



Effect of 1-butyl-1-methylpyrrolidinium hexafluorophosphate as a flame-retarding additive on the cycling performance and thermal properties of lithium-ion batteries

Ji-Ae Choi^a, Yang-Kook Sun^b, Eun-Gi Shim^c, Bruno Scrosati^d, Dong-Won Kim^{a,*}

^a Department of Chemical Engineering, Hanyang University, Seungdong-Gu, Seoul 133-791, Republic of Korea

^b Department of Energy Engineering, Hanyang University, Seungdong-gu, Seoul 133-791, Republic of Korea

^c Electrolyte Development Team, Techno SemiChem Co. Ltd, Yongin-si, Gyeonggi-do 446-599, Republic of Korea

^d Department of Chemistry, University of Rome "La Sapienza", Piazzale Aldo Moro 5, 00185 Rome, Italy

ARTICLE INFO

Article history:

Received 21 March 2011

Received in revised form 18 August 2011

Accepted 2 September 2011

Available online 9 September 2011

Keywords:

1-Butyl-1-methylpyrrolidinium phosphate

Lithium-ion battery

Flame retardant

Electrolyte additive

Thermal stability

ABSTRACT

1-Butyl-1-methylpyrrolidinium hexafluorophosphate (BMP-PF₆) was used as a flame-retarding additive in the liquid electrolyte, and the influence of BMP-PF₆ content on cycling performance and thermal properties of lithium-ion batteries was investigated. Self-extinguishing time and DSC studies demonstrated that the addition of BMP-PF₆ to the electrolyte provided a significant suppression in the flammability of the electrolyte and an improvement in the thermal stability of the cell. The optimum BMP-PF₆ content in the electrolyte was found to be 10 wt.% for improving safety without degrading cycling performance of the cell.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Lithium-ion batteries have rapidly become the dominant power source for portable electronic devices, power tools and electric vehicles due to their high energy density and long cycle life [1,2]. However, safety issues surrounding these batteries must be addressed before they can be widely utilized in large-scale cells, such as electric vehicles and energy storage systems. The highly flammable organic solvents that are contained in common electrolytes can be the major possible cause of fires and explosions when short circuiting or local overheating accidentally occurs. Thus, recent investigations have focused on the development of non-flammable electrolytes containing flame-retarding additives to improve the safety of such cells [3–17]. Although these additives can improve the safety of lithium-ion batteries, their addition is generally accompanied by deterioration in cell performance due to the reductive decomposition and low ionic conductivity of the electrolyte [18].

With the goal of developing less-flammable electrolytes for safe lithium-ion batteries, a small amount of 1-butyl-1-

methylpyrrolidinium hexafluorophosphate (BMP-PF₆) was added as a flame retarding additive into the liquid electrolyte. BMP-PF₆ is an ionic liquid that contains cations and anions whose non-volatile and non-flammable nature makes it especially desirable as a flame retarding additive for lithium-ion batteries. This study also illustrates that it is compatible with graphite/LiCoO₂ cells without deterioration in cell performance, if the proper amount of BMP-PF₆ has been added to the liquid electrolyte. To date, there has been no report published on the electrochemical performance and thermal stability of electrolytes containing BMP-PF₆ as an additive. With these less-flammable electrolytes, we assembled lithium-ion batteries composed of a graphite anode and a LiCoO₂ cathode. The cycling performance of the cells was evaluated and compared to that of the cell assembled with a base liquid electrolyte. The influences of BMP-PF₆ on the flammability of the electrolyte and the thermal stability of the charged cathode material were also investigated.

2. Experimental

2.1. Electrolyte preparation

BMP-PF₆ shown in Fig. 1 was purchased from Chem Tech Research Incorporation and was used after drying under a vacuum

* Corresponding author. Tel.: +82 2 2220 2337; fax: +82 2 2298 4101.

E-mail address: dongwonkim@hanyang.ac.kr (D.-W. Kim).

