glutaraldehyde. Resulting material is characterized by good chemical stability, high ionic conductivity, low swelling ratio and low liquid uptake [2, 10, 23–25].

C.-C. Yang [7] reported the use of ceramic fillers (TiO₂) with the aim of increasing the amorphous phase of polymer membrane. This process favors the creation of defects and free volume at interface between particles and polymer chains allowing the KOH adsorption and improved OH⁻ ionic conductivity.

[*] Corresponding author, helinando.oliveira@univasf.edu.br

Qiao et al. [26] reported that incorporation of interpenetrating poly (vinyl pyrrolidone) domains in PVA polymeric matrix, which contributes to improvement in the KOH adsorption in the interspaces created in PVA [27].

Based on these results, we have explored the influence of TiO₂ and PVP (isolated and combined contribution) in order to optimize the swelling, liquid uptake and ionic conductivity of KOH-doped and cross-linked PVA/PSSA membranes.

2 Materials and Methods

2.1 Reagents

Poly (vinyl alcohol), poly (vinyl pyrrolidone), sulfuric acid, HCl, KOH, acetone, titanium dioxide, PSSA and glutaraldehyde were purchased from Aldrich and used as received.

2.2 Preparation of Samples

The procedure for PVA-based AASEMs production was established according four steps *viz.* preparation of membrane, incorporation of additives, cross-linking and alkaline treatment [6, 7, 16, 26], as follows:

2.2.1 Polymeric Membrane Production

PVA powder (10 wt.%) is placed in 30 mL of water at 363.2 K during 2 h. Dissolved PVA in aqueous solution is poured into Petri dish allowing the water elimination under ambient temperature. The resulting film is peeled off from Petri dish, providing a free-standing membrane.

2.2.2 Additives Incorporation

Additives (PVP – varying amount from 0.2 g to 1.0 g, PSSA (2 mL) – and TiO₂ – varying amount from 0.0 g to 0.4 g) were introduced into aqueous solution at different relative concentration, previously to the dispersion of PVA (10 wt.%) which is mixed at 363.2 K during 2 h. The sequence of film preparation follows the same procedure as previously reported for PVA membranes.

2.2.3 Cross-linking

The cross-linking of polymer matrix with glutaraldehyde (GA) was established as follows:

Resulting PVA membrane is soaked into a reactor containing glutaraldehyde (GA) 10 wt.% and 50 μL of HCl (0.1M) in acetone at 303.2 K during 1 h, an adequate acidic environment for cross-linking between –OH group of PVA and –CHO group of GA [16].

2.2.4 Alkaline Treatment

The corresponding cross-linking procedure is followed by alkaline treatment: samples were soaked in KOH aqueous solution (4M) during 24 h for ion incorporation.

2.3 Characterization Techniques

2.3.1 Ionic Conductivity Measurement

The ionic conductivity of membranes was measured using electrical impedance spectroscopy with a potentiostat/galvanostat Autolab PGSTAT 302N in the range of frequency of 1 MHz–1 Hz, AC excitation of 10 mV and no external BIAS. The membrane was disposed in a Solartron 12962A sample holder (two-electrode configuration) at fixed temperature and humidity conditions. The bulk resistance R (intersection of semicircular arc at high frequency with Z' axis) is related with ionic conductivity according Eq. (1)

$$\sigma = \frac{L}{RA} \quad (1)$$

where L is the distance between two electrodes and A is the cross-sectional area of sample under test.

2.3.2 Raman Spectrum

Raman spectroscopy was performed in KOH-doped PVA/PSSA membranes in the absence/presence of TiO₂ in order to identify the incorporation of components. The spectrum of resulting material was determined using a Raman spectrometer (LabRam Horiba Evolution) with a 532 nm laser.

2.3.3 DSC Thermograms

DSC thermograms of membranes were performed by a Shimadzu DSC-60 using a scan rate of 10 K min⁻¹ and a temperature range of 298 K to 553 K under continuous flux of nitrogen.

