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Contributed Paper

Poly(oligoethylene Glycol Methacrylate): A Promising Electrolyte Polymer

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ABSTRACT

In this work, the polymer electrolyte based on poly(oligoethylene glycol methacrylate) was studied and found to be a promising electrolyte polymer. The polymer was synthesized using conventional free radical polymerization and characterized using Fourier transform infrared spectroscopy and thermogravimetric analysis. Ionic conductivity was measured using impedance spectroscopy as a function of polymer type, iodine/iodide concentration, additive type and concentration, and polymer blend composition. The additives used in this study were TiO_2 nanoparticles, propylene carbonate, γ -butyrolactone, and 1-methyl-3-propylimidazolium iodide, whereas poly(ethylene glycol) and poly(vinyl alcohol) were used to prepare the polymer blends with poly(oligoethylene glycol methacrylate). It was found that the ionic conductivity of poly(oligoethylene glycol methacrylate) was about 40 times higher than that of commonly used polymers, such as poly(ethylene glycol) and poly(vinyl alcohol). This work thus demonstrates that poly(oligoethylene glycol methacrylate) is a good candidate to be used as an electrolyte polymer for a variety of electronic applications.

Keywords: polymer electrolyte, poly(oligoethylene glycol methacrylate), impedance spectroscopy, ionic conductivity

1. INTRODUCTION

Polymer electrolytes are solid ionic conductors prepared by dissolution of salts and suitable polymeric materials. Since the

ionic conductivity of alkali metal salt complexes of poly(ethylene glycol) was discovered by Wright in 1973 [1], a variety of

solid polymer electrolytes (SPEs) have been of great interest and their potentials have been explored in a variety of applications including batteries [2-4], fuel cells [5, 6], electrochromic displays [7-9], dye-sensitized solar cells [10-12], and water desalination. [13-16] SPEs have shown several advantages over conventional, volatile liquid-based electrolytes in terms of long-term stability, large-scale production, and simple fabrication methods.

The ionic conductivity of SPEs is an important factor in determining the device's efficiency as the electrolyte is the medium that transport ions in the devices. The ionic conductivity of the SPEs depends on the mobility of the charge carrier, which is mostly associated with the interaction between ions and coordination sites in the polymer and the chain mobility of the polymer chains [17]. In recent years, PEG has been of interest because of its excellent chemical stability, ability to dissolve a variety of alkali salts, low glass transition temperature, and excellent processability for making thin film [18-22]. The ethylene glycol units ($-\text{CH}_2-\text{CH}_2-\text{O}-$) in the PEG main chains provide effective interaction between lone-pair electrons of the oxygen atoms and alkali metal cations or anions allowing the ion transport under the influence of electric field. However, electronic devices consisting of PEG electrolytes suffer low device performance because of the low ionic conductivity of PEG ($\sigma \sim 10^{-8} \text{ S cm}^{-1}$ at room temperature [11]). The low conductivity of PEG is caused by the high crystallinity due to the formation of helical structure of the PEG units in solid state.

In this work, poly(oligoethylene glycol methacrylate) (POEGM) was extensively studied as an electrolyte polymer to show that it is a promising electrolyte polymer. Unlike PEG where the ethylene glycol units

are present in the main chain, POEGM consisting of ethylene glycol units as side chains is expected to possess lower crystallinity, and therefore, higher ionic conductivity than PEG. The presence of side chains prevents the lamellae formation of polymer chains during crystallization [23]. In this study, POEGM was synthesized by conventional free radical polymerization using benzoyl peroxide as initiator. The polymer was characterized using Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The ionic conductivity of polymer electrolytes was measured using impedance spectroscopy as a function of polymer type, iodine/iodide concentration, additive type and concentration, and polymer blend composition and also compared with that of commonly used polymers including poly(ethylene glycol) (PEG) and poly(vinyl alcohol) (PVA). This work demonstrates that POEGM is a promising candidate to be used as solid polymer electrolytes for a variety of electronics applications.

