Int. J. Electrochem. Sci., 11 **(2016)** 1898 - 1906

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Characteristics of the electrolyte containing ethylene carbonate and dimethyl carbonate in zinc-polyaniline battery

*Yongli Li, Zhuan Hu, Yamei Ding, Jinqing Kan**

School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, 225002, China
*E-mail: jqkan@yzu.edu.cn

Received: 23 December 2015 / *Accepted:* 12 January 2016 / *Published:* 1 February 2016

Conducting polymers such as polyaniline (PANI) as active material of batteries possesses good electrochemical reversibility. It is a promising application for a rechargeable battery with an excellent performance. However, the instability of the structure resulting from repeated volumetric swelling and shrinking during the charge/discharge process, which has been a major shortcoming for their practical applications. This research proves a simple and general method to greatly enhance the cycling stability of PANI electrodes by developing a new electrolyte containing ethylene carbonate (EC) and dimethyl carbonate (DMC). Cyclic voltammetry revealed that polyaniline shows two pairs of redox peak in the organic electrolyte with pH 4.0. And redox peak current of polyaniline has not reduced with the increasing of cycle numbers. Electrochemical impedance spectra discovered the charge transfer resistance of polyaniline is smaller in the EC/DMC electrolyte than in aqueous electrolyte. Importantly, the discharge time of the 10th cycle has prolonged rather than reduced compared with that of the second cycle. The E_{corr} of Zn electrode in the organic electrolyte is more positive. The study provides an academic foundation and application prospect for the development of PANI secondary battery.

Keywords: ethylene carbonate, dimethyl carbonate, polyaniline, zinc, organic electrolyte

1. INTRODUCTION

Since the 1980s, conducting polymers have broken the traditional concept of “polymer cannot conduct electricity” [1]. Conducting polymers have shown wide application prospect in many fields, such as electrochemical energy [2], drug [3], biosensor [4-5] and so on. Polyaniline was synthesized 150 years ago, so it is the oldest one but is one of the most useful conducting polymers due to its ease of synthesis, environmental stability and unique acid/base doping/dedoping and reversible redox mechanism [6]. It can be readily synthesized by either chemical oxidation or electrochemical polymerization of aniline under mild conditions. As an important conducting polymer [7-10], PANI has been used in engineering structures, rechargeable batteries, electrochromic display devices, modified electrodes and electromagnetic interference shields and so on.

Ionic liquids composed of organic cations and organic or inorganic anions appear liquid salts at room temperature or near room temperature [11]. Ionic liquids have received extensive attention and been researched in recent years, since it has good performances, such as non-volatile, low vapor pressure, low melting point, wide liquid range, wide electrochemical window, low surface tension and good thermal stability [12]. And they have a wide range of applications in organic synthesis [13], extraction [14], chemistry of complex [15] and electrochemistry [16]. 1-ethyl-3-methylimidazolium ethyl sulfate (EMIES) as a representative of imidazoles ionic liquids gets the most extensive research and application because of its stability to air and water as well as high thermal stability. Kan [17] studied the electrochemical properties of magnesium electrode and polyaniline electrode in ionic liquid (EMIES) as the electrolyte. Mu [18] reported ionic liquid (EMIES) has a significant influence on the properties of polyaniline in aqueous solution electrolyte.

Electrolyte as a working medium of chemical batteries and electrolytic capacitors provides ion for their normal work, and ensures the chemical reaction reversible. At present there are aqueous electrolyte [19-20] and organic electrolyte [21-22]. Aqueous electrolyte has got more and more attention due to some advantages such as safety, no pollution. But for zinc-polyaniline battery, aqueous electrolyte has not yet achieved breakthrough development. In aqueous solution with high acidity, the electrochemical activity of polyaniline is higher, but the degradation rate of polyaniline is faster and the corrosion of negative zinc is easier due to hydrogen evolution reaction. On the contrary, in the aqueous solution of low acidity, zinc is not corroded easily, but the electrochemical activity of polyaniline is limited a lot. Now, there are little reports about zinc-polyaniline secondary battery in nonaqueous electrolyte [23]. Ethylene carbonate (EC) as a kind of annular solvent possesses high permittivity value, which is one of the indispensable compositions of lithium ion battery electrolyte at present. It does not decompose on the surface of highly graphitized carbon materials and has a very good film-forming effect. So it is the principal component of most of liquid electrolyte [24-25]. But, its viscosity is high, which reduces the speed of ion migration. Dimethyl carbonate (DMC) as a kind of chain type of solvent possesses low viscosity but with low permittivity. So the two kinds of solvent are mixed to complement each other.