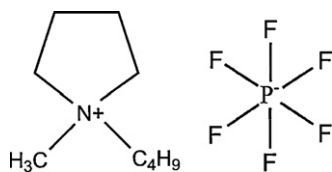


Fig. 1. Chemical structure of BMP-PF₆.

at 50 °C for 24 h. The BMP-PF₆ was solid at ambient temperature because its melting point is close to 80 °C. The base electrolyte, 1.4 M LiPF₆ in ethylene carbonate(EC)/fluoroethylene carbonate(FEC)/dimethyl carbonate(DMC)/ethylmethyl carbonate(EMC) (1:1:6:2 by volume, battery grade) was supplied by Techno SemiChem Co. Ltd. and used without further treatment. BMP-PF₆ was directly added to the base electrolyte in concentrations of 0, 10, 20 and 30 wt.% in an Ar-filled glove box. A porous poly(vinylidene fluoride-co-hexafluoropropylene)-coated polyethylene separator was prepared according to a procedure reported previously [19]. The polymer-coated separator was easily wetted by the electrolyte solution and retained the electrolyte solution well.

2.2. Electrode preparation and cell assembly

The cathode was prepared by coating an N-methyl pyrrolidone (NMP)-based slurry containing LiCoO₂ (Japan Chemical), PVdF, and super-P carbon (85:7.5:7.5) onto aluminum foil. Its active mass loading corresponded to a capacity of about 2.9 mAh cm⁻². The carbon anode was prepared by coating a NMP-based slurry of meso-carbon microbeads (MCMB, Osaka gas), PVdF and super-P carbon (88:8:4) onto copper foil. The cell composed of a carbon anode, a polymer-coated separator wetted with electrolyte solution and a LiCoO₂ cathode was assembled in a dry box filled with argon gas, enclosed in a pouch bag and vacuum-sealed.

2.3. Measurements

The self-extinguishing time (SET) was measured to quantify the flammability of the mixed electrolyte, as previously described [10–12,20–22]. Compared to the burning rate measurement, the SET measurement gave a better quantification of flammability. Briefly, SET was obtained by igniting the pre-weighed electrolytes soaked in an inert glass-fiber wick (3 cm × 3 cm), followed by recording the time it took for the flame to extinguish. The measurements were repeated at least five times to get reproducible SET values. The electrochemical behavior of a carbon electrode was analyzed by cyclic voltammetry in different electrolyte solutions. The voltammograms were obtained between 0 and 3.2 V at a scan rate of 0.5 mV s⁻¹; each cycling started from a respective open-circuit voltage. AC impedance measurements were performed using an impedance analyzer over a frequency range of 1 mHz to 100 kHz with an amplitude of 10 mV. Charge and discharge cycling tests of the lithium-ion cells were conducted at a current density of 1.45 mA cm⁻² (0.5C rate) over a voltage range of 3.0–4.2 V. For differential scanning calorimetry (DSC) experiments, the cells were fully recharged to 4.2 V after 100 cycles and were disassembled in the dry box. Approximately 5 mg of the cathode, scraped from the current collector, was hermetically sealed in a stainless steel pan, and measurements were performed at a heating rate of 1 °C min⁻¹. Before DSC measurements, the amounts of cathode active material and electrolyte solution were measured, and heat flow was calculated based on the weight of the cathode active material. The weight % of electrolyte solution in the cathode was almost the same (59.2–62.8 wt.% of total cathode material) irrespective of content of BMP-PF₆.