2.3.4 Methanol Uptake and Swelling Ratio

Methanol uptake and swelling ratio were determined as follows:

The weight and size (length) of membranes were determined at dry and wet condition (after immersion of membrane in methanol during 24 h). Liquid uptake and swelling ratio are given by Eqs. (2) and (3), respectively [9]:

$$\text{Liquid Uptake (LU)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \quad (2)$$

$$\text{Swelling ratio (SR)} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \quad (3)$$

where W_{wet} and L_{wet} are mass and length of wet membranes while W_{dry} and L_{dry} are mass and length of dry membranes, respectively.

3 Results and Discussion

The cross-linking provided by GA in PVA membrane improves the chemical stability and ionic conductivity in com-

parison with conventional method of annealing (thermal treatment at 373.2 K during 1 hour) [17]. The ionic conductivity of PVA/GA membrane is in order of $(0.745 \pm 0.166) \times 10^{-3} \text{ S cm}^{-1}$ while annealed sample returns corresponding conductivity of $(0.031 \pm 0.014) \times 10^{-3} \text{ S cm}^{-1}$. The incorporation of PSSA (2 mL) in composition of PVA membrane improves the resulting ionic conductivity to $(0.776 \pm 0.075) \times 10^{-3} \text{ S cm}^{-1}$. Based on this information, we have explored the influence of TiO_2 and PVP on KOH-doped PVA/PSSA membrane cross-linked with GA.

3.1 Influence of TiO_2

The influence of TiO_2 on electrical response of membrane is shown in the Figure 1. By comparison of curves, it is possible to verify that incorporation of PSSA improves the overall electrical response of membrane. The ionic conductivity of membrane reaches the maximum value (in order of $4.2 \times 10^{-3} \text{ S cm}^{-1}$) with incorporation of 0.02 g of TiO_2 . It is noteworthy that ceramic fillers contribute to increase in the amorphous phase of polymer (which affects positively the ionic conductivity). However, progressive incorporation of semiconductor nanoparticles reduces the free volume for ionic movement. This process takes place with reduction in the liquid uptake in the polymer membrane and reduction in the ionic conductivity. The maximum observed at 0.02 g represents the equilibrium point between these phenomena.

In addition to increase in the ionic conductivity (which is affected by creation of defects induced by semiconductor filler in polymeric matrix) [7], the incorporation of TiO_2 in polymeric matrix affects thermal properties of resulting membrane:

As shown in the Figure 2, the incorporation of TiO_2 (0.02 g) in membrane reduces the melting temperature of resulting material from 498.5 K to 496.9 K. In correspondence, the heat of fusion decreases from -51.40 J g^{-1} to -49.35 J g^{-1} , in agreement with data reported in the literature [7] indicating the

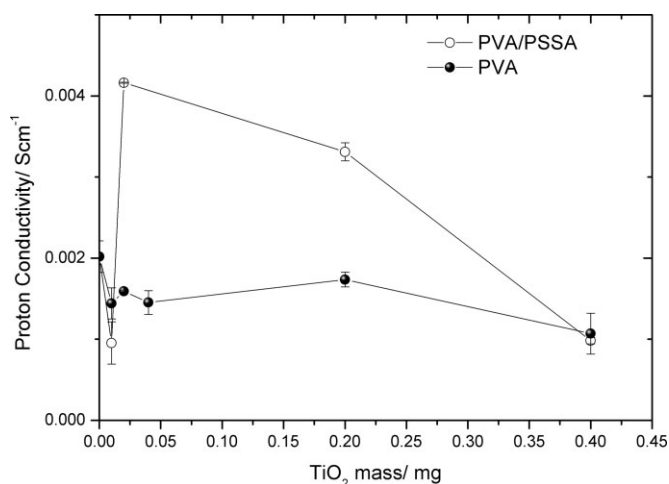


Fig. 1 Dependence of ionic conductivity of samples KOH-doped (PVA and PVA/PSSA) as a function of amount of TiO_2 .

