Journal of New Materials for Electrochemical Systems 17, 213-217 (2014)
© J. New Mat. Electrochem. Systems

Preparation and Characterization of Ultraviolet-cured Polymer Electrolyte Poly(glycidyl methacrylate-co-methyl methacrylate)

M. Imperiyka[1,2,5], A. Ahmad[1,2,†], S.A. Hanifah[1, 2], M.Y.A. Rahman[3,*] and N.S. Mohamed[4]

[1]School of Chemical Sciences and Food Technology, Faculty of Science and Technology,
Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia
[2]Polymer Research Center, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia
[3]Institute of Microengineering and Nanoelectronics (IMEN), Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia
[4]Center of Foundation Studies in Science, University of Malaya, 50603, Kuala Lumpur, Malaysia
[5]Faculty of Art and Science, Kufra Campus, University of Benghazi, PO Box 1308, Bneghazi, Libya

Received: February 06, 2014, Accepted: April 10, 2014, Available online: July 11, 2014

Abstract: *Effect of lithium triflate (LiTf) concentration on the properties of poly (glycidyl methacrylate-co-methyl methacrylate) P(GMA-co-MMA)-based solid polymer electrolyte was investigated. The copolymer of (GMA-co-MMA) was synthesized by photopolymerization method. P(GMA–MMA) was fixed at the ratio of 90:10 based on the conductivity result of the electrolyte film. The electrolyte samples were characterized using impedance spectroscopy (EIS), cyclic voltammetry (CV) and thermogravimetric analysis (TGA). The room temperature conductivity was improved about six orders upon the addition of 30 wt. % LiTf salt into the polymer host. The highest room temperature conductivity was* 1.4×10^{-6} *S* cm^{-1} *at 30 wt. % LiTf. The highest conductivity of* 1.25×10^{-4} *S* cm^{-1} *was achieved at 393 K. The polymer electrolyte system exhibits Arrhenius-like behavior with the pre-exponential factor of* 1.25×10^{-4} *S* cm^{-1} *and activation energy of 0.39 eV. The electrolyte showed electrochemical stability window up to 3 V. The thermal stability increases with the salt concentration. The above results indicate that the electrolyte has potential for lithium ion battery application.*

Keywords: glycidyl methacrylate (GMA), methyl methacrylate (MMA), ionic conductivity, solid polymer electrolyte, lithium triflate

1. INTRODUCTION

Many recent studies have been addressed to the preparation of polymer with high molecular weight and low cost. UV curing is one of the most widely applied processes for the preparation of polymeric materials as nearly 50% of all commercial synthetic polymers are produced by this method. It is an attractive method for building a polymeric network as it is a very fast and environmentally friendly polymerization process, which requires low energy and no solvents. Polymer researches have contributed to the electrochemical devices development especially as electrolyte. After the use of polyethylene oxide PEO as a polymer electrolyte material by Armand et al. in 1979 [1], polymer electrolytes have grabbed the attention of researchers owing to the possibility of applications in a diversity of electrochemical applications [2,3]. The importance of designing lithium ion polymer secondary batteries due to an increasing demand for safe, light weight and high performance has been well demonstrated in the recent years [4,5]. Lithium-ion batteries with long recycling life, low self-discharge rate, power capability and high energy density, are employed to power portable electronic devices for instance cellular phones and laptop computers. They have also long been considered as possible power source for electric vehicle (EV), hybrid electric vehicle (HEV) and high efficiency energy-storage systems [6,7]. Despite the high performance of lithium battery utilizing liquid electrolyte, difficulty caused by liquid electrolyte, such as leaks, evaporation, internal shorting and producing flammable reaction products at the electrode surfaces existing in the liquid electrolytes are eliminated by the presence of solid polymer electrolyte. Thus, numerous efforts have been made to replace liquid electrolytes with solid poly-

---

To whom correspondence should be addressed:
Email: *mohd.yusri@ukm.edu.my, †azizan@ukm.edu.my