In this paper, by comparing the properties of polyaniline in nonaqueous electrolyte ($Zn(ClO_4)_2$ / (EC+DMC)) and aqueous electrolyte ($Zn(ClO_4)_2$ / H_2O) with the method of cyclic voltammetry, electrochemical impedance spectroscopy, single electrode charge-discharge and so on. The study opens up a new realm of possibilities for zinc-polyaniline battery development.

2. EXPERIMENTAL

2.1. Materials

All chemicals used were analytical grade. Ethylene carbonate (EC) was purchased from Sigma-Aldrich chemie GmbH. Dimethyl carbonate (DMC), hydrochloric acid (36-38% (w/w)), ethanol and aniline were obtained from the Sinopharm Chemical Reagent Co., Ltd. The monomer aniline was distilled under reduced pressure and stored in refrigerator (about 4 °C) before usage. Zinc perchlorate hexahydrate was offered from Alfa Aesar Chemical Co., Ltd. 1-ethyl-3-methylimidazolium ethyl sulfate (EMIES) ionic liquid was synthesized base on literatures [26]. The others were used as received without further treatment. All of the aqueous solutions were prepared with doubly distilled water.

2.2. The preparation of electrodes

The electrochemical polymerization of the aniline was performed on a CHI 660D electrochemical workstation with a three-electrode system, two 10 mm×10 mm platinum plates and a saturated calomel electrode (SCE) as the working electrode, the counter electrode and the reference electrode, respectively. All potentials recorded are referred to SCE. PANI films were synthesized on the platinum working electrode by the cyclic voltammetry in an aqueous 1.0 mol dm^{-3} HCl solution with 0.2 mol dm^{-3} aniline. And the potential scan range of electrochemical polymerization was from -0.2 V to 1.0 V for 10 cycles at 50 mV s^{-1}. After the electrochemical polymerization of the aniline, the PANI electrode obtained was repeatedly washed with acetone and the doubly distilled water until the washing liquid was completely colorless to remove small molecular-weight contaminants generated during polymerization. Finally, the PANI electrode was dried at 60 ^{o}C.

2.3. Instrumentation and Characterization

Cyclic voltammetry (CV) were performed on a CHI 660D electroanalysis apparatus (CHI Instruments, USA) and electrochemical impedance spectroscopy (EIS) powered by an electrochemical workstation (AutoLab, Nova 1.9, Metrohm) were used to compare the electrochemical activities of the PANI in both 1 mol dm^{-3} $Zn(ClO_4)_2$ / (EC+DMC, volume ratio=1:1) and 1 mol dm^{-3} $Zn(ClO_4)_2$ aqueous electrolyte for 30 cycles. The cyclic voltammograms of the PANI were recorded in 1 mol dm^{-3} $Zn(ClO_4)_2$ / (EC+DMC) and the potential range was from -0.2 to 1.0 V at 0.01 V s^{-1}. The EIS spectras of PANI were got in the same electrolyte. The superimposed sinusoidal voltage signal was set up to 10 mV amplitude. Datas were collected within the frequency range from 10^4 to 10^{-1} Hz. The CV and EIS were performed in a standard one-compartment three-electrode cell with PANI electrode, Pt foil and Saturated calomel electrode (SCE), which served as working electrode, counter electrode and reference electrode, respectively. The charge and discharge tests of PANI electrode were carried out in the potential range from 0 V to 0.7 V (vs. SCE) at 0.1 mA cm^{-2} by the chronopotentiometry method on CHI 660D electrochemical workstation with a three-electrode system. The potentiodynamic polarization curves of the Zn electrode were measured by using the method of Tafel on CHI 660D at 5 mV s^{-1}.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry of electrolyte