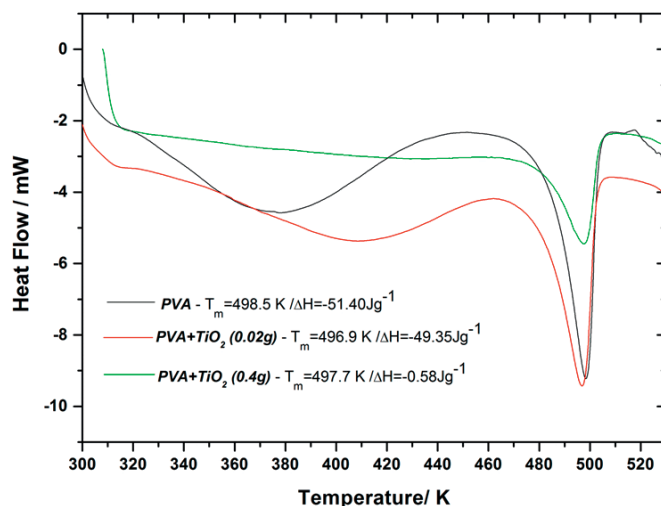


Fig. 2 DSC thermogram of KOH-doped PVA/PSSA/GA membrane (black line) in comparison with KOH-doped PVA/PSSA/ TiO_2 membrane (0.02 g - red line and 0.4 g - green line).

increase in the amorphous phase of polymeric matrix. The progressive incorporation of TiO_2 reduces strongly the heat of fusion to -0.58 J g^{-1} (in response of inclusion of 0.4 g of TiO_2), in agreement with previously reported data.

The Raman spectra of membranes (in the absence and presence of additive - TiO_2) shown in the Figure 3 reveals characteristic peaks of PVA at 1.438 cm^{-1} assigned to C-H and O-H bending and at $1.145, 919$ and 856 cm^{-1} (C-C and C-O stretching) [28, 29]. Other important aspect to be reported concerns to the reduction in the intensity of peaks by comparison of samples KOH-doped PVA/PSSA and KOH-doped PVA/PSSA/ TiO_2 , due to the increasing amorphous phase induced by TiO_2 (in agreement with data of heat of fusion of membranes).

Characteristic peaks of TiO_2 (phonon modes related with anatase phase) are identified at 142 cm^{-1} ($E_{g(1)}$), 194 cm^{-1} ($E_{g(2)}$), 396 cm^{-1} ($B_{1g(1)}$), 516 cm^{-1} ($A_{1g(1)} + B_{1g(2)}$) and 636 cm^{-1} ($E_{g(3)}$) [30].

3.2 Influence of PVP

The influence of PVP on membranes was compared for samples prepared in the absence and in the presence of semiconductor filler - TiO_2 (0.02 g).

In agreement with literature, it was observed that progressive inclusion of PVP in PVA matrix improves the swelling ratio of resulting matrix (see Figure 4).

By comparison with KOH-doped PVA/PSSA/ TiO_2 matrix, it is possible to verify that minimum in the swelling ratio is established with incorporation of 0.4 g of PVP in the resulting matrix. Progressive incorporation of PVP elevates the swelling ratio of matrix. The minimum in the swelling ratio of PVA/PSSA/ TiO_2 membrane can be described as a result of competition established between two mechanisms: the incorporation of ceramic filler at optimal concentration (0.02 g of TiO_2) results in reasonable increase in the swelling ratio of membrane. On the other side, the incorporation of an interpe-

