J Appl Electrochem (2009) 39:247–251
DOI 10.1007/s10800-008-9663-7

ORIGINAL PAPER

Preparation and electrochemical performance of gel polymer electrolytes with a novel star network

Qizhen Xiao · Zhaohui Li · Deshu Gao · Tao He · Hailiang Zhang

Received: 29 May 2008 / Accepted: 5 September 2008 / Published online: 1 October 2008

Abstract Well-defined star shaped polymers with α-Cyclodextrin (α-CD) core linking PMMA-block arms were synthesized by atom transfer radical polymerization (ATRP). Gel polymer electrolytes (GPEs) were prepared by encapsulating electrolyte solution of 1 mol L^{-1} of $LiClO_4$/EC-PC (volume 1:1) into the obtained star shaped polymer host. The ionic conductivity of the GPEs and the cycling characteristics of $LiCoO_2$/GPEs/Graphite cell were studied by electrochemical impedance spectroscopy and charge-discharge testing, respectively. The results indicate that the GPEs have a high ionic conductivity up to 1.63×10^{-3} S cm^{-1} at room temperature and exhibit a high electrochemical stability potential of 4.5 V (vs. Li/Li^{+}). The discharge capacity of $LiCoO_2$/GPEs/Graphite cell is about 98% of its initial discharge capacity after 20 cycles at 0.1 C rate. Discharge capacity of the model cell with GPEs is stable with charge-discharge cycling.

Keywords Gel polymer electrolytes · Star shaped polymers · α-Cyclodextrin · Lithium ion polymer battery

1 Introduction

A lithium ion polymer battery has high safety because a solid or gel-type electrolyte is used in the system, which overcomes the possibility of leakage of a liquid electrolyte. The high-rate and low-temperature performance decrease because the ionic conductivity of such electrolytes is low. Therefore, new types of advanced lithium ion battery with Gel polymer electrolytes (GPEs) have been studied to provide high power density and take advantage of the leak-free characteristics [1–4].

Recently, poly (methyl methacrylate) (PMMA) has been widely studied in the field of GPEs. It has good compatibility with the liquid electrolytes, leading to good absorbing ability of the carbonate-based liquid electrolytes [5–8]. Previous studies show that PMMA-based gel electrolytes could be achieved by immobilizing the solution [the solution of an inorganic salt ($LiClO_4$, $NaClO_4$) in an aprotic solvent (propylene carbonate)] in a polymer matrix. However, ionic conductivity was relatively low at ambient temperature. The low conductivity can be attributed to the low motion of Li^{+}, which originated from the complex effect of the carbonyl group and the low motion of polymer chain segment. Up to date, many attempts have been done to improve the ionic conductivity of PMMA-salt systems, such as modification of the composition of PMMA-salt systems by the addition of nanoparticles [9–13], modification of the structure of PMMA system by blending them with other polymers [14–16], copolymers [17–19]. A series of star polymers with new topology have been synthesized with the development of polymeric technology, such as ATRP. Its low glass transition temperature endowed a good chain segment motion capacity, with potential to increase the ionic conductivity [20–22].

Cyclodextrins (CDs) are cyclic molecules consisting of six to eight glucose units linked through 1–4 linkages. They form a conical cage with a hydrophobic cavity and a hydrophilic border, appealing to investigators in both pure research and applied technologies. Recently, Madhavan reported its nanoporous structure with pore sizes between

Q. Xiao · Z. Li · D. Gao · T. He · H. Zhang (✉)
College of Chemistry, Xiangtan University, Hunan,
Xiangtan 411105, People's Republic of China
e-mail: hlzhang2005@yahoo.cn

Q. Xiao · T. He · H. Zhang
Institute of Polymer Science, Xiangtan University, Hunan,
Xiangtan 411105, People's Republic of China

0.5 and 0.9 nm facilitating ion transportation and it could be used as ion channel [23]. Moreover, the CDs can be modified by esterification or etherification reactions with groups at the 2- and 3-positions (the secondary hydroxyl groups) and at the 6-positions (the primary hydroxyl groups) in the glucopyranose ring.

In this paper, the GPEs based on a novel star network polymeric host with α-CD core linking PMMA-block arms are reported. Firstly, a well-defined star polymer with α-CD core linking PMMA-block arms was prepared by ATRP method initiated by modified α-CD, which was prepared through an esterification process. Then GPEs were prepared by encapsulating electrolyte solution of 1 mol L^{-1} of $LiClO_4$/EC-PC (volume 1:1) into the star shaped polymer host. The ionic conductivity of the GPEs and the cycling characteristic of $LiCoO_2$/GPEs/Graphite cell were studied by electrochemical impedance spectroscopy and charge-discharge experiments, respectively.