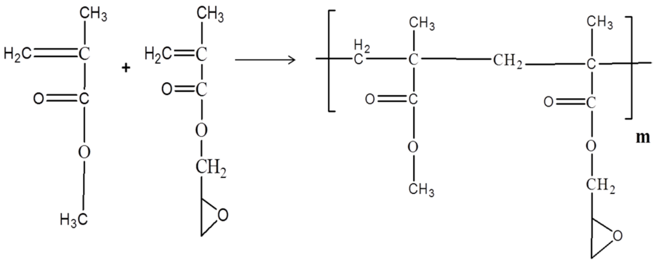

Figure 1. Scheme of poly (GMA-co-MMA) polymerization

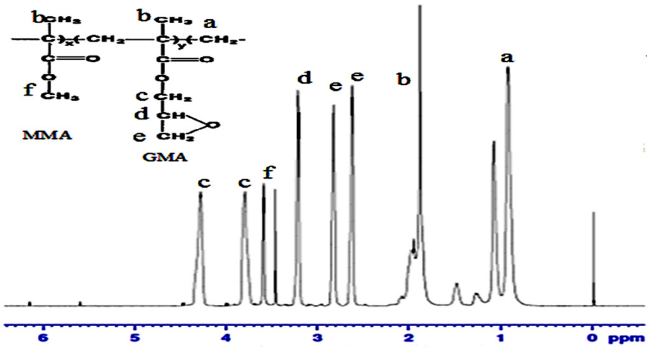

Figure 2. ^{1}H NMR spectrum of P(GMA-co-MMA)

mer electrolytes [8], gel polymer electrolytes (GPEs) [9] and ionic liquid-based gel electrolytes [10]. Solid polymer electrolytes have attracted huge interest as safer alternatives to liquid electrolyte for lithium secondary batteries [11]. Current research interest is on the development of novel solid polymer electrolytes with high ionic conductivities at ambient temperature, good electrochemical stability as well as thermal stability [11]. However, a number of methods have been reported for improving the electrochemical, thermal stability, mechanical and morphological characteristics of polymer electrolytes in higher temperature range and for improving conductivity in the lower temperature range. These include the use of blending, copolymer and addition of inert fillers. However, PMMA has been used as a polymer host due to its high stability at the lithium-electrolyte surface and because it is less reactive towards the lithium electrode, and it has been proposed for lithium battery application [3]. In an attempt to look for good lithium-ion-conducting polymer electrolytes, glycidyl methacrylate (GMA)-methyl methacrylate (MMA) copolymer has been synthesized via using photopolymerization techniques as a matrix polymer for preparing solid polymer electrolytes. We have investigated polymer electrolyte system of P(GMA-co-MMA)-LiTf by varying the concentration of LiTf. The electrolyte was prepared via solution casting technique.

2. MATERIALS AND METHODS

2.1. Materials

Glycidyl methacrylate (GMA), methyl methacrylate (MMA) and 2, 2-dimethoxy-2-phenyl-acetophenone (DMPP) as photoinitiator were purchased from Aldrich and used as received. Lithium triflate ($LiCF_3SO_3$) and tetrahydrofuran (THF) were supplied by Fluka and J. T. Baker, respectively.