The so-called electrochemical window is refers to the platform without any electrochemical reaction on the electrochemical cycle voltammetry curve, which means the electrode is in a state of charge and has no electrochemical reactions within the scope of the potential. Different electrodes have different electrochemical windows in different solutions. Figure 1 shows the cyclic voltammogram of the electrolyte (EC+DMC, volume ratio=1:1) containing 1 mol dm^{-3} $Zn(ClO_4)_2$ using a platinum plate as the working electrode, a platinum plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The results from a number of tests showed that the cycle voltammetry curve of the electrolyte has no redox peak in the potential range from -1.0 V to 2.0 V (vs. SCE), which means the property of the electrolyte is more stable and possesses a wider electrochemical window than that reported in other similar literatures [27-30]. So it is appropriate to choose the electrolyte of zinc-polyaniline battery. The curve is similar to a linear relationship between the current and potential besides small charge capacity, which is more like a resistor. 1 mol dm^{-3} $Zn(ClO_4)_2$ will be added to the solution (EC+DMC) due to its poor conductivity in application.

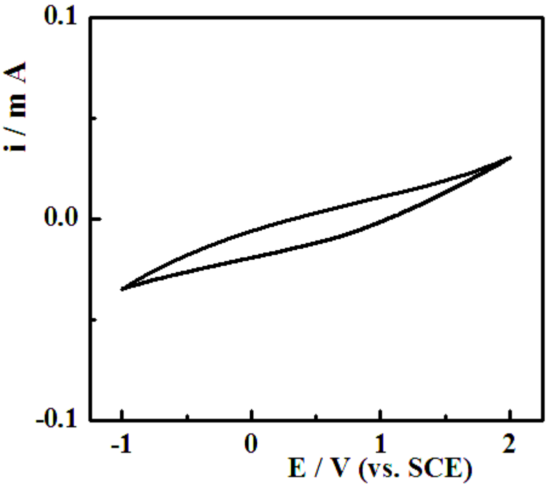

Figure 1. Cyclic voltammogram of the electrolyte (1 mol dm^{-3} $Zn(ClO_4)_2$ / EC + DMC)

3.2. Tafel plots of Zn electrode

Tafel plot is an important indicator to characterize the anticorrosion of electrode material [31-33]. It is seen from the figure 2 that the cathodic branches are under activation control and exhibit linearity consistent with Tafel relationship. The anodic branches are also in accord with Tafel law. As is well-known, the higher the E_{corr} is, the better the anticorrosion of electrode material is [34]. Figure 2 is Tafel plots of the Zn electrode in two different electrolytes (A 1 mol dm^{-3} $Zn(ClO_4)_2$ / (EC+DMC); B 1 mol dm^{-3} $Zn(ClO_4)_2$ / H_2O). According to the figure 2, the corrosion potential (E_{corr}) and the corrosion current (I_{corr}) is obtained (Table 1). The E_{corr} of Zn electrode in aqueous electrolyte (1 mol

dm^{-3} $Zn(ClO_4)_2$ / H_2O) is -0.934 V (vs.SCE), while the E_{corr} of Zn electrode in organic electrolyte (1 mol dm^{-3} $Zn(ClO_4)_2$ / (EC+DMC)) is -0.799 V (vs.SCE). The E_{corr} of Zn electrode in the organic electrolyte was obviously higher than that in the aqueous electrolyte. So the Zn electrode in the organic electrolyte is more stable than that in the aqueous electrolyte. Therefore, the organic electrolyte (EC+DMC) is selected as the research system.

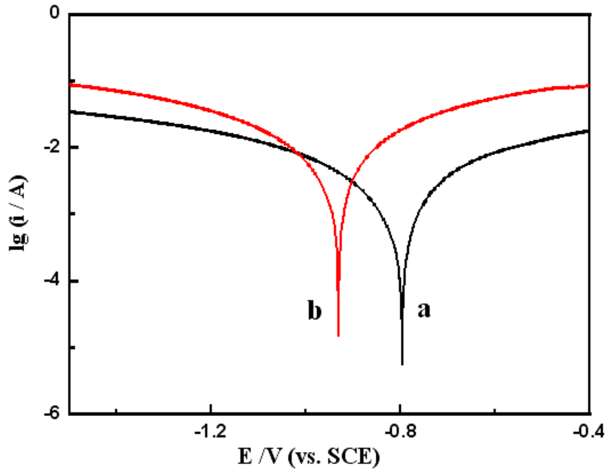

Figure 2. Tafel plots of Zn electrode in two different electrolyte (A 1 mol dm^{-3} $Zn(ClO_4)_2$ / (EC+DMC); B 1 mol dm^{-3} $Zn(ClO_4)_2$ / H_2O)