2. MATERIALS AND METHODS

2.1 Materials

All chemicals were purchased from Sigma-Aldrich. Oligoethylene glycol methacrylate ($M_n = 360$ and 500 g mol^{-1}) was purified by passing through silica gel columns. Benzoyl peroxide as free radical initiator was recrystallized in methanol and dried at room temperature. TiO_2 (particle size of less than 100 nm), propylene carbonate, γ -butyrolactone, and 1-methyl-3-propylimidazolium iodide, poly(ethylene glycol) (M.W. $100,000 \text{ g mol}^{-1}$), and poly(vinyl alcohol) (M.W. $86,000 \text{ g mol}^{-1}$) were used directly without further purifications.

2.2 Synthesis of Poly(oligoethylene glycol methacrylate)

Oligoethylene glycol methacrylate

(20 g), benzoyl peroxide (20 mg), and tetrahydrofuran (20 mL) were added to a round-bottom flask. The reaction mixture was heated at 80 °C until the solution became viscous. Then the solution was cooled down, filtered, and purified by soxhlet extraction in methanol and tetrahydrofuran to obtain clear solid as polymer product (16 g).

2.3 Preparation of Electrolyte Film

Polymer (0.6 g), NaI (0.054 g, 9 wt%), I_2 (0.054 g, 9 wt%), and acetone (10 mL) were added to a 20-mL vial. The mixture was allowed to mix using ultrasonicator (30 min) and a mechanical shaker (2 days). The mixture was then drop-cast on a cleaned aluminum sheet (3x3 inches) and allowed to dry at 35 °C for 2 days prior to the conductivity measurement. The sample thickness was in the range of 0.2-0.4 mm.

2.4 Characterization

The FTIR spectra were obtained using a Perkin Elmer FTIR (Spectrum 2000 model) and NaCl salt windows. The X-ray diffraction (XRD) patterns were obtained using PANalytical X-ray diffractometer (step angle = 0.02°; count time = 0.5 sec; D-, R- and S-slits 1°, 1/2° and 1/4°, respectively; target type: Cu; tube voltage = 45 kV; current = 45 mA). Thermogravimetric analysis (TGA) of the polymers was carried out with Perkin Elmer TGA7 analyzer. The samples were heated at a rate of 10 °C/min under air from 40 °C to 660 °C under nitrogen atmosphere. The ionic conductivity of electrolytes was measured at 25 °C using a Hewlett Packard 16451B Dielectric Test Fixture coupled to an Agilent 4294A Precision Impedance Analyzer over a frequency range of 40 Hz to 110 MHz. The applied voltage and current were 500 mV and 20 mA, respectively. A circular aluminum sheet (diameter = 38 mm) was placed on top of

the electrolyte films in each measurement (thus sandwiching electrolyte films with aluminum sheets). The ionic conductivity was calculated using the formula,

$$\sigma = \left(\frac{L}{AR_B} \right)$$

where σ is ionic conductivity (S cm⁻¹), R_B is the bulk resistance obtaining from the semicircle diameter in the Nyquist plot (by mathematical fitting, Ohm), L is thickness of the sample (cm) and A is the area of the sample (cm²)

3. RESULTS AND DISCUSSION

3.1 Synthesis of Poly(oligoethylene glycol methacrylate)

POEGM was prepared by solution free radical polymerization using benzoyl peroxide as free radical initiator (Figure 1). POEGM is not soluble in any organic solvents, but can be swollen in some solvents, such as dimethyl sulfoxide and acetone. Therefore, it cannot be characterized by conventional techniques for polymers, such as nuclear magnetic resonance spectroscopy and gel permeation chromatography. The FTIR spectra of both OEGM and POEGM showed peaks at 3480, 2960, 1734, and 1377 cm⁻¹ corresponding to the O-H, C-H, C=O, C-O stretches, respectively (Figure 2). The virtually disappearance of peak at 1638 cm⁻¹, corresponding to C=C stretch, in POEGM confirms the formation of the polymer.

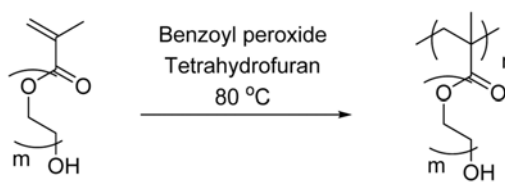


Figure 1. Synthesis of POEGM.