2.2. Synthesis of P(GMA-co-MMA) and Preparation of Solid Polymer Electrolyte

P(GMA-co-MMA) was prepared by using UV-photo curing. An appropriate amount of GMA and MMA were mixed and added into an appropriate amount of 2, 2-dimethoxy- 2-phenylacetophenone (DMPP) as photoinitiator. The mixture was exposed to UV radiation in a UV box (RS Ltd.) under continuous passing nitrogen gas for 5 minutes, adopting the method that was used by [12-14]. The P(GMA-co-MMA) polymerization scheme is illustrated in Figure 1. A series of solid polymer electrolyte samples were prepared using solution cast technique. P(GMA-co-MMA) with molecular weight of 393,177 g/mol was used as a host polymer. Tetrahydrofuran (THF) was used as solvent to dissolve P(GMA-co-MMA). Three grams of copolymer were added into 30 ml tetrahydrofuran (THF) and stirred using a magnetic stirrer for 24 hr. The salt solution was prepared by different content of $LiClO_4$ (5- 35) wt. %. and then stirred for 15 min. The two separate solutions were mixed and further stirred for 24 hr. The homogeneous solution was then poured onto teflon mould and was left to dry at ambient temperature until electrolyte films were formed. The films were then dried in a vacuum oven at 40°C for 2 hours. The films were then transferred into a desiccator for continuous drying.

2.3. Characterization of solid polymer electrolyte

High resolution ^{1}H NMR was utilized to confirm the chemical composition of copolymer. ^{1}HNMR spectra of polymer sample was recorded on a Bruker 600MHz FT-NMR spectrometer using TMS (Tetramethylsilane, $(CH_3)_4Si$) as internal reference with deuterated chloroform ($CDCl_3$). The ionic conductivity was determined by impedance spectroscopy model 1260 with operating ranging frequency from 1 MHz to 10 Hz at 1000 mV voltage amplitude. From the Cole-Cole plots obtained, the bulk resistance, R_b (Ω) of the samples was determined with Z-View software. The conductivity was measured at room temperature and in the temperature range from 303 K to 393 K. The conductivity was calculated using equation (1).

$$\sigma = l / R_b A \quad (1)$$

where l is the film thickness (cm) and A (cm^2) is the effective contact area of electrolyte and the electrode [14]. The electrochemical stability of polymer electrolyte was evaluated by cyclic voltammetry technique (CV) in the potential range from -5 to +5 V with a scan rate of 0.05 vs^{-1}.. The evaluation of the electrochemical stability of solid polymer electrolyte was carried out using two stainless steel electrodes cell configuration. Cyclic voltammetry was performed on a Wonatech Zive MP2 multichannel electrochemical workstation. The thermal stability analysis was performed on the samples by TGA. The samples were heated from 25 °C to 600 °C at a heating rate of 10 °C min^{-1}, under nitrogen flow at a rate of 10 °$Cmin^{-1}$. The samples weighing 15–22 mg were placed in an aluminum crucible.

3. RESULT AND DISCUSSION

3.1. NMR spectrum of copolymer

The ^{1}H NMR spectrum of copolymer is illustrated in Figure 2.