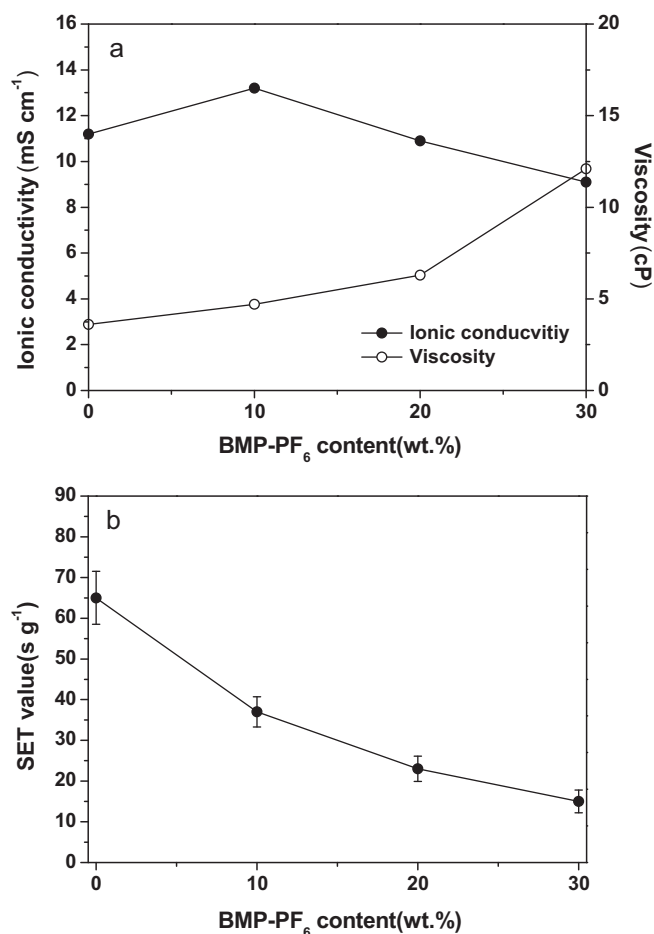


Fig. 2. (a) Ionic conductivities and viscosities, and (b) SET values of the electrolyte solutions as a function of BMP-PF₆ content.

3. Results and discussion

Fig. 2(a) shows the ionic conductivities and viscosities of the electrolyte solutions as a function of BMP-PF₆ content. The ionic conductivity increased with increasing content of BMP-PF₆, reaching a maximum ($1.3 \times 10^{-2} \text{ S cm}^{-1}$) at 10 wt.%. Since BMP-PF₆ itself has a lot of cations and anions, the number of ions in the electrolyte solution increased when BMP-PF₆ was added to the base electrolyte. As a result, the ionic conductivity initially increased with content of BMP-PF₆. On the other hand, the addition of BMP-PF₆ increased the viscosity of the resulting electrolyte solution due to the increase of ion-solvent interactions and coulombic interactions between ionic species. Thus, the decrease in ionic conductivity beyond 10 wt.% BMP-PF₆ was attributed to the increase in viscosity due to the addition of BMP-PF₆. In order to investigate the flammable behavior of the electrolyte solution containing BMP-PF₆, a flammability test was performed. The SET values of electrolyte solutions with varying BMP-PF₆ content are also shown in Fig. 2(b). For each composition, at least five measurements were done, and the average values were plotted as data points with error bars indicating deviations. The burning time here can be regarded as the self-extinguishing time. BMP-PF₆ itself did not exhibit any combustion, even during ignition with a flame source (i.e., SET value is 0 s g⁻¹). As BMP-PF₆ was added into the liquid electrolyte, both the burning time and the flame intensity decreased, and hence the flammability dropped. Accordingly, the SET of the electrolyte decreased from 65 s g⁻¹ for the base electrolyte to 37 s g⁻¹ when 10 wt.% BMP-PF₆ was added. When the content of the flame

