J Solid State Electrochem (2003) 7: 147–151
DOI 10.1007/s10008-002-0300-9

ORIGINAL PAPER

S.S. Zhang · K. Xu · T.R. Jow

Low-temperature performance of Li-ion cells with a $LiBF_4$-based electrolyte

Received: 29 March 2002 / Accepted: 14 May 2002 / Published online: 2 August 2002

Abstract The effect of $LiBF_4$ on the low-temperature performance of a Li-ion cell was studied by using a 1:1:1 (wt) EC/DMC/DEC mixed solvent. The results show that the $LiBF_4$-based electrolyte has a 2- to 3-fold lower ionic conductivity and shows rather higher freezing temperature compared with a $LiPF_6$-based electrolyte. Owing to electrolyte freezing, cycling performance of the Li-ion cell using $LiBF_4$ was significantly decreased when the temperature fell below –20 °C. However, impedance data show that at –20 °C the $LiBF_4$ cell has lower charge-transfer resistance than the $LiPF_6$ cell. In spite of the relatively lower conductivity of the $LiBF_4$-based electrolyte, the cell based on it shows slightly lower polarization and higher capacity in the liquid temperature range (above –20 °C) of the electrolyte. This fact reveals that ionic conductivity of the electrolytes is not a limitation to the low-temperature performance of the Li-ion cell. Therefore, $LiBF_4$ may be a good salt for the low-temperature electrolyte of a Li-ion cell if a solvent system that is of low freezing temperature, high solubility to $LiBF_4$, and good compatibility with a graphite anode can be formulated.

Keywords Li-ion cell · Lithium tetrafluoroborate · Lithium hexafluorophosphate · Electrolyte · Low temperature

Introduction

Li-ion batteries, with their high power density and good rechargeability, are increasingly entering the consumer market as a power source for portable electronics, such as cellular phones, camcorders, and laptop computers. However, application of these batteries is limited to a rather narrow temperature range of –20 to 60 °C [1]. At elevated temperatures (> 60 °C), cycling performance of Li-ion batteries deteriorates markedly. Known causes of performance deterioration at > 60 °C include the following:

1. Decomposition of electrolyte components. This is especially true for $LiPF_6$, which can decompose at temperatures as low as 80 °C in the presence of organic solvents. Products of this decomposition subsequently react with solvent molecules [2].
2. Dissolution (decomposition) of the solid electrolyte interface (SEI) film by electrolyte solvents [3, 4].
3. Acid (HF)-induced dissolution of cathode active materials [5].
4. Direct reactions between cathode active materials and the electrolyte [6].

It is obvious that the above phenomena are mainly related to the thermal stability of electrolytes, particularly in the case of $LiPF_6$ that has been a predominant solute for electrolytes of state-of-the-art Li-ion batteries. For the above reasons, we previously studied more thermally stable salts, such as $LiBF_4$ and lithium bis(oxalato)borate (LiBOB), which give improved high-temperature performance [7, 8].

On the other hand, at low temperatures (< –20 °C) the cycling capacities of Li-ion batteries are substantially decreased, although the discharge performance can be improved by charging the cells above –10 °C ([9, 10, 11, 12], Zhang SS, Xu K, Jow TR (2001) unpublished results). That is, there is a distinct gap in the cycling performance between above –10 °C and below –20 °C, and the charging temperature greatly affects the cell capacity. When cycling at –20 °C, for instance, a Li/graphite cell only achieves 12% of the capacity available at room temperature. However, the discharge capacity can be increased to 94% by charging the cell at 20 °C instead of at –20 °C (Zhang SS, Xu K, Jow TR (2001) unpublished work). The factors that affect the low-temperature

---

S.S. Zhang (✉) · K. Xu · T.R. Jow
U.S. Army Research Laboratory,
Adelphi, MD 20783, USA
E-mail: szhang@mail.com

performance of Li-ion batteries include: (1) low conductivity of the electrolyte and SEI film [9, 13, 14], (2) continuous growth of SEI resistance during cycling [10, 11], (3) high polarization of the graphite anode [11], and (4) low Li-ion diffusivity within the graphite ([12], Zhang SS, Xu K, Jow TR (2001) unpublished work). Previous approaches toward resolving these problems were mainly focused on the development of liquid electrolytes that had a lower freezing temperature [9, 13, 14, 15]. However, $LiPF_6$ was retained in these electrolytes and there was little attention given to the impact of the salt on low temperature performance. This was probably due to the limited selection of lithium salts available. As a solute of the electrolytes in Li-ion batteries, the salt should possess such properties as (1) forming a stable SEI film with the graphite anode, (2) passivating the Al cathode current collector, (3) being stable with respect to electrolyte solvents and electrode materials in a fully charged cell, and (4) providing high ionic conductivity over a wide temperature range.

