Short communication

Poly(ethene-1,1,2,2-tetrathiol): Novel cathode material with high specific capacity for rechargeable lithium batteries

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A R T I C L E   I N F O

A B S T R A C T

Novel thioether compound poly(ethene-1,1,2,2-tetrathiol) was synthesized, characterized and tested as cathode active material. The polymer was synthesized by facile one-step procedure and its chemical structure was confirmed by FT-IR, FT-Raman, element analysis, and XPS spectral analysis. The polymer had good electrochemical activity as cathode material for rechargeable lithium battery. It showed stable discharge specific capacity about $300 \, mAh \, g^{-1}$ and discharge voltage above 2 V. The thioether bond was deduced as the functional group. It was proposed that thioether bonds were oxidized to form thioether cations with the help of ether solvent, which offered energy storage.

1. Introduction

Sulfur is of high specific capacity, cheap, and environmentally benign as cathode material for rechargeable lithium batteries. It has attracted great interest and has being extensively studied. The shortcomings are its electric insulation, dissolution in solvents, and migration of S^{2-} from cathode. Since Liu and Visco et al. [1,2] found that organic disulfide compounds could be used as cathode materials for rechargeable lithium battery in late 1980s, many researches have been focused on organic disulfide materials. These disulfide compounds could be divided into five categories (Scheme 1): (1) Small organic compounds (Scheme 1a), from which small molecular anions ($^{-}SRS^{-}$) were formed in the reductive state [3–7]. Therefore this kind of organic disulfide compounds has the similar disadvantage to elemental sulfur. (2) Disulfide ladder polymers (Scheme 1b) have polymeric backbone linking disulfide bonds and do not dissolve in solvents during discharge process. But it is difficult to recombine perfectly during charging process, so that the cycling property is poor [8–10]. (3) Disulfide polymers have disulfide bonds as side-chains (Scheme 1c), in which the two S atoms of one disulfide bond (–S–S–) are linked to the same polymeric main chain. Hence the recombination of disulfide bonds could be improved [11–16]. (4) Polysulfide compounds [17–19]

(Scheme 1d) have high specific capacity in the first cycle and serious cycling fading due to its polysulfide structure. (5) Sulfurized polymers were synthesized through heating the mixture of organic polymer compounds and sulfur. Their structure is unclear; the electrochemical behaviors relied on the heating conditions. Some of them have high specific capacity and good cycling properties [20–23]. The electrode reactions of all these compounds are based on the same mechanism: the cleavage-recombination of disulfide (S–S) bonds. Nevertheless, recently we have found that the novel sulfide polymers, thioether compounds other than conventional disulfides, could also storage energy as cathode active materials [24]. That is, polymers contain thioether (C–S–C) bonds instead of disulfide (–C–S–S–C–) bonds. The redox reactions of thioether compounds do not involve bond cleavage, thus it may be expected to offer good stability as cathode active material. As a novel structure, it shows some advantage and need further study and exploration.

In this paper, we present novel thioether compound: poly(ethene-1,1,2,2-tetrathiol). It had several advantages as cathode active material. First, the polymer was prepared by facile "one-step polymerization" from convenient material (Scheme 2a). Second, its insolubility prevented migration of active material from cathode. Third, the simple polymeric structure consisting of S and C elements (Scheme 2b) benefited the exploration of the electrode reaction mechanism. Here we report the synthesis, characterization, and electrochemical behaviors of this novel cathode active material.

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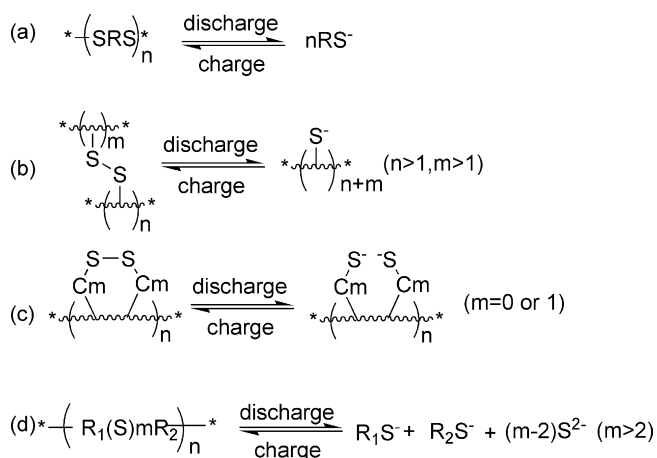
Scheme 1. Organic disulfide compounds for cathode active material in rechargeable lithium batteries.