2 Experimental

2.1 Materials

α-Cyclodextrin (analytical grade) was purchased from Tianjin Chemical Third Factory, and recrystallized twice before use. 2-Bromoisobutyryl bromide (BIBB) (98%, Alfa) was freshly distilled at room temperature under vacuum. Methyl methacrylate (MMA) was passed through a column with activated Al_2O_3 (120–160 mesh) to remove the inhibitor, stored over CaH_2, and then distilled under reduced pressure before polymerization. $LiClO_4$ (Shanghai Chemical Reactants Plant) was dried under vacuum at 100 °C for 48 h. Ethylene carbonate (EC) and Propylene carbonate (PC) (Shanghai Chemical Reactants Plant) were purified by distillation under reduced pressure. All other chemicals were purified according to conventional methods.

2.2 Synthesis of 18-arm functional poly(methacrylate) star polymer with α-CD-$(BIBB)_{18}$ core by ATRP

The α-CD-$(BIBB)_{18}$ macroinitiator, 18-Arm Functional Poly(methacrylate) Star Polymers were synthesized in a stepwise process. The overall synthetic protocol is presented in Scheme 1. Firstly, the macroinitiator α-CD-$(BIBB)_{18}$ was synthesized by reacting α-CD with 2-bromoisobutyryl bromide according to the literature [24]. Subsequently, the PMMA star polymer was prepared by using α-CD-$(BIBB)_{18}$ and CuCl/bpy complex as macroinitiator and catalyst, respectively, to catalyze atom transfer radical polymerization of MMA. The molar ratio of α-CD-$(BIBB)_{18}$, MMA, CuCl, 4,4′-bipyridine (Bpy) was 1/18:100:1:3. Its structure was confirmed by ^1H NMR (400 MHz, Bruker) spectra ($CDCl_3$,chemical shift, ppm relative to TMS): $\delta = 0.84–1.25$ (3H, $–CH_3$), 3.60 (3H, $–COOCH_3$), 1.5–2.08 (2H, $–CH_2–$).

2.3 Preparation of GPEs

The gel composition used for the electrolyte was PMMA Star Polymer: 30/PC:19/EC:46.5/$LiClO_4$:4.5 by mole ratio. The PMMA star polymer was dried under vacuum at 70 °C for 16 h before use in the electrolyte. All the components were transferred to a glove box with an argon atmosphere. The gels were prepared as follows: the PMMA star polymer was added to the EC/PC solution containing $LiClO_4$. The mixture was heated to 40 °C for 2 h, then to 70 °C for 1 h,and finally compressed into a 100–200 μm thick film at room temperature.

2.4 Electrochemical measurement of GPEs

The GPEs were sandwiched between two stainless steel backing electrodes, sealed in a module cell in the glove box and subjected to electrochemical impedance measurements. Ionic conductivity (σ) was determined by means of complex impedance measurements, using an EG & G Potentiostat/Golvannostat M273 in conjunction with a M5210 Lock-in amplifier over the frequency ranging 1 Hz to 100 kHz at an AC amplitude of 5 mV. The samples were thermally equilibrated at each temperature for at least 0.5 h prior to measurement. The bulk resistance of the polymer electrolyte, R_b can be obtained from the impedance spectrum. Thus, the ionic conductivity was calculated from Eq. 1:

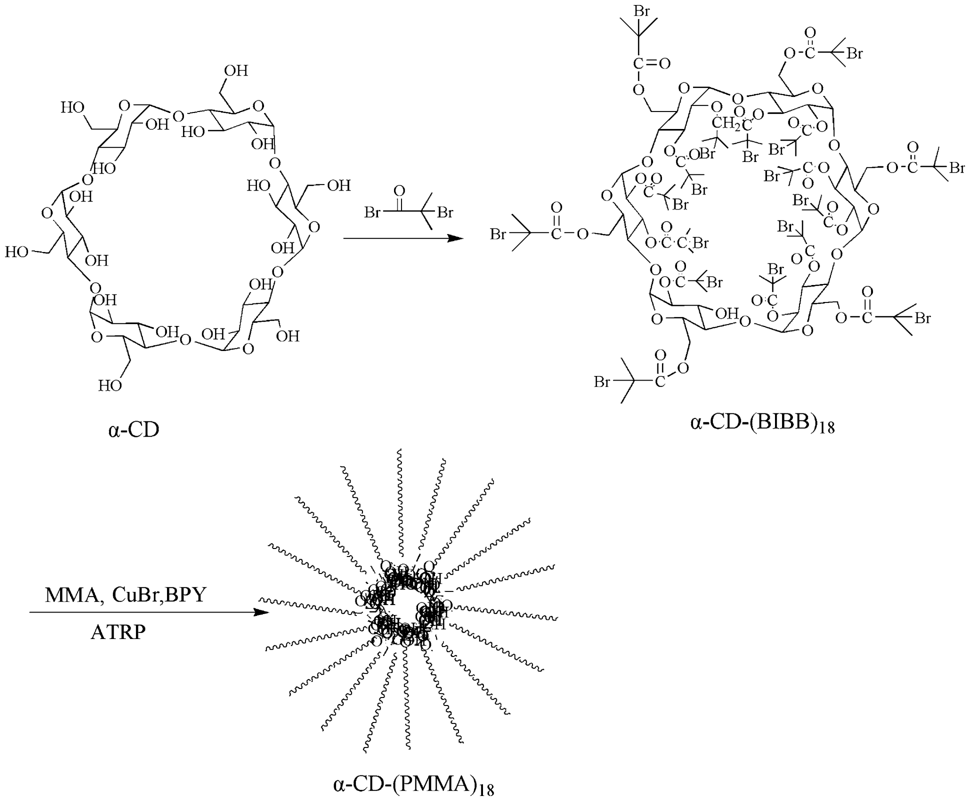
$$\sigma = d/(R_b \cdot S) \tag{1}$$

In this equation, σ is the ionic conductivity, R_b is the bulk resistance, d is the thickness of the GPEs and S is the area of the symmetrical electrode, respectively. The electrochemical stability window of polymer electrolyte was checked by linear sweep voltammetry using a stainless steel electrode as working electrode and a lithium piece as counter and reference electrode at a scan rate of 10 mV s^{-1}.

2.5 Preparation of the cell

Lithium cobalt oxide electrodes were prepared by mixing 85 wt% of $LiCoO_2$, 10 wt% of conducting acetylene black and 5 wt% of binder poly(vinylidene difluoride) (PVdF). Graphite electrodes were prepared by mixing 95 wt% MCF (milled carbon fiber) and 5 wt% PVdF. The cell consisted of the $LiCoO_2$ positive and Graphite negative electrodes separated by the GPEs. All test battery assembly was carried out in an argon-filled glove box, where water and oxygen concentration were kept to less than 5×10^{-6}.

Scheme 1 Synthetic route and sketch map of star network polymer



3 Results and discussion

3.1 Properties of the GPEs

FTIR spectra of pure PMMA and PMMA gel electrolytes are shown in Fig. 1. In PMMA, the C=O symmetrical stretch gives a sharp peak at ~1,730 cm^{-1}, asymmetric stretching vibrations of C–O–C bond are identified at ~1,240 and ~1,147 cm^{-1}, absorption of (C–O) of the OCH$_3$ group appears at ~1,190 cm^{-1}, and symmetrical stretch of the C–O bond in the C–O–C linkage of PMMA at ~987 cm^{-1}. In the gel electrolytes, the C=O stretch of PMMA at 1,725 cm^{-1} is invisible next to the C=O stretch of EC and PC molecules interacting with each other (1,797 and 1,771 cm^{-1}). These two peaks of EC and PC interaction arise from a splitting of the non-degenerate C=O stretch fundamental of a single molecule (EC or PC) into two components. Bands of PC similar to PMMA are also seen in the region between 1,100 and 1,300 cm^{-1}, but precise assignment of these peaks is difficult. Then (ClO$_4$$^{-1}$) internal mode of the LiClO$_4$ shows one peak at approximately 624 cm^{-1} which is assigned to the free anion which does not interact with the lithium cation. There is no peak at 635 cm^{-1} which may be considered as the contact ion pair. Lithium and perchlorate ions can migrate through the solvent domain surrounding the polymer matrix.