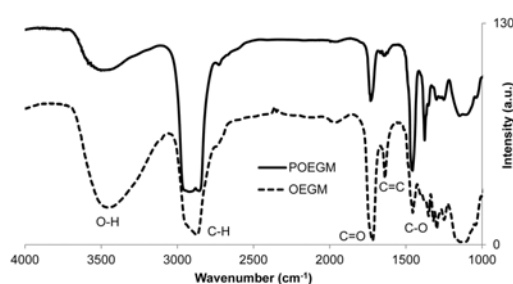


Figure 2. FTIR spectra of OEPM and POEPM.

3.2 Effect of Polymer Types

Polymer electrolyte samples based on POEPM were prepared and their ionic conductivities were measured and compared with those of the commonly used polymers, including PEO and PVA. Two types of POEPM with different side chain lengths were employed. They are denoted as POEPM360 and POEPM500 because the average molecular weights of their respective monomers are 360 and 500 g mol⁻¹. The Nyquist plots of the polymer electrolytes were obtained (Figure 3) and fitted and the ionic conductivities were calculated and reported (Table 1). A concentration of 9 wt% I₂/NaI was used, which is in the range used in the previous studies [24-26]. It was found that PEG and PVA possess similar ionic conductivities of about 5×10⁻⁸ S cm⁻¹, consistent with the values in previous studies [11]. POEPM360 and POEPM500 yielded the conductivities of 1.2×10⁻⁶ S cm⁻¹ and 2.3×10⁻⁶ S cm⁻¹, which are about 40 times higher than PEG and PVA. PEG and PVA were used for comparison because they are ones of the most studied electrolyte polymers [11, 13, 20, 21, 27]. POEPM500 has higher conductivity than POEPM360 possibly due to its lower crystallinity from the longer side chain length and also a higher density of ethylene glycol units in the side chain.

Table 1. Ionic conductivities of polymers with 9 wt% I₂ and 9 wt% NaI.

Polymer	Conductivity (S cm ⁻¹)
POEPM360	1.24×10 ⁻⁶
POEPM500	2.30×10 ⁻⁶
PEG	5.15×10 ⁻⁸
PVA	5.92×10 ⁻⁸

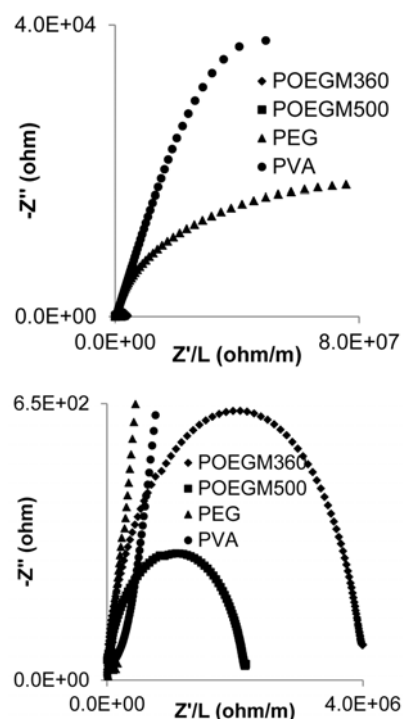


Figure 3. Nyquist plots of polymer electrolytes (with thickness-normalized Z' values) based on POEPM360, POEPM500, PEG, and PVA. The right-hand side picture is the magnification of the left-hand side one. These curves were fitted and the ionic conductivity values were reported in Table 1.

The XRD diffraction patterns of PEO, PVA, POEPM500, and POEPM360 were obtained (Figure 4). The XRD pattern of PEO shows two well-known semicrystalline peaks at 19.1° and 23.3° whereas the XRD pattern of PVA shows a peak at 23.7° [18]. Both POEPM360 and POEPM500 show

a broad peak centered at about 20.7° . Obviously from the XRD patterns of these polymers, PEO and PVA possess much higher crystallinities than POEGM360 and POEGM500. These XRD results agree with the ionic conductivity data where PEO and PVA yielded much lower ionic conductivities than the POEGM's. These results thus confirm that the presence of ethylene glycol units as side chains in POEGMs lower the crystallinity of the polymers in solid state, leading to higher ionic conductivities compared to the PEO where ethylene glycol units are present in the polymer main chains.