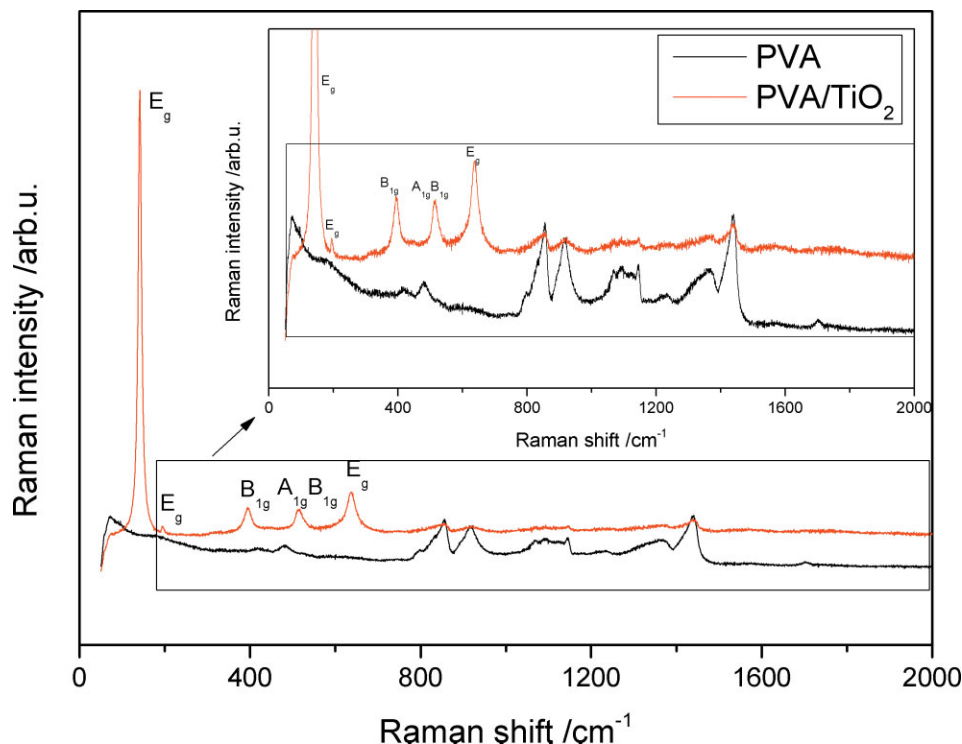


Fig. 3 Raman spectrum of KOH-doped PVA/PSSA membrane (black line) in comparison with KOH-doped PVA/PSSA/TiO₂ membrane (red line).

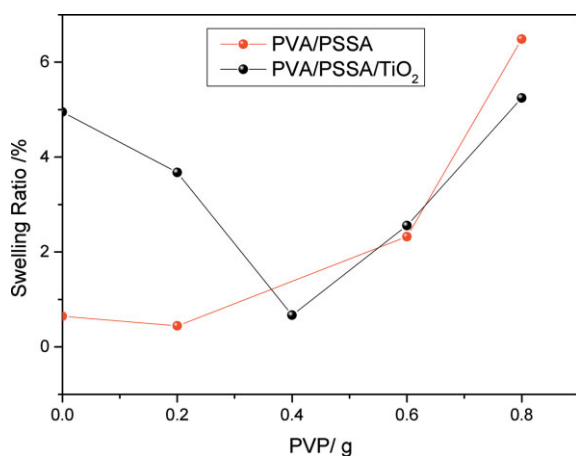


Fig. 4 Comparison of swelling ratio of methanol in KOH-doped (PVA/PSSA and PVA/PSSA/TiO₂) matrix as a function of amount of PVP in membrane.

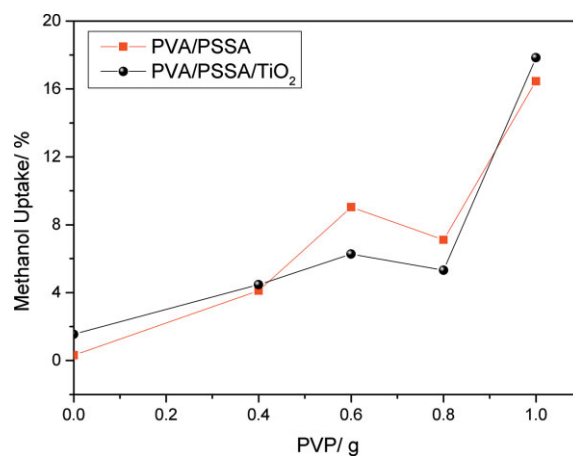


Fig. 5 Comparison of methanol uptake (%) of KOH-doped PVA/PSSA and KOH-doped PVA/PSSA/TiO₂ membranes as a function of amount of PVP in membrane.

netrating matrix (provided by PVP) provokes a reduction in the influence of particles on swelling of matrix due to the distribution of TiO₂ particles between PVP and PVA structure. The progressive incorporation of PVP contributes to hydrophilic behavior improvement in the resulting matrix followed by increase in the overall swelling ratio.

In terms of liquid uptake (as shown in the Figure 5), the progressive incorporation of PVP in both membranes (KOH-doped PVA/PSSA and KOH-doped PVA/PSSA/TiO₂) provokes a general increase in the corresponding value of methanol uptake.

The comparison with standard membrane reveals the typical advantage for use of PVA-based membrane with methanol as a feed-fuel (liquid uptake of Nafion is in order of 339%).