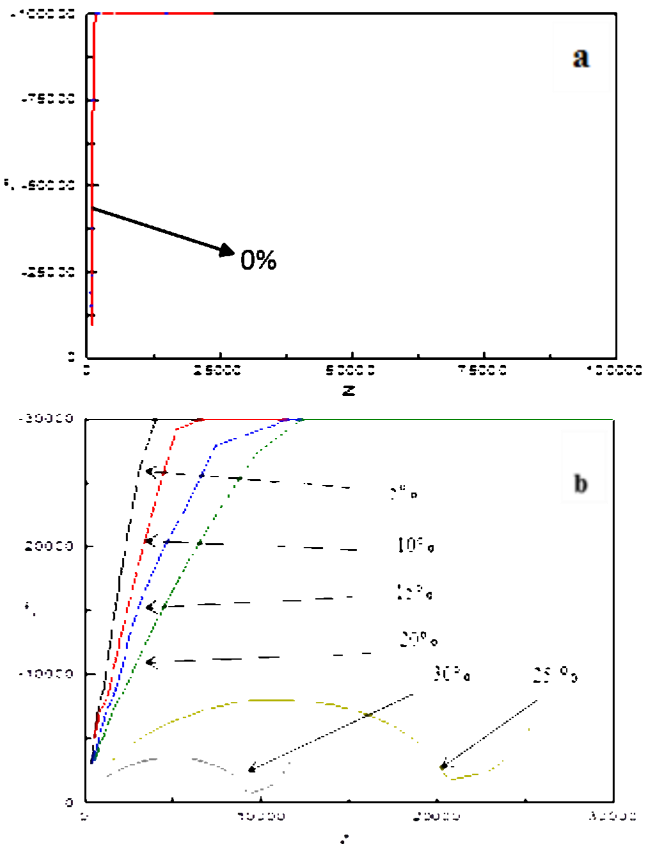

Figure 3. (a, b). Typical Cole-Cole of P (GMA-co-MMA)(90/10) with (0-30 wt. %) LiTf at 25°C

The chemical shifts at 3.214 ppm (d) 2.619 ppm (e) and 2.825 (e) ppm are attributed to epoxide group. While the signals at 3.793 (c) and 4.279 (c) ppm belong to methyne proton of GMA. The broad signal at 1.074 (a) and 0.918 (a) ppm correspond to α-methyl group of the copolymer. The peak at 3.587 ppm (f) is attributed to methoxy group in MMA. The methylene group of the backbone in copolymer for GMA, MMA shows a broad signal between 1.877 ppm (b) and 1.972 ppm (b) [15, 16].

3.3. Ambient Temperature–Ionic Conductivity Studies

Figure 3 shows the impedance spectra of solid polymer electrolyte with various LiTf content. The impedance plot for SPEs with 0 wt. % LiTf is shown in Figure. 3(a) and those for SPEs with 5–30 wt. % LiTf are shown in Figure 3(b). According to the impedance spectra, two regions were observed; semicircle portion in the high frequency range which is mainly the result of ions conduction and the linear region in the low frequency which is related to the bulk effect of blocking electrodes [17]. The ionic conductivity at 0 wt. % of LiTf salt content is 8.7×10^{-12} S cm^{-1} and the highest ionic conductivity is 1.4×10^{-6} at 30 wt. % LiTf salt. The room temperature conductivity is considered significant and comparable with the other solid polymeric electrolyte systems. The higher ionic conductivity in addition of 30 wt. % LiTf salt was caused by the large anion size and low lattice energy of LiTf salt is expected to promote greater dissociation of salts, thereby providing a higher concentration of ions [18]. The ionic conductivity increases as the salt loading increases up to its optimum level in the polymer host. This is due to the increase in the number of conducting species in the electrolyte. The coordination interactions between the carbonyl and ether O atoms from GMA-co-MMA chains and Li^+ cations, resulting in a reduction in crystallization of host polymer, is also responsible for the increase in ionic conductivity as reported in earlier work [13].

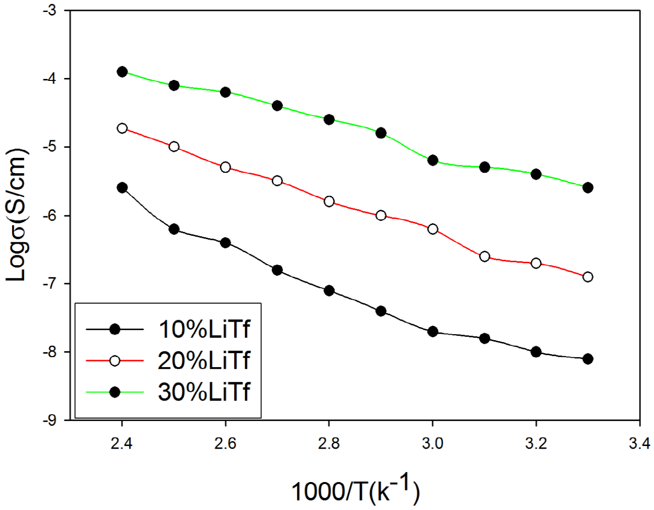

Figure 4. Arrhenius plot of P(GMA-co-MMA)(90/10) electrolyte containing 10, 20 and 30 wt. % LiTf