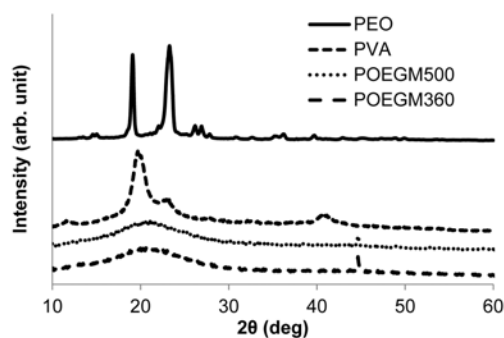


Figure 4. XRD patterns of PEO, PVA, POEGM500, and POEGM360.

3.3 Effect of I_2/NaI Concentrations

In this study, the effect of iodine concentration on the ionic conductivity of POEGM electrolytes was examined. It was found that for the samples with I_2/NaI the ionic conductivity was more than two orders of magnitude higher than the sample without the I_2/NaI (Table 2). As the concentration of I_2/NaI increases, the ionic conductivities of the polymer electrolytes increase, which agrees with the results from previous studies [11, 28]. These results confirm that the presence of iodine/iodide as ion carriers is essential for high ionic conductivity of polymer electrolyte.

Table 2. Ionic conductivities of polymer electrolytes based on POEGM500 with different I_2/NaI concentrations.

I_2/NaI concentration (wt%)	Conductivity ($S\ cm^{-1}$)
0	1.38×10^{-8}
4.5	2.16×10^{-6}
9	2.30×10^{-6}
18	8.80×10^{-6}

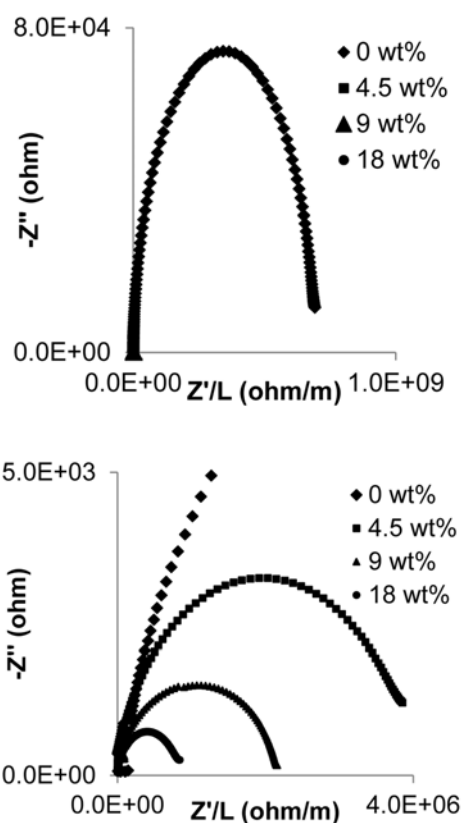


Figure 5. Nyquist plots of polymer electrolytes (with thickness-normalized Z' values) based on POEGM500 with different I_2/NaI concentrations. The right-hand side picture is the magnification of the left-hand side one. These curves were fitted and the ionic conductivity values were reported in Table 2.

3.4 Effect of Additive Types and Concentrations

The effect of additives on the ionic conductivity of POEGM electrolytes was investigated. Four types of commonly used additives in electronic applications, especially batteries [29] and dye-sensitized solar cells [11, 28], were mixed with POEGM500: TiO_2 , propylene carbonate (PC), γ -butyrolactone (GBL), and 1-methyl-3-propylimidazolium iodide (MPI). It was found that POEGM with TiO_2 and PC gave slightly lower conductivity than the pure POEGM500 whereas

POEGM500 with GBL or MPI gave higher conductivity than the pure POEGM500 (Table 3). The ionic conductivities of polymer electrolytes with different additives can be ranked as follows: $\text{MPI} > \text{GBL} > \text{PC} > \text{TiO}_2$. POEGM500 with TiO_2 gives the lowest ionic conductivity possibly due to the solid nature of TiO_2 decreasing chain mobility necessary for ion transport compared to MPI, GBL, and PC, which are liquid. MPI, which is an ionic liquid, gives the highest ionic conductivity possibly due to its ionic nature and also to its possessing iodide ion moiety.