The ionic conductivity of membranes in the absence and presence of TiO₂ was evaluated in order to establish the interaction of additives and corresponding influence on electrical response of membranes.

Results in the Figure 6 indicate that PVP affects positively the response of KOH-doped PVA/PSSA due to the improvement in the conductivity as a consequence of additive incorporation.

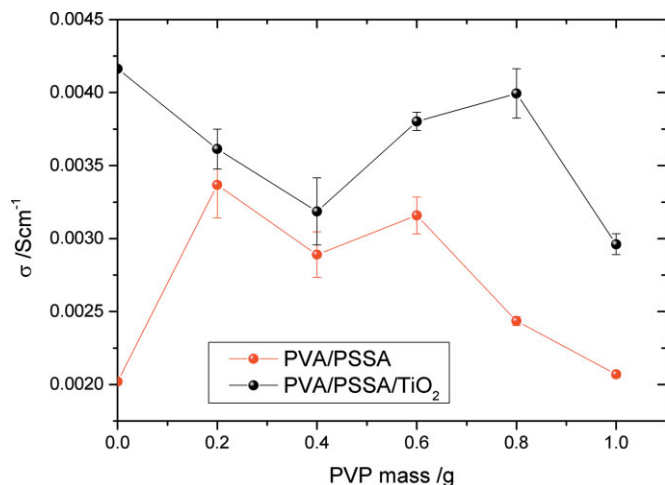


Fig. 6 Dependence of ionic conductivity of samples KOH-doped (PVA/PSSA and PVA/PSSA/TiO₂) as a function of amount of PVP.

However, as previously observed, the influence of TiO₂ on membrane ionic transport dominates and corresponding level of conductivity tends to be higher for sample prepared in the absence of additive (PVP). As a result, the progressive incorporation of PVP in association with TiO₂ returns a general decrease in the level of conductivity (the higher value of conductivity obtained for samples in the presence of PVP is lower than the value obtained in the absence of additive).

Based on these results, it is possible to establish that association of PVP and TiO₂ in PVA-based membranes affects negatively electrical and mechanical properties due to the decrease in the conductivity and progressive swelling ratio/liquid uptake.

The combined analysis of three factors (ionic conductivity, methanol uptake and swelling rate due to the methanol adsorption) indicates that sample KOH-doped PVA/PSSA/TiO₂ prepared using 0.02 g of TiO₂ can be considered as a potential candidate for application as membranes for DMFC due to the reasonable level of ionic conductivity and improved chemical/mechanical characteristics.

4 Conclusion

The competition established between creation of defects (increasing amorphous phase due to the incorporation of ceramic fillers) and interpenetrating domains (due to the action of PVP and PSSA) contributes to definition of best condition for production of cost-effective AASEMs.

The best concentration of components is reached at condition in which small variation in parameters is followed by dilution of charge carriers which affects strongly the mechanical and electrical response of resulting membranes.

The introduction of TiO₂ fillers (0.02 g) returns the best condition for filler incorporation in membranes and enables PVA/PSSA/TiO₂ as a potential candidate for use in DMFC membrane applications.