2. Experimental

2.1. Materials

Na$_2$S·9H$_2$O, dimethylsulfoxide (DMSO), perchloroethene were AR purity and all reagents were used as received unless otherwise indicated.

The synthetic route and structure of the polymer are described in Scheme 2a. The preparation procedure is described as follows. In a three-neck flask equipped with condenser, thermometer, funnel and temperature controller, Na$_2$S·9H$_2$O (15.3 g, 63.7 mmol) and 90 ml DMSO were stirred under nitrogen atmosphere at room temperature. 3 ml perchloroethene (4.86 g, 29 mmol) in 10 ml DMSO was added dropwise to the solution. The solution was stirred for 8 h at 80 °C. After the reaction was over, the mixture was filtered and black solid was collected. The solid powder was washed with distilled water (100 ml × 3) and 50 ml ethanol in sequence. The product was dried in oven at 50 °C for 12 h and 1.33 g black solid was obtained (yield 52%). IR: 1431, 1400, 1384, 1211, 858, and 521 cm^{-1}; Raman: 1442, 1256, and 493 cm^{-1}.
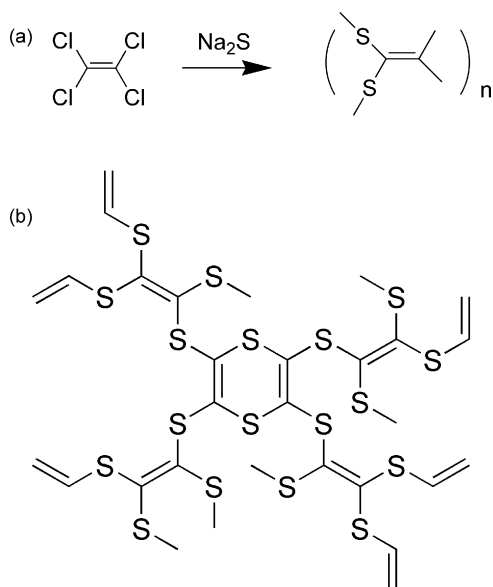
Scheme 2. (a) The synthetic routes of poly(ethene-1,1,2,2-tetrathiol). (b) The configuration of poly(ethene-1,1,2,2-tetrathiol).
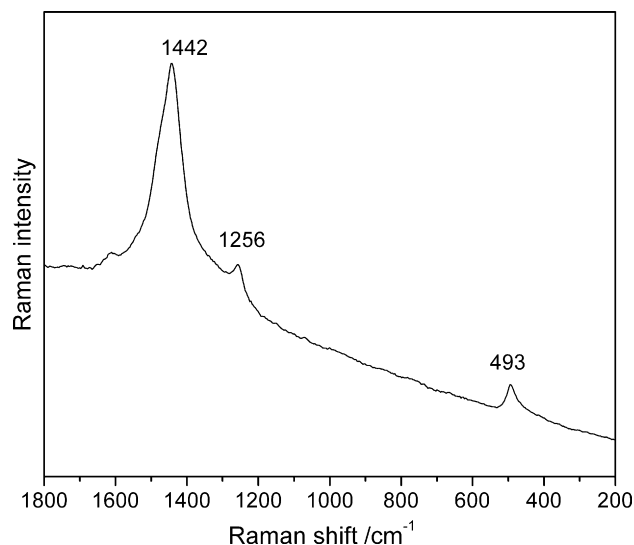
Fig. 1. FT-Raman spectrum of poly(ethene-1,1,2,2-tetrathiol).

2.2. Apparatus and procedures

FT-IR spectrum was recorded on a NICOLET AVATAR 360 FT-IR spectrometer with KBr pellets. FT-Raman spectrum was recorded on Confocal Raman Microspectroscopy. Thermal analysis was performed on a Diamond DSC TG-DTA 6300 instrument under nitrogen flow at a heating rate of 20 °C min^{-1}. XRD pattern of the powder specimen was obtained on a D8ADVANCE X-ray diffractometer.

The cyclic voltammetry (CV) test was carried out on CH Instrument electrochemical workstation (CHI 660B) using a scan rate of 50 μV s^{-1} at room temperature. The cathode was prepared by mixing polymer powder with carbon black and Teflon in a weight ratio of 4:4:2, the Li film was used as the reference electrode and counter electrode with 1 M LiN(CF$_3$SO$_2$)$_2$ (LiTFSI) in 1,2-dimethoxyethane (DME)/1,3-dioxolane(DOL) (1:2, by weight) as electrolyte.