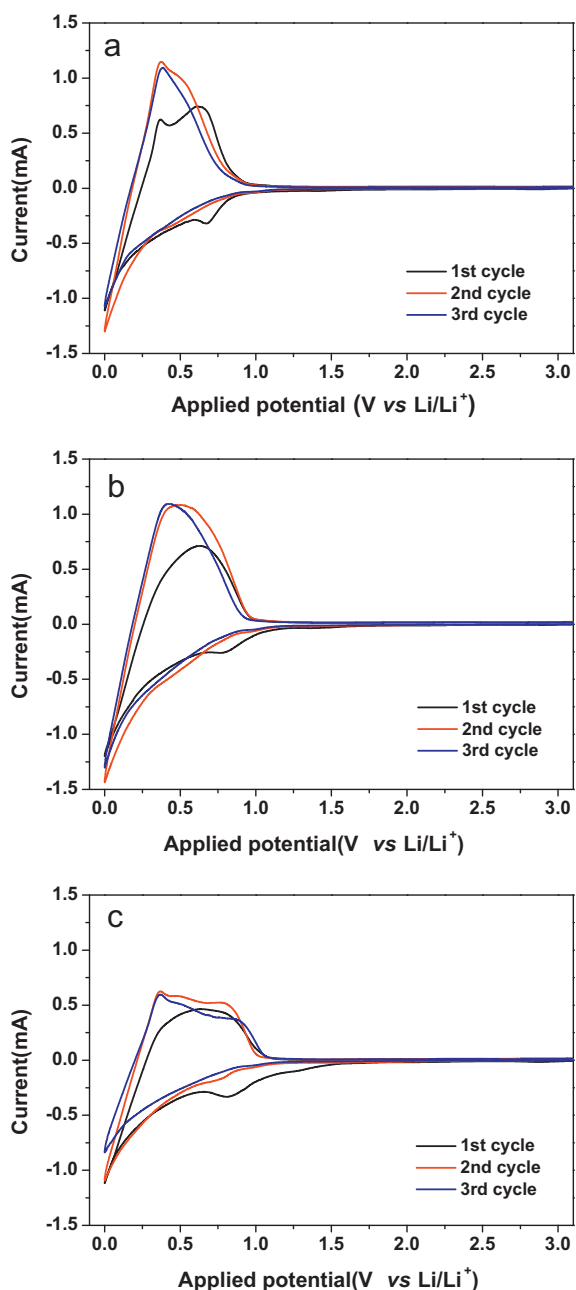


Fig. 3. Cyclic voltammograms of the carbon electrode in the electrolyte solution containing different content of BMP-PF₆. (a) 0 wt.% BMP-PF₆, (b) 10 wt.% BMP-PF₆, and (c) 30 wt.% BMP-PF₆.

retardant increased to 30 wt.%, the SET of the electrolyte decreased to 15 s g⁻¹. These results suggest that addition of BMP-PF₆ results in a reduction of the flammability of the electrolyte.

Fig. 3 shows cyclic voltammograms of the carbon electrode in the electrolyte solution containing different content of BMP-PF₆. The first cathodic process in liquid electrolyte without BMP-PF₆ (Fig. 3(a)) showed a small reduction peak around 0.69 V, which disappeared in the next cycles, attributed the reductive decomposition of electrolyte solvents [23,24]. It is plausible that FEC decomposes first on a graphite electrode at a higher potential than other solvents, because its lowest unoccupied molecular orbital (LUMO) energy is lower than those of other solvents. It provides the surface film for suppressing the reductive decomposition of other solvents. Profatilova et al. also reported that the reduction peak of the electrolyte (1 M LiPF₆ in EC/EMC, 3:7 by volume)

containing 10% FEC was observed around 0.65 V on a graphite electrode and the decomposition products of FEC mainly constituted the solid electrolyte interphase (SEI) layer on graphite electrode [25]. In the electrolyte solution containing 10 wt.% BMP-PF₆, the reduction peak was shifted toward higher potential of 0.78 V, which may arise from the reductive decomposition of BMP-PF₆ with electrolyte solvent. Reversible intercalation and deintercalation of lithium could be observed in this electrolyte system. Judging from this result, the SEI layer formed at the first cycle in the electrolyte containing 10 wt.% BMP-PF₆ would be stable. In contrast, an irreversible cathodic current started to increase at around 1.5 V and the relatively large reduction peak was observed around 0.83 V at the first cycle in the electrolyte solution containing 30 wt.% BMP-PF₆. The cathodic current started around 1.5 V corresponds to reductive decomposition of the 1-butyl-1-methylpyrrolidinium cation. This value of cathodic decomposition is in agreement with that observed in the ionic liquid electrolyte based on BMP-TFSI [26]. The irreversible reduction peak also did appear at the second cycle. The peak currents corresponding to intercalation/deintercalation of lithium were about half as large as those for the above two electrolyte systems. These results suggest that the SEI layer is not so effective for protecting a carbon electrode against an undesirable irreversible reaction in the electrolyte solution containing high amount of BMP-PF₆.