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References

- [1] C. Wang, M. Waje, X. Wang, J. M. Tang, R. C. Haddon, Y. Yan, *Nano Letters* **2004**, *4*, 345–348.
- [2] J.-W. Rhim, H. B. Park, C.-S. Lee, J.-H. Jun, D. S. Kim, Y. M. Lee, *Journal of Membrane Science* **2004**, *238*, 143–151.
- [3] M. Zhou, H. Wang, D. J. Hassett, T. Gu, *Journal of Chemical Technology Biotechnology* **2013**, *88*, 508–518.
- [4] S. Holmberg, A. Perebikovskiy, L. Kulinsky, M. Madou, *Micromachines* **2014**, *5*, 171–203.
- [5] Y.-S. Ye, J. Rick, B.-J. Hwang, *Polymers* **2012**, *4*, 913–963.
- [6] S. D. Bhat, A. K. Sahu, C. George, S. Pitchumani, P. Sridhar, N. Chandrakumar, K. K. Singh, N. Krishna, A. K. Shukla, *Journal of Membrane Science* **2009**, *340*, 73–83.
- [7] C.-C. Yang, *Journal of Membrane Science* **2007**, *288*, 51–60.
- [8] Moon-Sung Kang, J. H. Kim, J. Won, Seung-Hyeon Moon, Y. S. Kang, *Journal of Membrane Science* **2005**, *247*, 127–135.
- [9] B. Chen, G. Li, L. Wang, R. Chen, F. Yin, *International Journal of Hydrogen Energy* **2013**, *38*, 7913–7923.
- [10] A. K. Sahu, G. Selvarani, S. D. Bhat, S. Pitchumani, P. Sridhar, A. K. Shukla, N. Narayanan, A. Banerjee, N. Chandrakumar, *Journal of Membrane Science* **2008**, *319*, 298–305.
- [11] J. K. Park, Y. S. Kang, J. Won, *Journal of Membrane Science* **2008**, *313*, 217–223.
- [12] F. F. Hatta, M. Z. A. Yahya, A. M. M. Ali, R. H. Y. Subban, M. K. Harun, A. A. Mohamad, *Ionics* **2005**, *11*, 418–422.
- [13] J. Fu, J. Qiao, H. Lv, J. Ma, X.-Z. Yuan, H. Wang, *ECS Transactions* **2010**, *25* (13), 15–23.
- [14] R. Boonpoo-nga, M. Sriring, P. Nasomjai, S. Martwiset, *Science Asia* **2014**, *40*, 232–237.
- [15] M. S. Boroglu, S. Cavus, I. Boz, A. Ata, *Polymer Letters* **2011**, *5*, 470–478.
- [16] J. Fu, J. Qiao, X. Wang, J. Ma, T. Okada, *Synthetic Metals* **2010**, *160*, 193–199.
- [17] M. D. Abu Sayeed, K. Talukdar, H. J. Kim, Y. Park, A. I. Gopalan, Y. H. Kim, K.-P. Lee, S.-J. Choi, *Journal of Nanoscience and Nanotechnology* **2014**, *14*, 9329–9334.
- [18] A. M. Attaran, M. Javanbakht, K. Hooshyari, M. Enhessari, *Solid State Ionics* **2015**, *269*, 98–105.
- [19] D. L. Zugic, I. M. Perovic, V. M. Nikolic, S. Lj. Maslovara, M. P. Marceta Kaninski, *International Journal of Electrochemical Science* **2013**, *8*, 949–957.
- [20] Chien-Shun Wu, Fan-Yen Lin, Chih-Yuan Chen, P. P. Chu, *Journal of Power Sources* **2006**, *160*, 1204–1210.
- [21] D. S. Kim, M. D. Guiver, S. Y. Nam, T. I. Yun, M. Y. Seo, S. J. Kim, H. S. Hwang, J. W. Rhim, *Journal of Membrane Science* **2006**, *281*, 156–162.

- [22] C.-P. Liu, C.-A. Dai, C.-Y. Chao, S.-J. Chang, *Journal of Power Sources* **2014**, 249, 285–298.
- [23] M. Higa, S. Feng, N. Endo, Y. Kakihana, *Electrochimica Acta* **2015**, 153, 83–89.
- [24] B. Bolto, T. Tran, M. Hoang, Z. Xie, *Progress in Polymer Science* **2009**, 34, 969–981.
- [25] Moon-Sung Kang, Young-Jin Choi, Seung-Hyeon Moon, *Journal of Membrane Science* **2002**, 207, 157–170.
- [26] J. Qiao, J. Fu, R. Lin, J. Ma, J. Liu, *Polymer* **2010**, 51, 4850–4859.
- [27] Y. F. Huang, L. C. Chuang, A. M. Kannan, C. W. Lin, *Journal of Power Sources* **2009**, 186, 22–28.
- [28] C.-C. Yang, W.-C. Chien, Y. James Li, *Journal of Power Sources* **2010**, 195, 3407–3415.
- [29] C.-C. Yang, C.-T. Lin, S.-J. Chiu, *Desalination* **2008**, 233, 137–146.
- [30] R. Palomino-Merino, P. Trejo-Garcia, O. Portillo-Moreno, S. Jiménez-Sandoval, S. A. Tomás, O. Zelaya-Angel, R. Lozada-Morales, V. M. Castaño, *Optical Materials* **2015**, 46, 345–349.
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