For electrochemical evaluation, the charge–discharge tests were performed on Land Battery test system. Working cathodes were prepared by mixing specific polymer powder with carbon black and Teflon in a weight ratio of 4:4:2. Lithium foil was used as the anode and the tests were processed at a rate of 50 mA g^{-1} in 1 M LiN(CF$_3$SO$_2$)$_2$ (LiTFSI) in 1,2-dimethoxyethane (DME)/1,3-dioxolane(DOL) (1:2, by weight) solution. The cut-off voltages were 1.5 and 4.4 V.

3. Results and discussion

3.1. Material characterization

The polymer was insoluble and was characterized by FT-IR, FT-Raman spectra, XRD, X-ray photoelectron spectroscopy (XPS), and TGA. The FT-IR spectrum showed simple vibration mode due to its simple symmetric molecular structure. There was no vibration below 1000 cm^{-1} and at 2480 cm^{-1}, indicating that the polymer did not contain C–Cl, S–H bonds and asymmetric C–S bonds. The FT-Raman spectrum (Fig. 1) showed strong band at 1442 cm^{-1}, which was assigned to the C=C stretching vibration. A thioether molecule (CF$_3$S)$_2$C=C(SCF$_3$)$_2$, with similar molecular structure to that of the unit of poly(ethene-1,1,2,2-tetrathiol), exhibited C=C vibration band at 1450 cm^{-1} [25]. The band at 493 cm^{-1} was assigned to the –C–S–C– vibration.

The X-ray photoelectron spectroscopy (XPS) of poly(ethene-1,1,2,2-tetrathiol) (Fig. 2) was examined. The bonding energy of S 2p
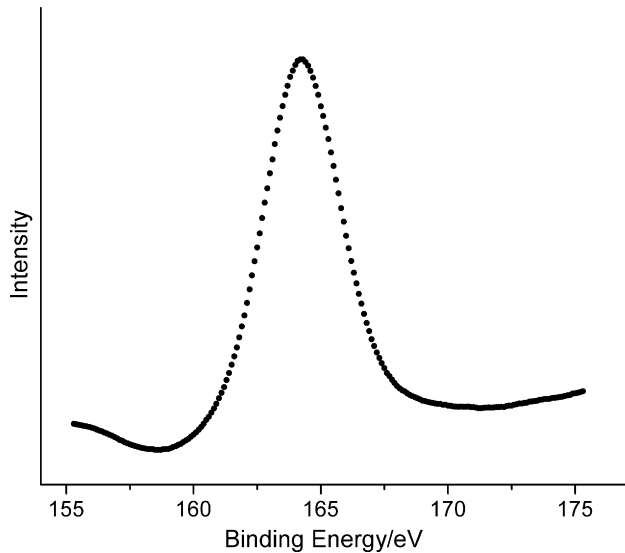
Fig. 2. X-ray photoelectron spectroscopy (XPS) spectrum of poly(ethene-1,1,2,2-tetrathiol).

was located 164.3 eV and showed that sulfur in polymers had only one valence state. Hence FT-Raman, XPS spectra of poly(ethane-1,1,2,2-tetrathiol) suggested the successful polymerization and the polymeric structure (Scheme 2b).

Thermal gravity analysis (TGA) of poly(ethene-1,1,2,2-tetrathiol) showed the 5% weight loss at 239 °C; the thermostability was better than general sulfide polymers. This stability was due to the thioether structure of poly(ethane-1,1,2,2-tetrathiol), the S atoms were in main chain and there was not disulfide bond.

The X-ray diffraction (XRD) pattern manifested poly(ethene-1,1,2,2-tetrathiol) was completely amorphous. The morphology was compatible to its hyperbranch structure (Scheme 2b). The irregular molecule was difficult to stack in regularity.