In our early work [7], we have found that $LiBF_4$ gave improved high-temperature performance in Li-ion cells. However, its impact on low-temperature performance was not investigated. In addition, it has been proven that at low temperatures the ternary solvent EC/DMC/DEC can provide higher conductivity and better SEI characteristics as compared to the binary analogues [9]. Therefore, in this work, a 1:1:1 (wt) EC/DMC/DEC mixed solvent was used to evaluate the ability of $LiBF_4$ to function as a solute for the low-temperature electrolyte. A comparison of the low-temperature performance of $LiBF_4$ in Li-ion cells versus that of $LiPF_6$ in such cells is reported.

Experimental

The electrolyte starting materials ethylene carbonate (EC) (Grant Chemical), $LiPF_6$ (Stella Chemifa), and $LiBF_4$ (Stella Chemifa) were used as received, while dimethyl carbonate (DMC) (EM Industries) and diethyl carbonate (DEC) (EM Industries) were dried over activated aluminum oxide (neutral) before use. Electrolytes with a composition of 1 m (mole solute per kilogram solvent) salt dissolved in a 1:1:1 EC/DMC/DEC mixture were prepared in an argon-filled glove box and their water content as determined by Karl-Fischer titration was 10–20 ppm. Both a lithium nickel mixed-oxide cathode and a graphite anode, provided by SAFT America, were cut into small disks and dried at 105 °C under vacuum for 16 h prior to use. BR2335-type Li-ion button cells with cathode and anode areas of 0.97 cm^2 and 1.27 cm^2, respectively, were assembled in the same glove box and filled with 150 μL of electrolyte.

A Solartron SI 1287 Electrochemical Interface and a SI 1260 Impedance/Gain-Phase Analyzer, controlled by Zplot software, were used to measure the impedance of the cells. A Tenney Environmental Oven Series 942 was employed to control the testing temperature. The ionic conductivity of the electrolytes was determined by measuring the impedance of the electrolytes in a two-platinum-electrode cell having a cell constant of 1.586 cm^{-1}. Button cells were galvanostatically cycled between 2.5 V and 3.9 V on a Maccor Series 4000 tester, in which the discharging processes were carried out under different conditions as specified in the discussion. All the charging processes were conducted at 20 °C at 0.5 mA/cm^2 with a total 3-h limit, during which the cell was constantly kept at 3.9 V after its voltage reached 3.9 V. As a definition, we took "relative capacity" as the ratio of discharge capacity at a certain temperature to the capacity accessed at 20 °C. The AC impedances of the button cells were potentiostatically measured by applying a DC bias, which was equal to the open-circuit voltage (OCV) of the cells, and an AC oscillation of 5 mV over the frequencies from 100 kHz to 0.01 Hz. The obtained impedance spectra were analyzed by using ZView software (Scribner Associates).

Results and discussion

Arrhenius plots of ionic conductivities for the various electrolytes are shown in Fig. 1. The dotted line represents extrapolation of the conductivity change above –20 °C. The $LiBF_4$-based electrolyte has a 2- to 3-fold lower conductivity than the $LiPF_6$ one over the entire temperature range investigated. The Arrhenius plot for the conductivity of the $LiPF_6$ system has a constant slope, while a significant drop in conductivity is observed at temperatures below –20 °C for the $LiBF_4$-based electrolyte. The negative deviation of the measured conductivity from the extrapolated Arrhenius plot below this temperature can be ascribed to freezing of the liquid electrolyte, which is associated with either EC crystallization, $LiBF_4$ precipitation, or a combination of both. This was confirmed by lowering the temperature to –40 °C and noting that the $LiBF_4$ electrolyte solution froze within 30 min, while the $LiPF_6$ system remained in the liquid state. Thus, the $LiBF_4$ electrolyte solution resists surpercooling.