Table 1. Corrosion potential and corrosion currents of Zn in different electrolytes

Electrolyt	E_{corr} / V	I_{corr} ×10 ^{4}/ A
$Zn(ClO_4)_2$ / (EC+DMC)	-0.799	1.79
$Zn(ClO_4)_2$ / H_2O	-0.934	6.32

3.3. Cyclic voltammetry of PANI electrode

Figure 3 shows the cycle voltammetry curves of PANI film electrode in 1mol dm^{-3} $Zn(ClO_4)_2$ / (EC+DMC) and 1 mol dm^{-3} $Zn(ClO_4)_2$ / H_2O, respectively. There are two pairs of redox peaks in figure 3(A), the two anodic peaks at 0.19 and 0.78 versus SCE correspond to the conversions between leucoemeraldine and emeraldine and between emeraldine and pernigraniline, respectively [35-37]. Two main cathodic peaks of the 5th cycle at -0.12 and 0.77 correspond to the reverse process, respectively. However, with the increasing of the cycle numbers, the reductive peaks at lower potential move to the higher potential, and the reductive peaks at higher potential move to the lower potential, which may be caused by the polarization effect. It is worth noting that the redox peak current has not reduced. There is only one pair of redox peak in figure 3(B), which is in accord with the results reported in literatures that the cyclic voltammetry curve of PANI in aqueous solution of pH 4 shows only one pair of redox peak [38-39]. The only one pair of redox peak is due to a merger of two pairs of redox peak. However, the redox peak current decreases with the increasing of cycle numbers. It is accountable for that PANI has degraded gradually [40-41]. The above phenomenon does not appear in

1 mol dm^{-3} $Zn(ClO_4)_2$ / (EC+DMC) electrolyte. Therefore, this kind of organic electrolyte can restrain the degradation of PANI in some degree.

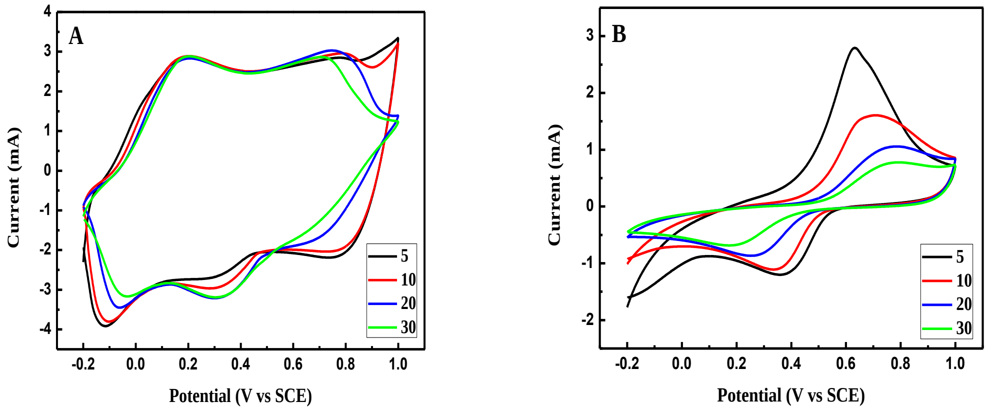

Figure 3. Cyclic voltammogram of PANI in two different electrolyte (A 1 mol dm^{-3} $Zn(ClO_4)_2$ / (EC+DMC); B 1 mol dm^{-3} $Zn(ClO_4)_2$ / H_2O)

3.4. Electrochemical Impedance Spectra of PANI electrode

Figure 4 shows the electrochemical impedance spectra of polyaniline cycled 30 cycles in two different electrolyte (1 mol dm^{-3} $Zn(ClO_4)_2$ / (EC+DMC) and 1 mol dm^{-3} $Zn(ClO_4)_2$ / H_2O) respectively. The Nyquist plot of figure 4(A) includes two different regions [42-43]: the straight line in the low frequency region and the semicircle in the high frequency range. The straight line stands for the Warburg impedance of PANI, which shows the reaction is controlled by interface diffusion between the electrode and electrolyte. The semicircle in the high frequency range represents charge transfer resistance and double-layer capacitance. The diameter of the semicircle represents the charge transfer resistance.