3.2. Electrochemical properties

Fig. 3 exhibits the cyclic voltammograms (CVs) of the first cycle of poly(ethene-1,1,2,2-tetrathiol) at a scan rate of 50 μV s^{-1}
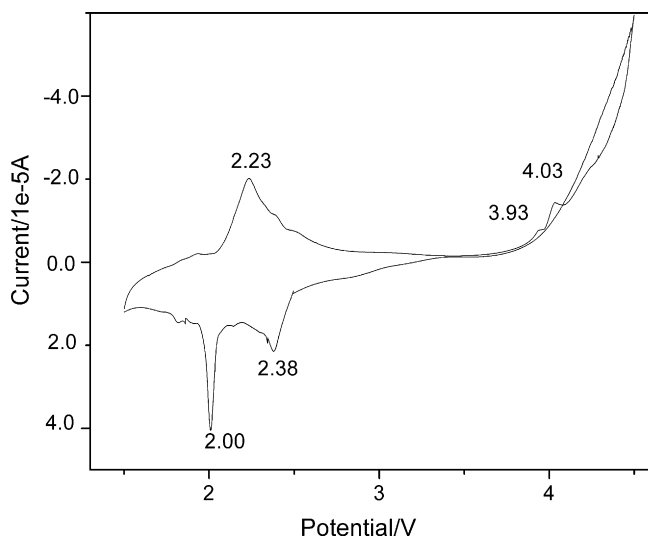

Fig. 3. Cyclic voltammogram of poly(ethene-1,1,2,2-tetrathiol) vs. Li$^+$/Li. Li film as the reference and counter electrode with 1 M LiTFSI/DME/DOL as electrolyte; scan rate 50 μV s^{-1}.
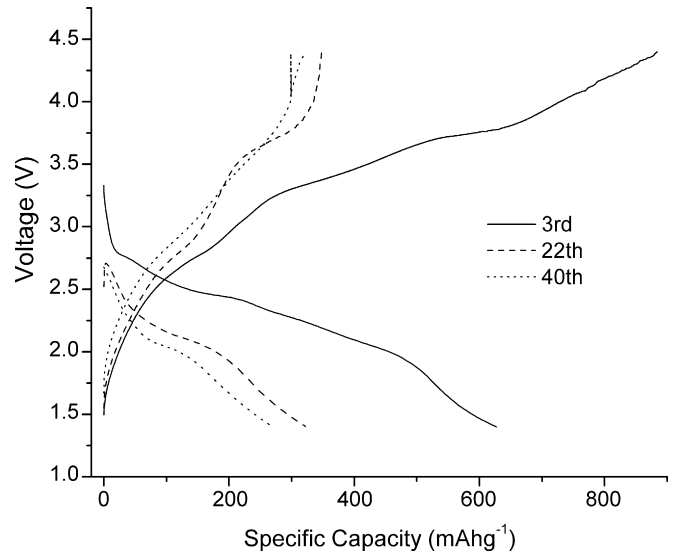

Fig. 4. The capacity–voltage curves of charge–discharge of poly(ethene-1,1,2,2-tetrathiol).

between 1.5 and 4.4 V at room temperature. It can be seen that the polymer has two oxidation peaks appeared at 2.23 and 4.03 V vs. Li/Li$^+$ and two reduction peaks at 2.0 and 2.38 V vs. Li/Li$^+$. The high oxidative peak indicates that the polymer may be charged at high voltage as cathode material. But the reductive peaks are in low voltage, which imply a low discharge voltage.

The charge–discharge curves of poly(ethene-1,1,2,2-tetrathiol) are shown in Fig. 4. The charge curve contains two plateaus: the low plateaus are at 2.6–2.8 V and the high plateaus are between 3.3 and 3.8 V. But the discharge voltage is at 2.7–2.0 V. The charge voltage and discharge voltage are corresponding to the oxidative potential and reduction potential in CV (Fig. 3). However, the discharge voltage is higher than disulfide polymers and elemental sulfur. The charge–discharge behavior is similar to our previously reported thioether-containing polymers, poly(2-phenyl-1,3-dithiolane) and poly[1,4-di(1,3-dithiolan-2-yl)benzene] [24].