Figure 4 illustrates Arrhenius plot for the polymer electrolyte system of P(GMA-MMA) at 10, 20 and 30 wt. % LiTf salt. The conductivity increases with temperature from 303 K to 393 K. Table 1 summarizes the conductivity and the respective E_a values of PGMA-co-MMA-$LiCF_3SO_3$ at various compositions. The highest conductivity was 1.25×10^{-4} S cm^{-1} at 393 K at 30 wt % LiTf salt. The conductivity is also considered significant and comparable with the other solid polymeric electrolyte systems. The enhancement of conductivity with temperature can be linked to the decrease in viscosity and hence increase in chain flexibility [19]. In solid polymer electrolytes, the increase in conductivity with temperature is due to the segmental motion, which results in an increase in the free volume of the system. The increase in free volume facilitates the motion of ionic charge [20, 21]. However, as shown in Figure 4, the relationship between conductivity and temperature was linear. This implies that the polymer electrolyte system exhibit Arrhenius-like behavior thus; activation energy (E_a) of the electrolyte can

Table 1. Ionic conductivity and activation energy of the electrolyte at 10, 20 and 30 wt. % LiTf.

%wt. LiTf	σ (S cm^{-1})	R^2	E_a (eV)
10	2.5×10^{-6}	0.964	0.54
20	1.86×10^{-5}	0.994	0.47
30	1.25×10^{-4}	0.986	0.39

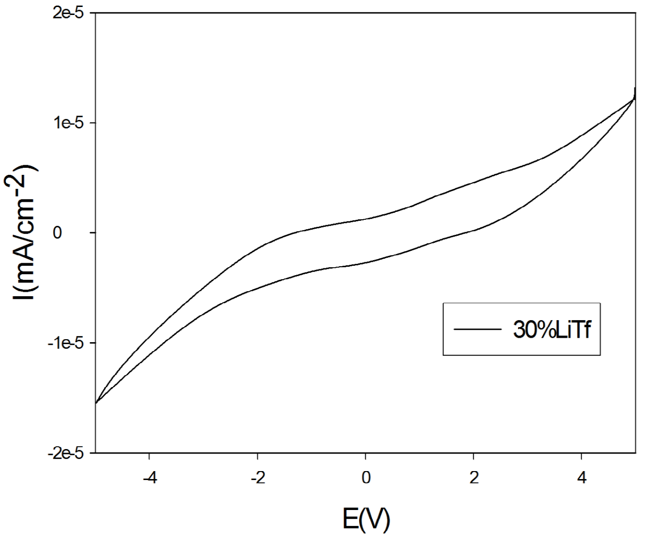

Figure 5. Cyclic voltammogram of the P(GMA-co-MMA) with 30 wt. % LiTf

be estimated from the plot. Arrhenius equation is shown in Equation (2).

$$\sigma = \sigma_0 \, e^{(-Ea/kT)} \tag{2}$$

where σ is the conductivity of the polymer electrolyte, σ_0 is a pre-exponential factor, E_a is the activation energy, K is Boltzmann constant, and T is the absolute temperature. The E_a for these systems are 0.54, 0.47 and 0.39 eV with regression (R^2) of 0.964, 0.994 and 0.986 respectively as illustrated in Table 1 It is observed that the E_a reduces as the amount of salt increases. Basically, the activation energy is the combination of the energy of defect formation and the energy of defect migration. Therefore, it can be proposed that the value of E_a is the energy required to provide a conductive condition for the migration of ions [22]. As expected, the E_a for the P(GMA-co-MMA)-30% LiTf is the lowest. Low activation energy for the lithium ion transport of P(GMA-co-MMA)-30% LiTf was due to the complete amorphous nature of the polymer electrolyte that facilitates fast Li^+ ions motion in the polymer network [23].