Table 3. Ionic conductivities (S cm^{-1}) of polymer electrolytes based on POEGM500 with 9% NaI, 9% I_2 , and different additives and concentrations.

Concentration (wt%)	Additive			
	TiO_2	PC	GBL	MPI
2.5	1.2×10^{-6}	1.6×10^{-6}	3.4×10^{-6}	5.0×10^{-6}
5	8.2×10^{-7}	2.8×10^{-6}	3.1×10^{-6}	3.7×10^{-6}

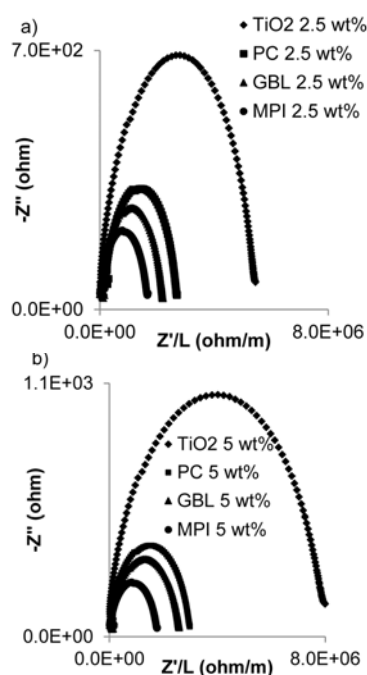


Figure 6. Nyquist plots of polymer electrolytes (with thickness-normalized Z' values) based on POEGM500 with additives a) 2.5 wt% and b) 5 wt%. These curves were fitted and the ionic conductivity values were reported in Table 3.

The effect of additive concentration on ionic conductivity of POEGM was investigated. For each additive, two concentrations were employed: 2.5% and 5% by weight with respect to the POEGM500 polymer. It was found that higher concentration of PC led to slightly higher conductivity whereas higher concentration of TiO_2 , GBL, and MPI resulted in lower conductivity. Molecular-level computational studies, for example, are required to confirm the effects on the conductivity of POEGM, but they are not the scope of this work. These results indicate that the type and concentration of additives affect the ionic conductivity of POEGM, and therefore, the additives must be chosen carefully when using the POEGM for actual applications.

3.5 Effect of Polymer Blends

In this study, POEGM500 was mixed with PEG and PVA to prepare polymer blend samples in order to investigate the

compatibility effect on the ionic conductivity. It was found that the POEGM500/PEG blend gave an ionic conductivity about two orders of magnitude higher than the POEGM500/PVA, despite the fact that pure PVA has a slightly higher conductivity than pure PEO (Table 4). This result is possibly due to the fact that POEGM is more compatible with PEG than PVA because of the similarity in chemical structure of their ethylene glycol units.

The effect of blend composition on ionic

conductivity was studied using two different concentrations (1:1 and 3:1) of both types of polymer blends. It was found that higher concentrations of POEGM500 in the blends led to about three times lower ionic conductivities. Nevertheless, all blend samples yield lower ionic conductivity than the pure POEGM500. This is because both pure PEG and PVA possess lower conductivities than POEGM500, and therefore, they are detrimental to the conductivity of the polymer electrolytes.

Table 4. Ionic conductivities of polymer blend electrolytes based on POEGM500 and PEG and PVA with 9% NaI and 9% I₂.

Polymer blend	Ratio (by wt)	Conductivity (S cm ⁻¹)
POEGM500:PEG	1:1	8.89×10 ⁻⁷
	3:1	2.46×10 ⁻⁷
POEGM500:PVA	1:1	5.84×10 ⁻⁹
	3:1	1.77×10 ⁻⁹

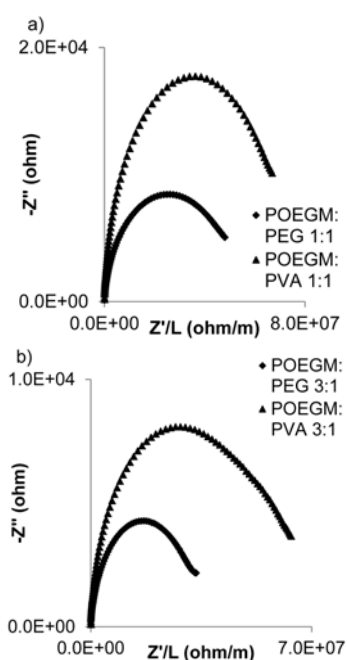


Figure 7. Nyquist plots of polymer electrolytes (with thickness-normalized Z' values) based on POEGM:PEG and POEGM:PVA blends with a) 1:1 ratio and b) 3:1 ratio. These curves were fitted and the ionic conductivity values were reported in Table 4.