Cycling performance of lithium-ion cells assembled with electrolytes containing different amounts of BMP-PF₆ was evaluated. The assembled cells were initially subjected to a preconditioning cycle with a cut-off voltage of 3.0–4.2 V at a rate of 0.1C (0.29 mA cm⁻²), and the results are summarized in Table 1. The first discharge capacity of the lithium-ion cell using electrolyte without additive was 145.9 mAh g⁻¹ based on the LiCoO₂ active cathode material. The discharge capacities of the lithium-ion cells assembled with electrolyte containing BMP-PF₆ ranged from 121.2 to 146.6 mAh g⁻¹, depending on the content of BMP-PF₆. It should be noted that the cell containing 10 wt.% BMP-PF₆ exhibit high discharge capacity and coulombic efficiency, comparable to those of a cell using electrolyte without additive. The irreversible capacity loss in the first cycle was caused by the decomposition of electrolyte on the surface of the anode electrode, resulting in formation of a SEI layer [27,28]. Thus, the above result indicates that a stable SEI film is formed in the cell containing 10 wt.% BMP-PF₆. Decreases in discharge capacity and coulombic efficiency with further addition of BMP-PF₆ indicates that further increasing the BMP-PF₆ content does not help in improving the electrochemical characteristics of the SEI layer but instead increases the irreversible capacity due to the decomposition of the additive. Optimum additive content leading to stable SEI formation has been also reported for other flame retardant additives such as allyl tris(2,2,2-trifluoroethyl) carbonate [10] and diphenyloctyl phosphate [16].

After two preconditioning cycles, the cell was charged at a current density of 1.45 mA cm⁻² (0.5C rate) to 4.2 V. This was followed by a constant voltage charge with a decline in the current until a final current of 20% of the charging current was reached. The cell was then discharged to 3.0 V at the same current density. Fig. 4 shows the charge–discharge curves of the 1st, 20th, 50th and 100th cycles of a lithium-ion cell assembled with an electrolyte solution containing 10 wt.% BMP-PF₆. The cycling behavior of the cell was comparable to that of the cell assembled with a base liquid electrolyte with respect to the charge–discharge profiles and the reversible capacity. The cell had a first discharge capacity of 144.9 mAh g⁻¹, which then declined to 124.3 mAh g⁻¹ after 100 cycles, while the coulombic efficiency steadily increased with cycle number. Fig. 5 shows the discharge capacity as a function of cycle number in the cells prepared with electrolyte containing different amounts of additive. It is clear that the cycling characteristics of the cells are dependent on the content of BMP-PF₆. The

Table 1
The first preconditioning cycle data of cells with different electrolyte solutions.

Electrolyte	First charge capacity (mAh g ⁻¹)	First discharge capacity (mAh g ⁻¹)	Efficiency (%)
Base electrolyte	156.2	145.9	93.4
Base electrolyte + 10 wt.% BMP-PF ₆	156.6	146.6	93.6
Base electrolyte + 20 wt.% BMP-PF ₆	153.1	140.4	91.7
Base electrolyte + 30 wt.% BMP-PF ₆	138.8	121.2	87.3