3.4. Electrochemical studies

The electrochemical potential window of the electrolyte in working voltage range, for electrolytes is another important parameter to be evaluated from their application point of view in ionic devices. Similar experiment results have already been carried out [3, 24]. Figure 5 represents the cyclic voltammograms of PGMA-co-MMA-30% LiTf solid polymer electrolyte. The cathodic and anodic peaks of the cell are not observed. This could be due to non-interaction of the lithium ions in the polymer electrolyte with the SS electrodes. The cyclic voltammograms exhibit firmly about the reversibility of electrolyte film. The electrochemical stability is in the range from about −3 to 3 V, which is an acceptable working voltage range for device applications, particularly as an electrolyte in rechargeable batteries. The electrochemical window of 3 V is significant.

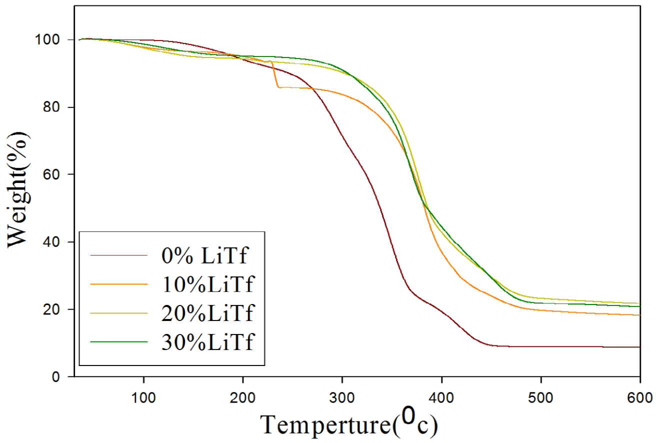

Figure 6. TGA thermograms polymer electrolyte samples with different LiTf content

3.5. Thermogravimetric Analysis (TGA)

Figure 6 shows the TGA curve of the electrolyte samples containing different lithium salt content. For lithium ion battery, it is necessary for the polymer electrolyte to have high thermal stability. The TGA curve of P(GMA-co-MMA) shows two decomposition steps. The first step is due to the decomposition of polymer glycidyl methacrylate PGMA which is in the range of 188 −230°C [25, 26] and another step is attributed to the degradation of poly methyl methacrylate PMMA which is in the range of 370 −440 °C [27]. As the concentration of the salt increases, the initial decomposition temperature of the electrolyte increases accordingly. The residual mass increases accordingly with the increase in the concentration of LiTf. In general, the result clearly indicates that this kind of electrolyte is thermally stable up to 480 °C which is remarkably higher than that of liquid electrolytes which is currently used in lithium ion batteries at 80 °C [28]. This electrolyte system possesses better thermal stability and thus may enhance the practical performance and safety of lithium ion battery.

4. CONCLUSIONS

The highest room temperature conductivity achieved in this work was 1.4×10^{-6} S cm^{-1} and 1.2×10^{-4} S cm^{-1} was obtained at 393 K with the addition of 30 wt. LiTf into P(GMA-co-MMA). It was found that this electrolyte showed good electrochemical stability (±3 V). Infrared analysis revealed that the interaction between lithium ions and oxygen atoms occurred at the carbonyl group, the ether group and epoxy group in both GMA and EMA. The thermal stability of P(GMA-co-MMA) increased when lithium salt was added. SEM analysis revealed that the decrease in the number of pores of the P(GMA-co-MMA) as the rough surface changes to smooth surface upon the addition of salt into the polymer host. The results from this work showed that P(GMA-co-MMA) has potential for Li ion battery application.

5. ACKNOWLEDGMENTS

The authors are thankful to the Universiti Kebangsaan Malaysia for allowing this research to be carried out in various laboratories. This work was supported by the UKM grant UKM-DLP-2012-021.