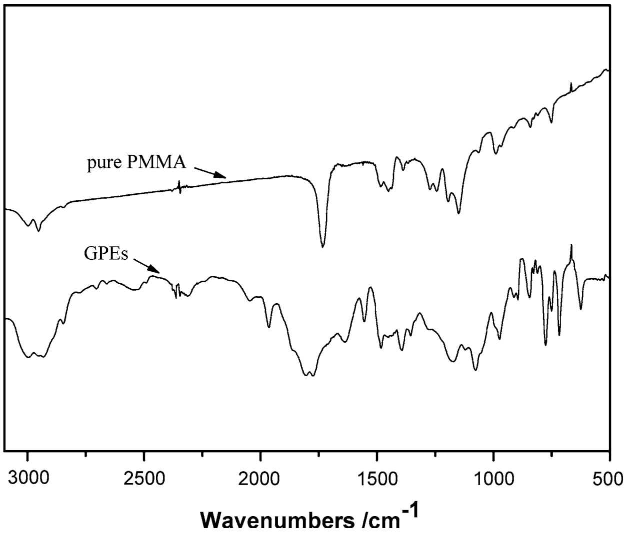


Fig. 1 FTIR spectra of pure PMMA and PMMA GPEs

Figure 2 shows an AC impedance spectrum of the SS/GPEs/SS cell at deferent temperatures. At room temperature, the intercept on the real axis gives the electrolyte resistance, viz. 15.6 Ω. From this value, the ionic conductivity was calculated to be 1.63 × 10^{-3} S cm^{-1} from Eq. 1, the ionic conductivity of the GPEs at different temperatures is depicted in Fig. 3. The ionic conductivity increases with increasing temperature. This behavior can be understood in terms of the free volume model [25]. As the temperature increases, the polymer can expand easily and produce free volume. Thus, ions, solvated molecules,

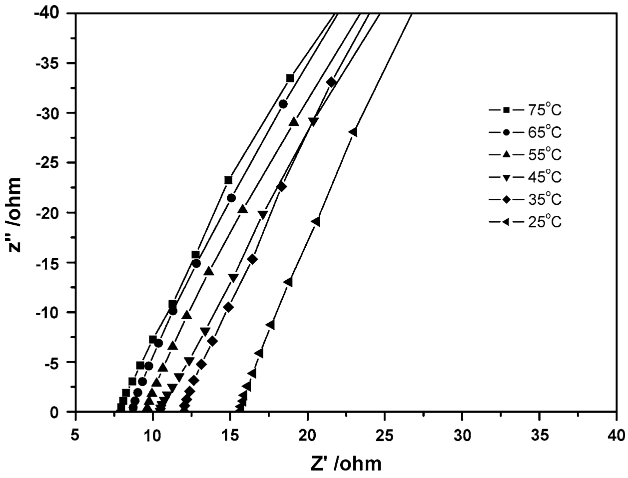


Fig. 2 AC impedence spectra of SS/GPEs/SS cell with GPEs

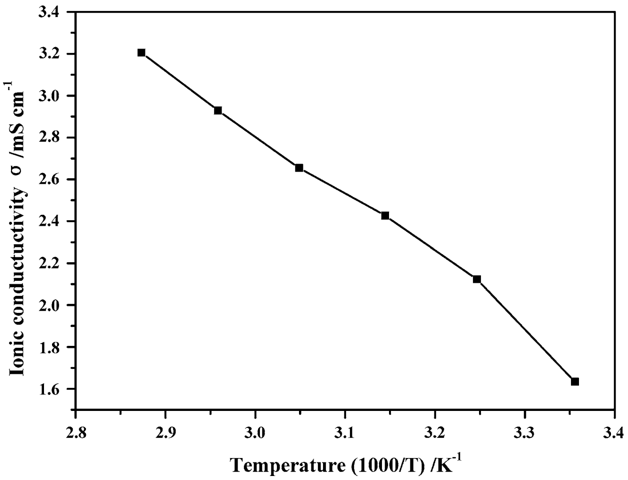


Fig. 3 Ionic conducticity of the GPEs at various temperatures

or polymer segments can move into the free volume. The resulting conductivity, represented by the overall mobility of ions and the polymer, is determined by the free volume around the polymer chains. Therefore, the free volume increases as temperature increases. This leads to an increase in ion mobility and polymer chain segmental motion that will assist ion transport and virtually compensate for the retarding effect of the ion clouds. As shown in Fig. 3, the Arrhenius plots of the temperature dependency of the σ exhibits convex upward curved profiles, and fits the Vogel–Tamman–Fulcher (VTF) equation (2) for such electrolytic materials,

$$\sigma T^{1/2} = A\exp(-E_a/R(T - T_0)) \tag{2}$$

where A is a fitting parameter, E_a is activation energy, R is the gas constant, T_0 is often related to equilibrium glass-transition temperature (T_g—50 K), respectively.