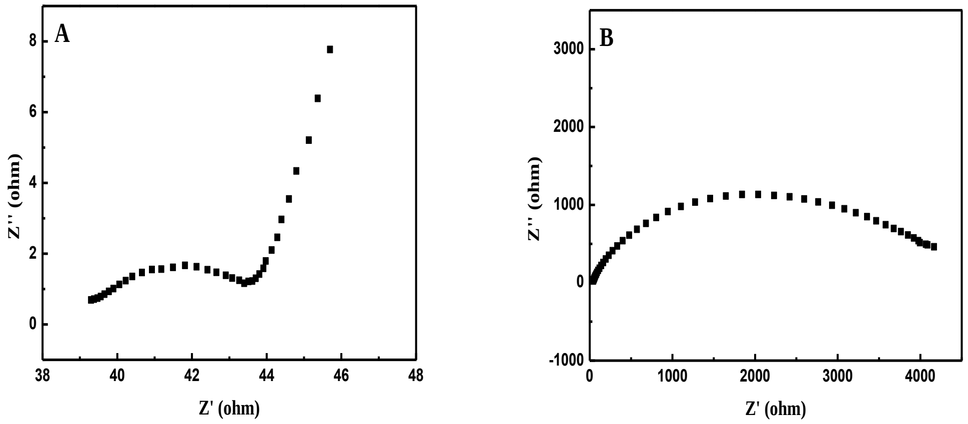

Figure 4. The electrochemical impedance spectra of polyaniline cycled 30 cycles A: 1 mol dm^{-3} $Zn(ClO_4)_2$ / (EC+DMC); B: 1 mol dm^{-3} $Zn(ClO_4)_2$ / H_2O)

The charge transfer resistance of polyaniline cycled 30 cycles in the organic electrolyte is about 4.5 ohm. However, the charge transfer resistance of polyaniline cycled 30 cycles in the aqueous electrolyte is about 4000 ohm (figure 4(B)), which is close to 1000 times of the charge transfer resistance cycled 30 cycles in the organic electrolyte. This show that the charge transfer resistance of polyaniline in 1 mol dm^{-3} $Zn(ClO_4)_2$ / (EC+DMC) is much less than that in 1 mol dm^{-3} $Zn(ClO_4)_2$ / H_2O.

3.5. Charge and discharge of PANI electrode

Figure 5 shows the charge and discharge profiles of polyaniline in organic electrolyte and aqueous electrolyte, respectively. No matter in an organic electrolyte (1mol dm^{-3} $Zn(ClO_4)_2$ / EC+DMC) or aqueous electrolyte (1 mol dm^{-3} $Zn(ClO_4)_2$ / H_2O), both the charge and discharge curves have good symmetry, which indicates that polyaniline has good electrochemical reversibility in the two kinds of different electrolyte. In figure 5(A), the discharge time of the 10th cycle of polyaniline in the organic electrolyte does not decrease, but slightly longer, compared with the discharge time of the second circle. However, the discharge time of polyaniline in aqueous electrolyte gradually reduces with the increasing of cycle numbers. As is shown in figure 5(B), the discharge time of the 10th cycle of polyaniline in the aqueous electrolyte has reduced by 15.8% compared with that of in the second cycle. Therefore, polyaniline in the organic electrolyte can keep higher electrochemical activity.