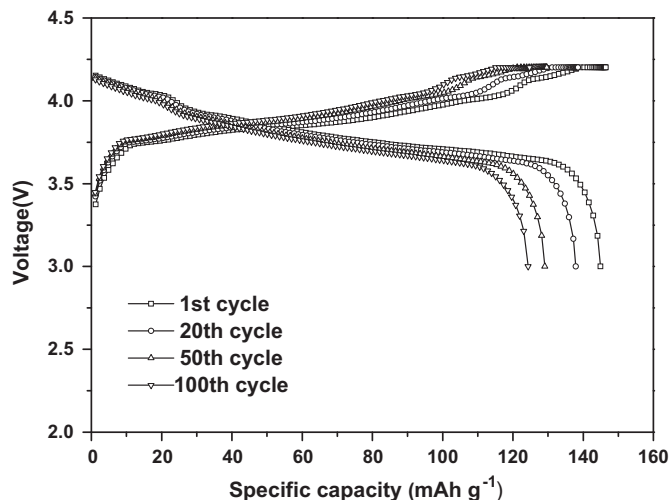


Fig. 4. Charge and discharge curves of the lithium-ion cell assembled with the electrolyte containing 10 wt.% BMP-PF₆ (0.5C CC and CV charge, 0.5C CC discharge, cut-off: 3.0–4.2 V).

initial discharge capacity exhibited a maximum at 10 wt.% and then decreased with further increase in BMP-PF₆ content. With respect to capacity retention, the cell with 30 wt.% BMP-PF₆ showed significant capacity fading during cycling. As explained earlier, excessive addition of BMP-PF₆ caused a reduction in ionic conductivity and irreversible reactions on the electrode surface, resulting in a low initial capacity and a large capacity decline. From these results, it can be concluded that the optimum content of BMP-PF₆ in the electrolyte for efficient cell operation is 10 wt.%.

In order to understand the effect of BMP-PF₆ content on cycling performance, the ac impedance of the cells before and after the repeated cycles (100 cycles) was measured. The resultant ac impedance spectra are shown in Fig. 6. Before cycling, there are

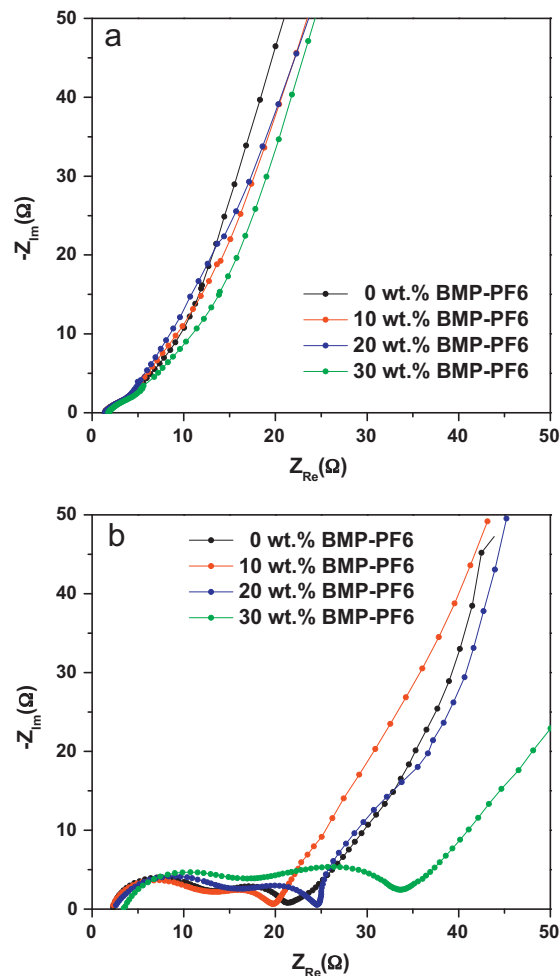


Fig. 6. AC impedance spectra (a) before and (b) after 100 charge–discharge cycles in the lithium-ion cells assembled with electrolyte solutions containing different amounts of BMP-PF₆.