Figure 2 compares the effect of the lithium salts on the relative capacity of Li-ion cells. The cells were galvanostatically charged at 20 °C and discharged at various temperatures at 0.5 mA/cm^2 ($\sim C/2$). At temperatures below –20 °C the $LiBF_4$ cell demonstrated a

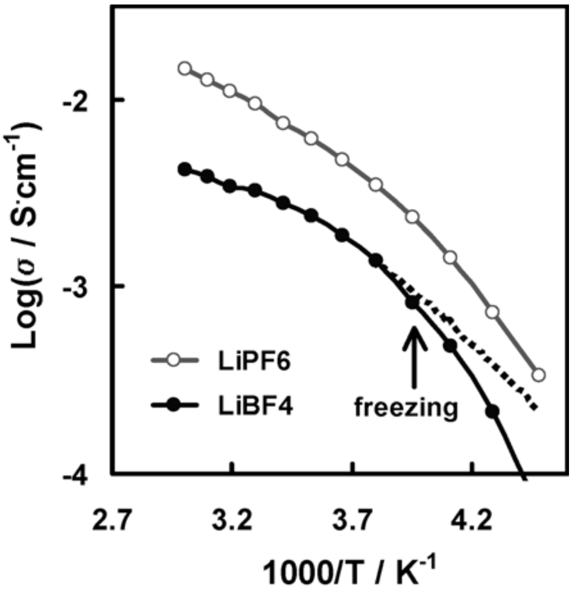

Fig. 1 Arrhenius plots of ionic conductivities for the electrolytes composed of 1 m lithium salt dissolved in a 1:1:1 EC/DMC/DEC mixture

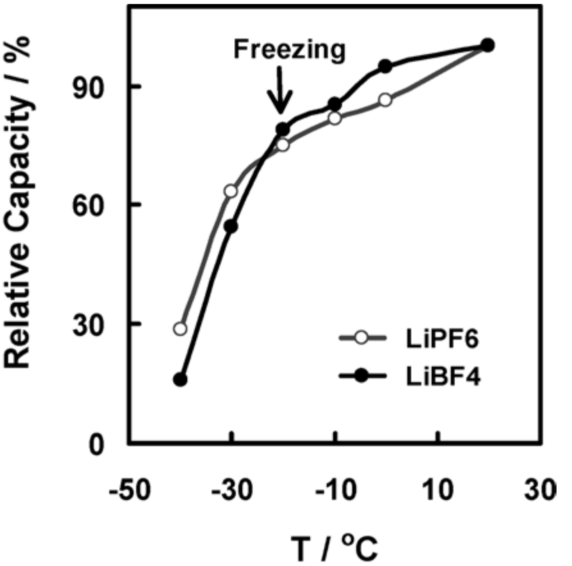

Fig. 2 Effect of temperature on the relative capacity of the Li-ion cells using either 1 m $LiPF_6$ or 1 M $LiBF_4$ salt dissolved in a 1:1:1 EC/DMC/DEC mixture

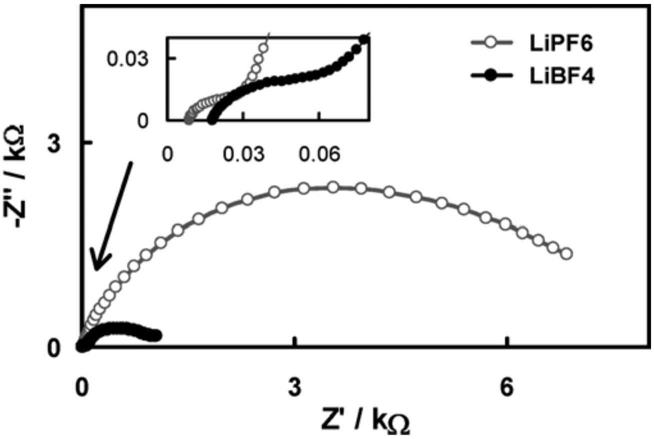

Fig. 3 Impedance spectra of the fully charged Li-ion cells using different salts at –20 °C. The *inset* shows the parts of the impedance spectra in the high-frequency region

lower relative capacity than the $LiPF_6$ cell. This can be attributed to the lower conductivity of the $LiBF_4$-based electrolyte, as indicated in Fig. 1, due to freezing of the electrolyte. When the temperature rose to above –20 °C (the temperature at which the electrolyte became liquid), the $LiBF_4$ cell demonstrated a higher relative capacity than the $LiPF_6$ cell, although the conductivity of the $LiBF_4$-based electrolyte was lower. This observation suggests that the ionic conductivity of the electrolytes may not be the only limiting factor of the low-temperature performance of Li-ion cells. It could be practical to use $LiBF_4$ as a solute for the low-temperature electrolyte of the Li-ion cells if a solvent mixture of low freezing temperature and high solubility to $LiBF_4$ can be formulated. It should be mentioned here that at 20 °C the current density (0.5 mA/cm^2) used in these cycling tests is not high enough to distinguish any capacity difference caused by the salts.