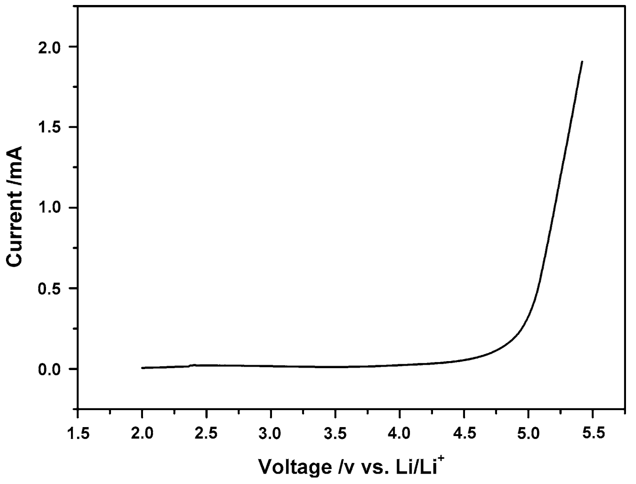


Fig. 4 Linear sweep voltammmetry of GPEs

Figure 4 shows the linear sweep voltammmetry plots of the polymer electrolytes. It was found that the current flow in the GPEs was very small when the voltage was below 4.5 V (vs. Li/Li$^+$), indicating that no decomposition of the components of polymer electrolyte occurs below this potential. Oxidation occurs at potentials higher than 4.75 V (vs. Li/Li$^+$). There is no problem with the electrochemical stability, because the charging voltage for a lithium ion battery is about 4.2 V. These results suggest that the as-prepared GPEs are very suitable for applications in lithium ion batteries.

3.2 Cell performance

The discharge curves obtained at different current rates are shown in Fig. 5. Polarization increases as the current rate increases, which results in a decreasing capacity. The

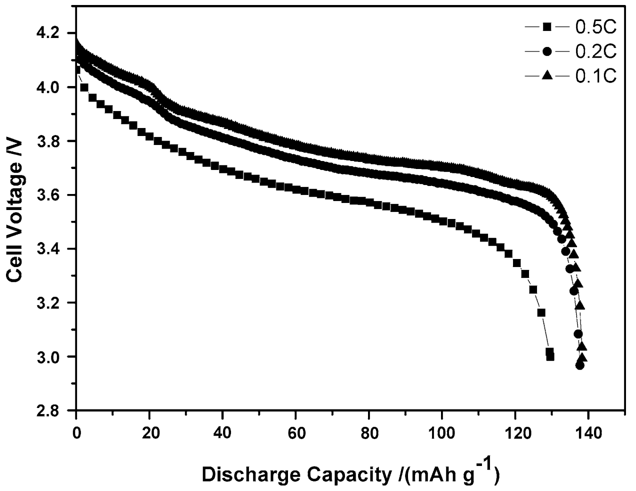


Fig. 5 Typical discharge curves for LiCoO$_2$/GPEs/graphite cell at various current densities at 25 °C

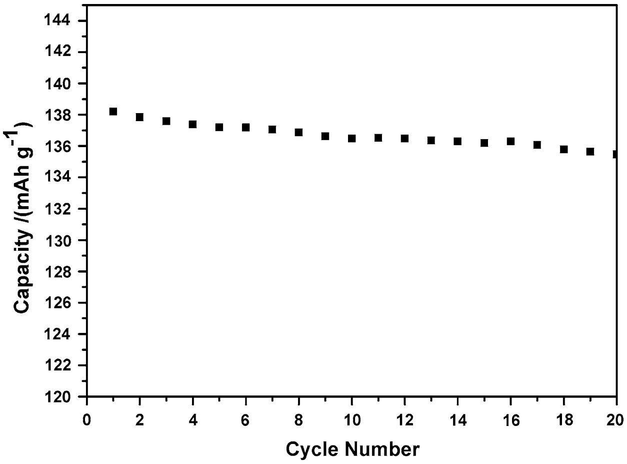


Fig. 6 Discharge capacity upon cycling for $LiCoO_2$/GPEs/graphite cell at 0.1 C rate at 25 °C

discharge capacity based on the weight of the cathode $LiCoO_2$ is 138.2 mAh g^{-1} at a current density of 0.1 C and falls to 129.6 mAh g^{-1} at 0.5 C. The reduced capacity at high current rate is due to the lower diffusion rate of lithium ions in the GPEs [26]. The lower diffusion rate of lithium ions may limit the cycling rate of the $LiCoO_2$/GPEs/graphite cell. More efforts to improve the high-rate performance, such as incorporation of highly conductive liquid electrolyte into GPEs and minimization of the GPEs membrane thickness are in progress.