no semicircles in the high frequency region. The almost identical ac impedance spectra, except for small difference in electrolyte resistance, indicate that addition of BMP-PF₆ into the base electrolyte had little effect on the interfacial behavior of the cell before cycling. After charge and discharge cycling, two overlapped semicircles were observed, as shown in Fig. 6(b). According to previous studies of ac impedance analysis [29,30], the semicircle in the high frequency range can be attributed to the resistance due to Li⁺ ion migration through the surface film on the electrode, and the semicircle in the medium-to-low frequency range is due to charge transfer resistance between the electrode and electrolyte. The cell containing 10 wt.% BMP-PF₆ exhibited the lowest surface film resistance (11.2 Ω) and charge transfer resistance (6.2 Ω). This result implies that the addition of 10 wt.% BMP-PF₆ has a beneficial influence to the formation of a stable interface between the electrode and electrolyte. When BMP-PF₆ was present at greater than 10 wt.%, both the surface film resistance and the charge transfer resistance increased. In the electrolyte solution containing 30 wt.%

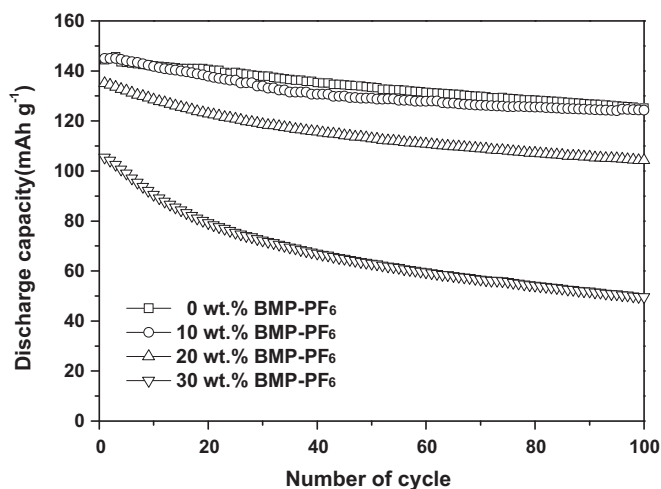


Fig. 5. Discharge capacities as a function of cycle number for lithium-ion cells assembled with electrolytes containing different amounts of BMP-PF₆ (room temperature, 0.5C CC and CV charge, 0.5C CC discharge, cut-off voltage range: 3.0–4.2 V).

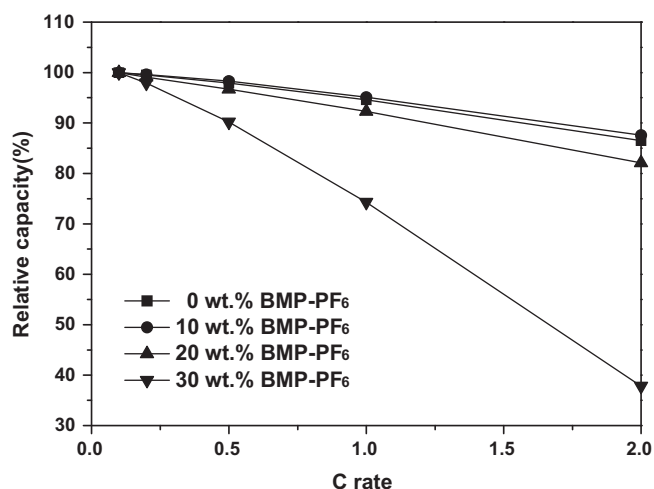


Fig. 7. Relative capacities, as a function of the current rate, of lithium-ion cells assembled with different amounts of BMP-PF₆.

BMP-PF₆, surface film resistance and charge transfer resistance increased to 14.1 and 16.0 Ω, respectively. These results suggest that in the presence of excess BMP-PF₆, the resistive surface film formed at electrode surface hampers charge transport at the electrode and electrolyte interface, which causes an increase in charge transfer resistance. Also an additional contribution to charge transfer resistance from a loss of interfacial contact between the electrode materials and the electrolyte solution, arising from the viscous nature of the electrolyte, cannot be excluded. Thus, proper control of the BMP-PF₆ content is very important for achieving stable interfacial behavior.