3.6 Thermal Stability

TGA thermographs of POEGM500, POEGM360, PEO, and PVA were obtained. It was found that the onset temperatures of POEGM500, POEGM360, PEO, and PVA are 321, 290, 360, and 254 °C, respectively (Figure 8). It can be noted that POEGM500 and POEGM360 are relatively stable, compared with PEO and PVA. This result indicates that POEGM-based polymers are sufficiently stable to be used as polymer electrolytes for actual electronic applications.

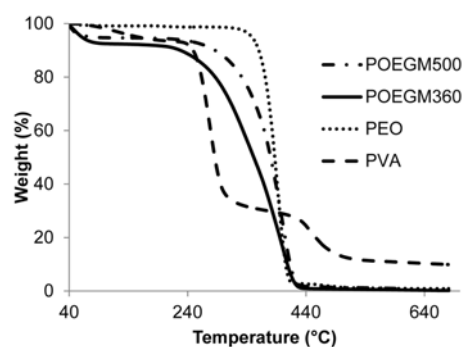


Figure 8. TGA thermographs of POEGM500, POEGM360, PEO, and PVA.

4. CONCLUSIONS

In this work, POEGMs were investigated as polymer electrolytes and their ionic conductivities were measured. It was found that POEGMs possess higher conductivities than the commonly used polymers such as PEG and PVA. The effect of iodine/iodide concentration, additive type and concentration, and polymer blend composition on the ionic conductivity of POEGM was examined and it was found that all of these factors affect the ionic conductivities of POEGM-based electrolytes. Possessing a higher ionic conductivity than the commonly used polymers, POEGM is shown to be an excellent candidate as a material for solid-state electrolyte in several electronics applications. Future work includes the study of POEGM as polymer electrolytes in dye-sensitized solar cells and lithium-ion batteries.

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REFERENCES

- [1] Fenton D., Parker J.M. and Wright P.V., *J. Polym.*, 1973; **14**: 589. DOI 10.1016/0032-3861(73) 90146-8.
- [2] Young W.S. and Kuan W.F., *J. Polym. Sci., Part B: Polym. Phys.*, 2014; **52**: 1-16. DOI 10.1002/polb.23404.
- [3] Park M.J., Choi I., Hong J. and Kim O., *J. Appl. Polym. Sci.*, 2013; **129**: 2363-2376. DOI 10.1002/app.39064.
- [4] Jin Z., Xie K. and Hong X., *Acta Chim. Sinica*, 2014; **72**: 11-20. DOI 10.6023/A13101097.
- [5] Qi Z., Gong C., Liang Y., Li H., Zhang S. and Li Y., *Prog. Chem.*, 2013; **25**: 2103-2111. DOI 10.7536/PC130438.
- [6] Lufrano F., Baglio V., Staiti P., Antonucci V. and Arico A.S., *J. Power Sources*, 2013; **243**: 519-534. DOI 10.1016/j.jpowsour.2013.05.180.
- [7] Assis L.M.N., Ponez L., Januszko A., Grudzinski K. and Pawlicka A., *Electrochim. Acta*, 2013; **111**: 299-304. DOI 10.1016/j.electacta.2013.07.203.
- [8] Yang S., Zheng J., Wu Z. and Xu C., *Acta Chim. Sinica*, 2013; **71**: 1041-1046. DOI 10.6023/A13020168.
- [9] Thakur V.K., Ding G., Ma J., Lee P.S. and Lu Z., *Adv. Mater.*, 2012; **24**: 4071-4096. DOI 10.1002/adma.201200213.
- [10] Nogueira A.F., Durrant J.R. and Paoli M.A.D., *Adv. Mater.*, 2001; **13**: 826-830. DOI 10.1002/1521-4095 (200106)13:11.
- [11] Freitas J.N.d., Nogueira A.F. and Paoli M.A.D., *J. Mater. Chem.*, 2009; **19**: 5279-5294. DOI 10.1039/B900928K.
- [12] Peter L.M., *J. Phys. Chem. Lett.*, 2011; **2**: 1861-1867. DOI 10.1021/jz200668q.
- [13] Hallinan Jr. D.T. and Balsara N.P., *Annu. Rev. Mater. Res.*, 2013; **43**: 503-525. DOI 10.1146/annurev-matsci-071312-121705.
- [14] Yaroshchuk A., Martinez-Llado X., Llenas L., Rovira M., Pablo J.d., Flores J. and Rubio P., *Desalin. Water Treat.*, 2009; **6**: 48-53. DOI 10.5004/dwt.2009.642.