The cycling life of poly(ethene-1,1,2,2-tetrathiol) is shown in Fig. 5. It displays a stable discharge specific capacity value of ca. 300 mAh g^{-1} from the 10th cycle to the 40th cycle and shows maximal specific capacity of 632 mAh g^{-1} at the second cycle. The coulomb efficiency of poly(ethene-1,1,2,2-tetrathiol) (about
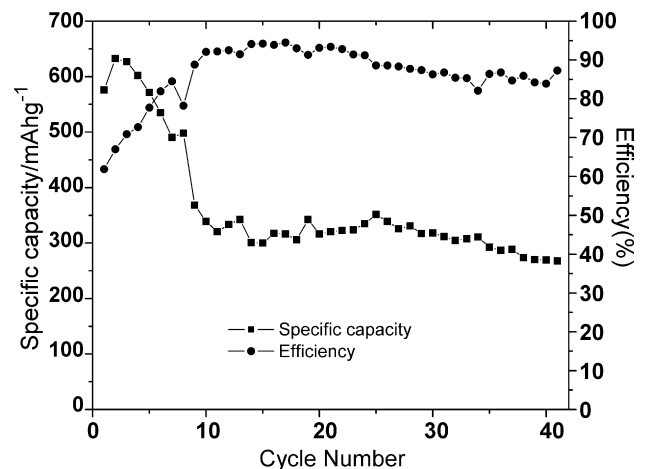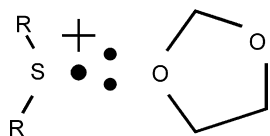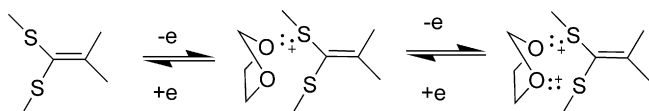

Fig. 5. Cycle life and coulomb efficiency of poly(ethene-1,1,2,2-tetrathiol) (current density 50 mA g^{-1}).

Scheme 3. The possible thioether cation in electrolyte.

Scheme 4. The proposed redox reaction of poly(ethene-1,1,2,2-tetrathiol) in cathode.

90% from the 10th cycle to the 40th cycle) is higher than that of poly(2-phenyl-1,3-dithiolane) and poly[1,4-di(1,3-dithiolan-2-yl)benzene] [24]. The electrochemical behaviors (maximal specific capacity and cycling performance) of poly(ethene-1,1,2,2-tetrathiol) are better than some of the disulfide polymers [11–16].

3.3. Mechanism of electrode reaction

The mechanism of electrode reaction is unclear at moments; here we can only present our preliminary understanding. First, thioether bonds are proposed as the function groups to offer reversible electrode reaction. There are only two kinds of bonds in the polymer: C=C and C–S–C bonds. It is impossible that vinyl bonds (C=C) afford so high specific capacity. The well known conducting polymer polyacetylene consisting of conjugated vinyl groups affords specific capacity of 144 mAh g^{-1} without counterions [26]. If the weight of S atom is calculated, the value will be of 60 mAh g^{-1}; hence we must consider the function of thioether.

Second, the oxidation of thioether has been studied extensively and reviewed, which illustrated that thioether bond can be easily oxidized to form thioether cation [27–30]. Furthermore, thioether radical cations can be stabilized by electron donation from the solvents [31]. In LiTFSI/DME/DOL electrolyte/solvents, DOL may act as electron donor to stabilize thioether cations (Scheme 3). Therefore it is reasonable to propose that thioether is the electrochemical active group and the tentatively proposed electrode reaction is depicted in Scheme 4. According to this mechanism, the oxidation of one polymeric unit is consisted of two steps, which is in good agreement with the CV test. Moreover, the discharge process is the reduction of S cation, which offers low discharge voltage at ca. 2 V, like sulfur-containing materials, such as disulfide and elemental sulfur. The theoretic specific capacity is 595 mAh g^{-1}, which agrees roughly to the test values. The maximal specific capacity (632 mAh g^{-1}) exceeds its theoretical value, which may be attributed to the contribution of vinyl groups.

4. Conclusions

In conclusion, poly(ethene-1,1,2,2-tetrathiol) is a facile-synthesized, thermally stable, novel cathode active polymer. The electrochemical tests show that poly(ethene-1,1,2,2-tetrathiol) is cathode active; its specific capacity and discharge voltage is higher than that of general disulfide polymer cathode materials. It is proposed that thioether bonds are the function groups and thoiether cations are their oxidized state.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2008.10.023.