To understand the effect of the lithium salts on low-temperature performance, we measured impedances of the Li-ion cells at both fully charged and discharged states. Impedance spectra of the fully charged Li-ion cells, recorded at –20 °C over the frequencies of 100 kHz to 0.01 Hz, are presented in Fig. 3. Typically, the impedance spectra of Li-ion cells are composed of two overlapped semicircles at high and medium frequencies and a sloping straight line at low frequencies. Sometimes, the sloping straight line at low frequencies may be absent since the low-frequency limit (0.01 Hz) used for the measurement may be still too high to induce the diffusion process of lithium ions in solids. In accordance with general analyses ([8, 9, 10], Zhang SS, Xu K, Jow TR (2001) unpublished work), the semicircle at high frequencies reflects the surface layer (SEI film) resistance (R_f) on both electrodes. The semicircle at medium frequencies reflects the charge-transfer resistance (R_{ct}), which takes place at the electrolyte-electrode interface, and the intercept of the semicircle at the far high-frequency end on the real impedance axis reflects the electrolyte and electrodes bulk resistance (R_e). Using this model, we fitted R_e, R_f, and R_{ct} of the impedance spectra in Fig. 3. It is estimated from the inset of Fig. 3 that R_e and R_f for the $LiBF_4$ cell are 18.0 Ω and 53.9 Ω, respectively, in comparison to 8.6 Ω and 23.4 Ω, respectively, for the $LiPF_6$ cell. These results reflect the difference in conductivity of these two electrolytes at –20 °C. However, Fig. 3 indicates that $LiBF_4$ results in a much lower R_{ct} (808 Ω) as compared to $LiPF_6$ (6289 Ω). In addition, we measured and fitted impedance spectra of the fully discharged cells and found that both R_e and R_f remained nearly constant but the R_{ct} value increased significantly. However, the large difference in the R_{ct} values for $LiBF_4$ and $LiPF_6$ remained. Thus, the low-temperature performance of the Li-ion cells is probably more associated with the R_{ct} value than with R_e and R_f. Better low-temperature performance of the $LiBF_4$ cell is shown to be related to its lower R_{ct}, the value of which depends on the composition of Li_xC_6 (i.e., charged state of the cell).

Voltage-capacity curves of two Li-ion cells using $LiPF_6$ and $LiBF_4$ were recorded at –20 °C on discharging the cells at 0.5 mA/cm^2 (Fig. 4). As indicated by a slightly higher discharge voltage, the $LiBF_4$ cell is less polarized. Obviously, the conductivity (Fig. 1) of the electrolyte does not explain this observation, and neither do the R_e and R_f values (Fig. 3) of the cell. The only evidence that could be responsible for this observation is the much lower R_{ct} value. It appears that, for the $LiBF_4$ cell, the much lower R_{ct} not only compensates for the high R_e and R_f but also facilitates cell operation, as indicated by the higher discharge voltage in Fig. 4. It should be mentioned that although $LiBF_4$ may result in a lower R_{ct} as compared with $LiPF_6$, the R_{ct} at low temperatures is still rather high for the operation of the Li-ion cells.

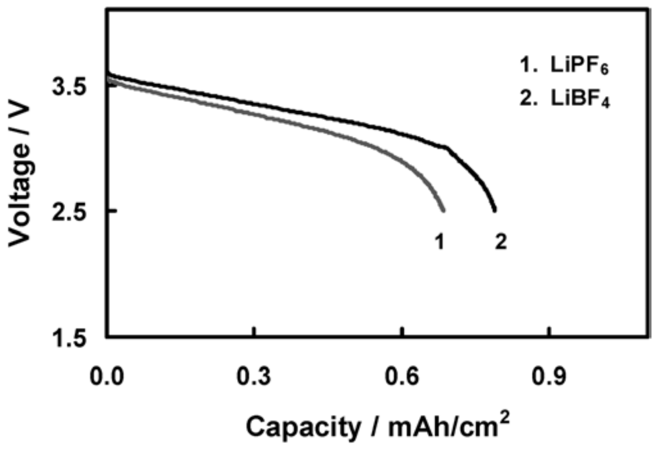

Fig. 4 Comparison of voltage-capacity curves of the Li-ion cells using different salts, which were recorded at –20 °C during discharging at 0.5 mA/cm^2