- [15] Kumar R., Ismail A.F., Kassim M.A. and Isloor A.M., *Desalination*, 2013; **317**: 108-115. DOI 10.1016/j.desal.2013.03.008.
- [16] Blasi A.D., Andaloro L., Siracusano S., Briguglio N., Brunaccini G., Stassi A., Arico A.S. and Antonucci V., *Int. J. Hydrogen Energy*, 2013; **38**: 7612-7615. DOI 10.1016/j.ijhydene.2012.10.062.
- [17] Kang M.S., Kim J.H., Won J. and Kang Y.S., *J. Phys. Chem. C.*, 2007; **111**: 5222-5228. DOI 10.1021/jp067621k.
- [18] Singh P.K., Kim K.I., Park N.G. and Rhee H.W., *Macromol. Symp.*, 2007; **249-250**: 162-166. DOI 10.1002/masy.200750327.
- [19] Kohjiya S. and Ikeda Y., *Mater. Sci. Res. Int.*, 1998; **4**: 73-78. DOI 10.2472/jsms.47. 6Appendix_73.
- [20] Florjanczyk Z., Marcinek M., Wieczorek W. and Langwald N., *Pol. J. Chem.*, 2004; **78**: 1279-1304. DOI 10.1016/j.polymer.2006.05.069.
- [21] Ileperuma O.A., *Mater. Technol.*, 2013; **28**: 65-70. DOI <http://dx.doi.org/10.1179/1753555712Y.00000000043>.
- [22] Somsongkul V., Saekung C., Thang S.H., Wongchaisuwat A. and Arunchaiya M., *Chiang Mai J. Sci.*, 2011; **38**: 223-230.
- [23] Marzantowicz M., Dygas J.R., Kroka F., Tomaszewskab A., Florjanczyk Z., Zygodlo-Monikowska E. and Lapienis G., *J. Power Sources*, 2009; **194**: 51-57. DOI 10.1016/j.jpowsour.2009.01.011.
- [24] Nogueira A.F., Spinace M.A.S., Gazotti W.A., Girotto E.M. and Paoli M.A.D., *Solid State Ionics*, 2001; **140**: 327-335. DOI 10.1016/S0167-2738(01)00813-X.
- [25] Freitas J.N.d., Nogueira V.C., Ito B.I., Soto-Oviedo M.A., Longo C., Paoli M.A.D. and Nogueira A.F., *Int. J. Photoenergy*, 2006; **75483**. DOI 10.1155/IJP/2006/75483.
- [26] Nogueira V.C., Longo C., Nogueira A.F., Soto-Oviedo M.A. and Paoli M.A.D., *J. Photochem. Photobiol. A*, 2006; **181**: 226-232. DOI 10.1016/j.jphotochem.2005.11.028.
- [27] Bhad S.N. and Sangawar V.S., *Chem. Sci. Trans.*, 2012; **1**: 653-657. DOI 10.7598/cst2012.253.
- [28] Nazeeruddin M.K., Baranoff E. and Gratzel M., *Sol. Energy*, 2011; **85**: 1172-1178. DOI 10.1016/j.solener.2011.01.018.
- [29] Matsuo Y., Fumita K., Fukutsuka T., Sugie Y., Koyama H. and Inoue K., *J. Power Sources*, 2003; **119**: 373-377. DOI 10.1016/S0378-7753(03)00271-4.