Figure 6 shows the discharge capacity as a function of cycle number for a $LiCoO_2$/GPEs/graphite cell at a current density 0.1 C. The discharge capacity is 138.2 mAh g^{-1} for the first cycle and falls to 135.5 mAh g^{-1} after the 20th cycles, the reversible capacity maintains about 98% of its initial discharge capacity. The discharge capacity of the cell with GPEs remains stable for 20 cycles of charging and discharging. It can be expected that the star polymer may decrease the interface resistance between the electrode and the GPEs.

4 Conclusions

Well-defined star shaped polymers were synthesized by the ATRP method. GPEs were prepared by encapsulating electrolyte solution into the star shaped polymer host. The ionic conductivity of the GPEs was around 1.63×10^{-3} S cm^{-1} at 25°C. The GPEs had good electrochemical stability up to 4.5 V (vs. Li/Li^+). Discharge curves of the $LiCoO_2$/GPEs/graphite cells exhibited well-defined voltage profiles; the discharge capacity was 138.2 mAh g^{-1} for the first cycle and fell to 135.5 mAh g^{-1} after the 20th cycle; the reversible capacity maintained about 98% of its initial discharge capacity. The discharge capacity of the cell with GPE remained stable with cycling. These results show that this kind of polymer electrolyte has potential application in lithium ion batteries.

Acknowledgment The authors thank the Hunan Province Education Research Foundation of China (06C819) for support of this work.

References

1. Li ZH, Zhang HP, Zhang P, Wu YP (2008) J Appl Electrochem 38:109
2. Scrosati B, Croce F, Persi L (2000) J Electrochem Soc 147:1718
3. Zhang HP, Zhang P, Li ZH, Sun M, Wu YP et al (2007) Electrochem Commun 9:1700
4. Wang XJ, Kang JJ, Wu YP, Fang SB (2003) Electrochem Commun 5:1025
5. Reiter J, Vondrák J, Mička Z (2005) Electrochim Acta 50:4469
6. Vondrák J, Reiter J, Velická J, Sedlaříková M (2004) Solid State Ionics 170:79
7. Vondrák J, Sedlaříková M, Velická J et al (2003) Electrochim Acta 48:1001
8. Kim D, Oh B, Choio Y (1999) Solid State Ionics 123:243
9. Kumara R, Subramania A, Sundaram NTK et al (2007) J Membrane Sci 300:104
10. Sharma JP, Sekhon SS (2007) Solid State Ionics 178:439
11. Meneghettia P, Qutubuddina S, Webber A (2004) Electrochim Acta 49:4923
12. Adebahr J, Byrne N, Forsyth M et al (2003) Electrochim Acta 48:2099
13. Meneghetti P, Qutubuddin S (2006) Thermochim Acta 442:74
14. Lin DJ, Chang CL, Lee CK, Cheng LP (2006) Eur Polym J 42:2407
15. Li ZM, Wei JG, Shan F et al (2008) J Polym Sci: Part B: Poly Phy 46:751
16. Zhang SP, Fu XK, Gong YF (2007) J Appl Polym Sci 106:4091
17. Gao K, Hu XG, Yi TF, Dai CS (2006) Electrochimi Acta 52:443
18. Joa SI, Sohna HJ, Kang DW, Kim DW (2003) J Power Sources 478:119–121
19. Wang MK, Dong SJ (2007) J Power Sources 170:425
20. Liang WJ, Kao HM, Kuo PL (2004) Macromol Chem Phys 205:600
21. Zhang Z, Sherlock D, West R et al (2003) Macromolecules 36:9176
22. Siska DP, Shriver DF (2001) Chem Mater 13:4698
23. Madhavan N, Robert EC, Gin MS (2005) Angew Chem Int Edit 44:7584
24. Ohao K, Wong B, Haddleton DM (2001) Polym Sci: Part A: Polym Chem 39:2206
25. Rajendran S, Uma T (2000) J Power Sources 88:282
26. Kim D (2000) J Power Sources 87:78