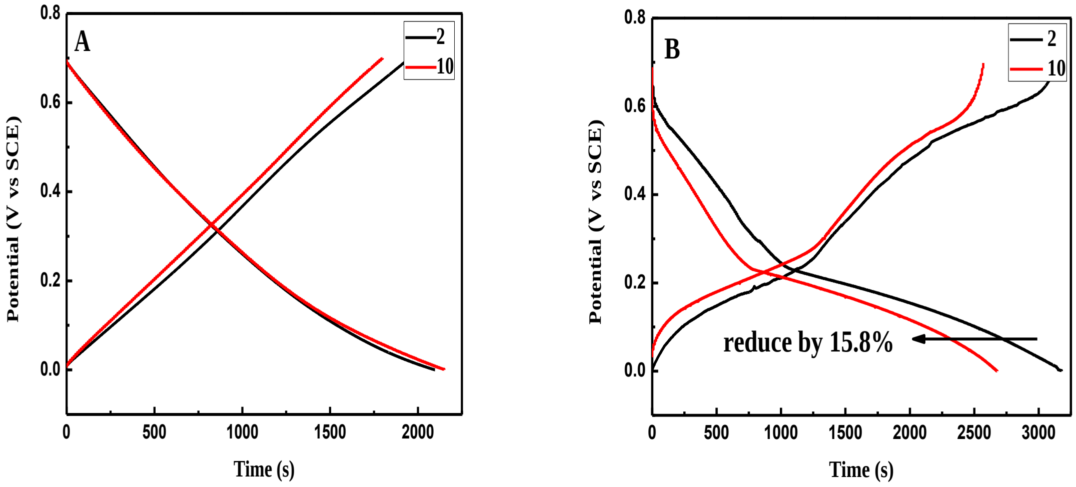

Figure 5. Charge and discharge profiles of polyaniline in two different electrolyte (A 1 mol dm^{-3} $Zn(ClO_4)_2$ / (EC+DMC); B 1 mol dm^{-3} $Zn(ClO_4)_2$ / H_2O)

4. CONCLUSION

In conclusion, polyaniline shows higher electrochemical activity in the organic electrolyte by comparing the properties of polyaniline in the organic electrolyte (1 mol dm^{-3} $Zn(ClO_4)_2$ / (EC+DMC)) and the aqueous electrolyte (1 mol dm^{-3} $Zn(ClO_4)_2$ / H_2O). The E_{corr} of Zn electrode in the organic electrolyte is more positive. The concrete manifestation of polyaniline in the organic electrolyte with pH 4.0 is as follows: (i) polyaniline shows two pairs of redox peak; (ii) redox peak current of polyaniline has not reduced with the increasing of cycle numbers; (iii) the charge transfer resistance of polyaniline is less than that in the aqueous electrolyte; (iv) the discharge time of the 10th cycle has prolonged rather than reduced compared with that of the second cycle. We consider that more research concerning how to suppress the formation of zinc dendrite should be made so as to accelerate the commercialization of Zn/PANI secondary battery.

ACKNOWLEDGEMENTS

This project was supported by the National Science Foundation of China (No. 20873119), and by the Priority Academic Program Development of Jiangsu Higher Education Institutions. Part of the datas were from Testing Center of Yangzhou University.