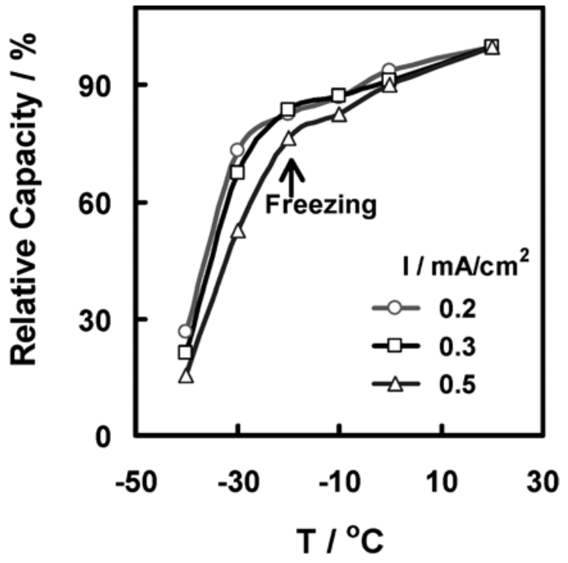

Fig. 6 Temperature effect of the relative capacity for the Li-ion cell using 1 m LiBF$_4$ in a 1:1:1 EC/DMC/DEC electrolyte, in which the cell was charged at 20 °C and discharged at specified temperatures and current densities

The effect of current density on the discharge voltage and the relative capacity of the cells using 1 M LiBF$_4$ in 1:1:1 EC/DMC/DEC electrolyte at –20 °C is illustrated in Figs. 5 and 6, respectively. We found that, with the LiBF$_4$ salt, the current density did not affect cell performance as much as expected. Between 0.3 and 0.5 mA/cm^2, the current density has negligible impact on the discharge voltage (Fig. 5). When the current density was decreased to 0.2 mA/cm^2 (*C*/5), we observed an increase in the discharge voltage. It is noted from Fig. 6 that, as the temperature was lowered below –20 °C, the relative capacity of the cells was considerably decreased even for the case of low current density (0.2 mA/cm^2). The small impact of the current density on the discharge voltage and relative capacity is more likely associated with freezing of the LiBF$_4$-based electrolyte rather than with the low diffusivity of lithium ions within the graphite anode, as reported elsewhere ([12], Zhang SS, Xu K, Jow TR (2001) unpublished work). If the latter case is true, the current density should considerably affect the discharge voltage of the cells.

Figure 7 compares discharge capacities of the Li-ion cells using LiPF$_6$ and LiBF$_4$, respectively, before and after the cycling test at low temperatures. After the cycling test at low temperatures, both cells lost some capacity. This phenomenon is often observed in Li-ion batteries, and the mechanism is as yet unknown. We can see from Fig. 7 that, after the cycling test at low temperatures, the LiBF$_4$ cell loses less capacity and shows slower capacity fading for the extended cycles. This makes the use of LiBF$_4$ advantageous, and more work is needed to understand the phenomenon.

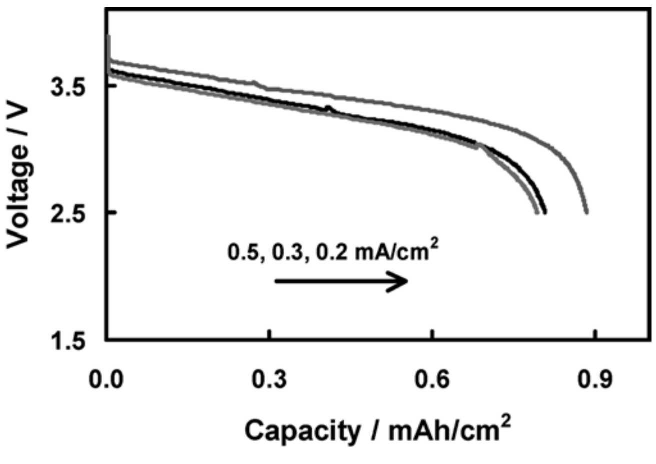

Fig. 5 Influence of current density on discharge voltage of the Li-ion cells using 1 m LiBF$_4$ in a 1:1:1 EC/DMC/DEC electrolyte, in which the cell was charged at 20 °C and discharged at –20 °C with a constant current density of 0.5 mA/cm^2