References

[1] M. Liu, S.J. Visco, L.C. De Jonghe, J. Electrochem. Soc. 136 (1989) 2570.
[2] S.J. Visco, C.C. Mailhe, L.C.D. Jonghe, M.B. Armand, J. Electrochem. Soc. 136 (1989) 661.
[3] T. Maddanimath, Y.B. Khollam, A. Aslam, I.S. Mulla, K. Vijayamohanan, J. Power Sources 124 (2003) 133.
[4] H. Tsutsumi, K. Okada, T. Oishi, Electrochim. Acta 41 (1996) 2657.
[5] H. Tsutsumi, Y. Oyari, K. Onimura, T. Oishi, J. Power Sources 92 (2001) 228.
[6] H. Tsutsumi, K. Okada, K. Fujita, T. Oishi, J. Power Sources 68 (1997) 735.
[7] Z.J. Liu, L.B. Kong, L.M. Wang, Y.H. Zhou, C.M. Zhan, J. New Mater. Electrochem. Syst. 8 (2005) 269.
[8] L.M. Huang, T.C. Wen, C.H. Yang, Mater. Chem. Phys. 77 (2003) 434.
[9] Y.Z. Su, Y.P. Niu, Y.Z. Xiao, M. Xiao, Z.X. Liang, K.C. Gong, J. Polym. Sci. Part A: Polym. Chem. 42 (2004) 2329.
[10] K. Naoi, K.-I. Kawase, M. Mori, M. Komiyama, Mater. Res. Soc. Symp. Proc. 496 (1998) 309.
[11] J.X. Li, H. Zhan, L. Zhou, S.R. Deng, Z.Y. Li, Y.H. Zhou, Electrochem. Commun. 6 (2004) 515.
[12] L.J. Xue, J.X. Li, S.Q. Hu, M.X. Zhang, Y.H. Zhou, C.M. Zhan, Electrochem. Commun. 5 (2003) 903.
[13] S.R. Deng, L.B. Kong, G.Q. Hu, T. Wu, D. Li, Y.H. Zhou, Z.Y. Li, Electrochim. Acta 51 (2006) 2589.
[14] G.X. Xu, L. Qi, B.T. Yu, L. Wen, Chin. J. Polym. Sci. 24 (2006) 307.
[15] M. Amaike, T. Iihama, Synth. Met. 156 (2006) 239.
[16] H. Uemachi, Y. Iwasa, T. Mitani, Electrochim. Acta 46 (2001) 2305.
[17] G.F. Myachina, S.A. Korzhova, L.K. Papernaya, E.N. Deryagina, T.A. Skotheim, B.A. Trofimov, Phosphorus, Sulfur Silicon Relat. Elem. 181 (2006) 1241.
[18] B.A. Trofimov, L.V. Morozova, M.V. Markova, A.I. Mikhaleva, G.F. Myachina, I.V. Tatarinova, T.A. Skotheim, J. Appl. Polym. Sci. 101 (2006) 4051.
[19] B.A. Trofimov, E.N. Deryagina, E.N. Sukhomazova, E.P. Levanova, G.F. Myachina, S.A. Korzhova, Y.V. Mikhaylik, T.A. Skotheim, Sulfur Lett. 25 (2002) 229.
[20] J.L. Wang, J. Yang, C.R. Wan, K. Du, J.Y. Xie, N.X. Xu, Adv. Funct. Mater. 13 (2003) 487.
[21] J.L. Wang, J. Yang, J.Y. Xie, N.X. Xu, Adv. Mater. 14 (2002) 963.
[22] B.A. Trofimov, A.M. Vasil'tsov, O.V. Petrova, A.I. Mikhaleva, G.F. Myachina, S.A. Korzhova, T.A. Skotheim, Y.V. Mikhailik, T.I. Vakul'skaya, Russ. Chem. Bull. 51 (2002) 1709.
[23] B.A. Trofimov, Sulfur Reports 24 (2003) 283.
[24] J.Y. Zhang, L.B. Kong, L.Z. Zhan, J. Tang, H. Zhan, Y.H. Zhou, C.M. Zhan, J. Power Sources 168 (2007) 278.
[25] J.F. Harris Jr., J. Org. Chem. 32 (1967) 2063.
[26] P. Novak, K. Mueller, K.S.V. Santhanam, O. Haas, Chem. Rev. 97 (1997) 207.
[27] W.K. Musker, Acc. Chem. Res. 13 (1980) 200.
[28] W.K. Musker, P.B. Roush, J. Am. Chem. Soc. 98 (1976) 6745.
[29] G.S. Wilson, D.D. Swanson, J.T. Klug, R.S. Glass, M.D. Ryan, W.K. Musker, J. Am. Chem. Soc. 101 (1979) 1040.
[30] W.K. Musker, T.L. Wolford, J. Am. Chem. Soc. 98 (1976) 3055.
[31] D.W. Werst, J. Am. Chem. Soc. 113 (1991) 4345.