REFERENCES

[1] M.B. Armand, J.M. Chabagno, M. Duclot, In Fast on Transport in Solids (eds), P. Vashista, J.N. Mundy and G.K. Shenoy (New York: Elsevier) 131, 1979.
[2] M. Armand, Solid State Ionics, 69, 309 (1994).
[3] A.M.M. Ali, M.Z.A. Yahya, H. Bahron, R.H.Y. Subban, Ionics, 12, 303 (2006).
[4] J.M. Tarascon, M. Armand, Nature, 414, 359 (2001).
[5] K. Murata, S. Izuchi, Y.Y. Youetsu, Electrochimica Acta, 45, 1501 (2000).
[6] J. Xu, H.R. Thomas, R.W. Francis, Journal of Power Sources, 177, 512 (2008).
[7] M.A. Stephan, K.S. Nahm, Polymer, 47, 5952 (2006).
[8] S. Anandan, S. Pitchumani, B. Muthuraaman, P. Maruthamuthu, Solar Energy Materials and Solar Cells, 90, 1715 (2006).
[9] S.A.M. Noor, A. Ahmad, M.Y.A. Rahman, I.A. Talib, Journal of Applied Polymer Science, 113, 855 (2009).
[10]M.Y.A. Rahman, A. Ahmad, L.H.C. Ismail, M.M. Salleh, Journal of Applied Polymer Science, 115, 2144 (2009).
[11]S.A.M. Noor, A. Ahmad, M.Y.A. Rahman, Current Trends in Polymer Science, 13, 17 (2009).
[12]M.Y.A. Rahman, A. Ahmad, T.K. Lee, Y. Farina, H.M. Dahlan, Journal of Applied Polymer Sciences, 124, 2227 (2012).
[13]A. Ahmad, M.Y.A. Rahman, M.S. Su'ait, Journal of Applied Polymer Sciences, 124, 4222 (2012).
[14]T.K. Lee, A. Ahmad, Y. Farina, H.M. Dahlan, M.Y.A. Rahman, Journal of Applied Polymer Sciences, 126, E159 (2012).
[15]D.W. Kang, D.W. Kim, S.K. Jo, H.J. Sohn, Journal of Power Sources, 112, 1 (2002).
[16]J. Fuller, A.C. Bred, T.R. Carlin, Journal of Electroanalytical Chemistry, 459, 29 (1998).
[17]Y. Wang, X. Ma, Q. Zhang, N. Tian, Journal of Membrane Science, 349, 279 (2010).
[18]S.A. Hanifah, L.Y. Heng, M. Ahmad, Analytical Science, 25, 779 (2009).
[19]M. Imperiyka, M. Ahmad, S.A. Hanifah, M.Y.A. Rahman, Advanced Science Letters, 19, 194 (2010).
[20]M. Imperiyka, A. Ahmad, S.A. Hanifah, M.Y.A. Rahman, Advanced Materials Research, 626, 454 (2012).
[21]H.M.S. Nasirtabrizi, Mohebalizadeh, P.A. Jadid, Iranian Polymer Journal, 20, 579 (2011).
[22]S.I. Kaya, Z. I˙lterb, S.D. Enol, Polymer, 43, 6455 (2002).
[23]N. Ataollahi, A. Ahmad, H. Hamzah, M.Y.A. Rahman, N.S. Mohamed, International Journal of Electrochemical Science, 7, 6693 (2012).
[24]F. Latif, M. Aziz, N. Katun, M.M. Ali, M.Z. Yahya, Journal of Power Sources, 159, 1401 (2006).
[25]K.B. Ahmad, M.D. Isa, Z. Osman, Sains Malaysiana, 40, 691 (2011).
[26]F. Wu, T. Feng, Y. Bai, C. Wu, L. Ye, Z. Feng, Solid State Ionics, 180, 677 (2009).
[27]P. Ragavendran, A. Kalyani, S. Veluchamy, R., Banumathi, T. Thirunakaran, Journal Benedict Portugaliae Electrochimica Acta, 22, 149 (2004).
[28]D. Kumar, S.A. Hashmi, Journal of Power Sources, 195, 5101 (2010).