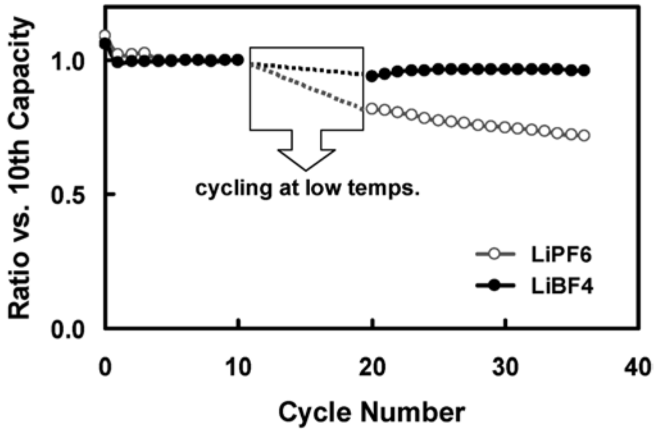

Fig. 7 Change in the discharge capacities of the Li-ion cells using LiPF$_6$ and LiBF$_4$, respectively, before and after the cycling test at low temperatures. The data were obtained by cycling the cells at 0.5 mA/cm^2 at 20 °C between 2.5 V and 3.9 V

Conclusions

It may be concluded that the ionic conductivity of the electrolytes is probably not the source of the limitation on the low-temperature performance of Li-ion cells. The electrolyte made of the $LiBF_4$ salt has a lower conductivity than that made of $LiPF_6$; however, it provides better low-temperature performance in its liquid temperature range. This behavior can be ascribed to the lower charge-transfer resistance arising from the use of $LiBF_4$. Unfortunately, the $LiBF_4$-based electrolyte has a rather high freezing temperature, which limits its application at low temperatures.

Acknowledgements The gift of the lithium nickel mixed-oxide cathode and graphite anode films from SAFT America is gratefully acknowledged.

References

1. Molicel (2000) Product data sheet for IMR-18650 Li-ion cell. Molicel,
2. Sloop SE, Pugh JK, Wang S, Kerr JB, Kinoshita K (2001) Electrochem Solid-State Lett 4:A42
3. Pasquier AD, Disma F, Bowmer T, Gozdz AS, Amatucci GG, Tarascon JM (1988) J Electrochem Soc 145:472
4. Zheng T, Gozdz AS, Amatucci GG (1999) J Electrochem Soc 146:4014
5. Jang DH, Shin YJ, Oh SM (1996) J Electrochem Soc 143:2204
6. Matsuo Y, Kostecki R, McLarnon F (2001) J Electrochem Soc 148:A687
7. Zhang SS, Xu K, Jow TR (2002) J Electrochem Soc 149:A586
8. Xu K, Zhang SS, Jow TR, Xu W, Angell CA (2002) Electrochem Solid-State Lett 5:A26
9. Smart MC, Ratnakumar BV, Surampudi S (1999) J Electrochem Soc 146:486
10. Smart MC, Ratnakumar BV, Surampudi S, Wang Y, Zhang X, Greenbaum SG, Hightower A, Ahn CC, Fultz B (1999) J Electrochem Soc 146:3963
11. Lin HP, Chua D, Salomon M, Shiao HC, Hendrickson M, Plichta E, Slane S (2001) Electrochem Solid-State Lett 4:A71
12. Huang CK, Sakamoto JS, Wolfenstine J, Surampudi S (2000) J Electrochem Soc 147:2893
13. Shiao HC, Chua D, Lin HP, Slane S, Salomon M (2000) J Power Sources 87:167
14. Plichta EJ, Hendrickson M, Thompson R, Au G, Behl WK, Smart MC, Ratnakumar BV, Surampudi S (2001) J Power Sources 94:160
15. Herreyre S, Huchet O, Barusseau S, Perton F, Bodet JM, Biensan P (2001) J Power Sources 97–98:576