References

1. M.E. Galvin and G.E. Wnek, *Polymer*, 23 (1982) 795.
2. Z. Ma and J. Kan, *Synth. Met*., 174 (2013) 58.
3. S.C.Wuang, K.G.Neoh, E.T.Kang, D.W.Pack and D.E.Leckband, *Biomaterials*, 29 (2008) 2270.
4. Y.Jiang, A.Wang and J.Kan, *Sensors and Actuators* B, 124 (2007) 529.
5. M.V. Kulkarni, N.A. Charhate, K.V. Bhavsar, M.A. Tathe and B.B. Kale, *Mater. Res., Innov*., 17 (2013) 238.
6. Y.Zhao, S.Si, L.Wang, P.Tang and H.Cao, *J. Electrochem. Soc*., 161 (3) (2014) A330.
7. A.Tiwari and V.Singh, *Express Polym. Lett*., 1 (2007) 308.
8. C.S.Wu, *Express Polym. Lett*., 6 (2012) 465.
9. N.H.Khdary, M.E.Abdesalam and G.E.Enany, *J. Electrochem. Soc*., 161 (9) (2014) G63.
10. M.S.Tamboli, M.V.Kulkarni, S.P.Deshmukh and B.B.Kale, *Mater. Res. Innov*., 17 (2013) 112.
11. K.R.Seddon, *Chem.Biotechnol*., 2 (1997) 351.
12. N.D.Khupse and A.Kumar, *Indian J. Chem*., 49 (2010) 635.
13. J.D.Paul, J.E.David and W.Thomas, *Can. J. Chem*., 79 (2001) 705.
14. H.T.Wong, C.J.Pink and F.C.Ferreira, *Green Chem*., 8 (2006) 373.
15. M. J. Earle, R. B. Mclormzc and K. R. Seddon, *Green Chem*., 1 (1999) 23.
16. K.P.Doyle, C.M.Lang, K.Kim and P.A.Kohl, *J. Electrochem. Soc*., 153 (2006) A1353.
17. Q.Ju, Y.Shi and J.Kan, *Synth. Met*., 178 (2013) 27.
18. S.L.Mu, *Electrochim. Acta*, 52 (2007) 7827.
19. X.Y.Wang, Y.Y.Hou, Y.S.Zhu, Y.P.Wu and R.Holze, *Sci. Rep*., 3 (2013) 1401.
20. L.Jiang, L.Sheng, C.Long and Z.Fan, *Nano Energy*, 11 (2015) 471.
21. O.C.Compton, A.Abouimrane, Z.An, M.J.Palmeri, L.C.Brinson, K.Amine and S.T.Nguyen, *Small*, 8 (2012) 1110.
22. C.O.Laoire, S.Mukerjee and K.M.Abraham, *J. Phys. Chem*. C, 114 (2010) 9178.
23. A.Guerfi, J.Trottier, I.Boyano, I.De Meatza, J.A.Blazquez, S.Brewer, K.S.Ryder, A.Vijh and K.Zaghib, *J. Power Sources,* 248 (2014) 1099.
24. K.Xu, *Chem. Rev*., 104 (2004) 4303.
25. M.Wu, H.Luan and W.Yao, *Mining & Metallurgy*, 13 (2004) 57.
26. J.D.Holbrey, W.M.Reichert, R.P.Swatloski, G.A.Broker, W.R.Pitner, K.R.Seddon and R.D.Rogers, Green Chem., 4 (2002) 407.
27. G.Mengoli, M.M. Musiani, D. Pletcher and S. Valcher, *J. Appl. Electrochem*,, 17(1987) 515.
28. Y.Zhao, S. Si and C. Liao, *J. Power Sources*, 241(2013) 449.
29. G.Mengoli, M.M. Musiani, D. Pletcher and S. Valcher, *J. Appl. Electrochem*,, 17(1987) 525.

30. S.Wu, Y.Zhao, D.Li, Y.Xia and S. Si, *J. Power Sources*, 275 (2015) 305.
31. M.S.Rahmanifar, M.F.Mousavi, M.Shamsipur and M.Ghaemi, *J. Power Sources*, 132 (2004) 296.
32. S.Sathyanarayana and N.Munichandraiah, *J. Appl. Electrochem*., 11 (1981) 33.
33. B.C.Dalui, I.N.Basumallick and S.Ghosh, *Indian J. Chem. Technol*., 15 (2008) 576.
34. E.M.Sherif, *Int. J. Electrochem. Sci*., 6 (2011) 2284.
35. W.S.Huang, B.D.Humphrey and A.G.MacDiarmid, *J. Chem. Soc., Faraday Trans*., 82 (1986) 2385.
36. A.S.Sarac, M.Ates and B.Kilic, *Int. J. Electrochem. Sci*., 3 (2008) 777.
37. E.M.Genies and C.Tsintavis, *J. Electroanal. Chem. Interfac*., 195 (1985) 109.
38. G. ang, Y.Liu, W.Hou, H.Ji and Y.Li, *J. Appl. Polym. Sci*., 113 (2009) 78.
39. T.Liu, L.Finn, M.Yu, H.Wang, T.Zhai, X.Lu, Y.Tong and Y.Li, *Nano Lett*., 14 (2014) 2522.
40. E.Büttner and R.Holze, *J. Electroanal. Chem*., 508 (2001) 150.
41. D.Park and Y.Shim, *J. Electrochem. Soc*., 140 (1993) 609.
42. S.Luo, Z.Tang, J.Lu, Z.Zhang and J.Yan, *Rare Metal Mat. Eng*., 36 (2007) 835.
43. W.Shao, R.Jamal, F.Xu, A.Ubul and T.Abdiryim, *Materials*, 5 (2012) 1811.