Rate capabilities of lithium-ion cells prepared with electrolytes containing different amounts of BMP-PF₆ were evaluated. Fig. 7 compares the rate capabilities of the lithium-ion cells using these electrolyte solutions. For this test, the cells were charged to 4.2 V at a constant rate of 0.2C and discharged at rates varying from 0.1 to 2.0C. In this figure, the relative capacity is defined as the ratio of the discharge capacity at a specific C rate to the discharge capacity delivered at a 0.1C rate. The results showed that the content of the BMP-PF₆ affected high rate performance. When 10 wt.% BMP-PF₆ was added into the base electrolyte, the relative capacity at 2.0C rate was the highest. This was explained by the favorable interfacial charge transport kinetics and the high ionic conductivity of the

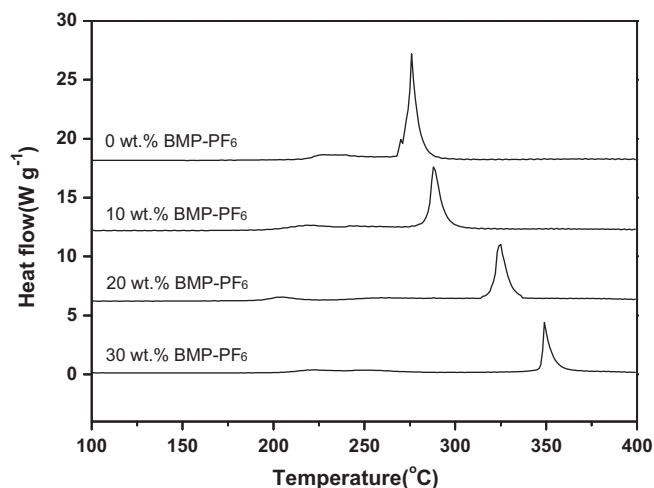


Fig. 8. DSC profiles of Li_{1-x}CoO₂ cathode materials charged to 4.2 V in the electrolyte solutions containing different amounts of BMP-PF₆.

electrolyte containing 10 wt.% BMP-PF₆. A large reduction in the rate performance of the cell containing 30 wt.% BMP-PF₆ may have arisen from the high internal resistance of the cell, as explained in Fig. 6(b).

Fig. 8 compares the DSC profiles of the charged cathode materials in the electrolytes containing different amounts of BMP-PF₆. The main exothermic peaks occurring between 250 and 360 °C are associated with oxidation reactions of the organic solvents with oxygen released from the charge Li_{1-x}CoO₂ lattice [31–33]. The onset temperature of the main exothermic reaction shifted to a high temperature, and the heat generated by the thermal reaction of the charged cathode with the electrolyte was reduced when the content of BMP-PF₆ increased. These results suggested that an increase in the content of BMP-PF₆ mitigated the exothermic reaction. A very small and broad exothermic peak prior to main peak is believed to decomposition of the surface films formed on the cathode [15,17]. Accordingly, it may affect thermal behavior of the lithium-ion batteries. Further detailed studies on thermal decomposition of surface film for enhancing thermal safety of the cells are necessary.

4. Conclusions

Electrolyte solutions prepared with different amounts of a flame retardant, BMP-PF₆, were investigated. Self-extinguishing time and DSC studies demonstrated that BMP-PF₆ was efficient in reducing the flammability of the electrolytes and improving the thermal stability of the charged LiCoO₂ cathode. It was very encouraging that the addition of 10 wt.% BMP-PF₆ to the base electrolyte could improve the safety without degrading cycling performance of the cell. These results demonstrate that BMP-PF₆ is a promising flame-retarding additive for improving the cell performance and thermal stability of the cell.

Acknowledgments

This work was supported by the IT R&D program of MKE/KEIT (KI002176-2010-02) and by a grant from the National Research Foundation of Korea funded by the MEST of the Korean Government (NRF-2009-0092780 and NRF-2009-C1AAA001-0093307).

References

- [1] W.A. van Schalkwijk, B. Scrosati (Eds.), *Advances in Lithium-ion Batteries*, Kluwer Academic/Plenum Publishers, New York, 2002.
- [2] G.-A. Nazri, G. Pistoia (Eds.), *Lithium Batteries*, Kluwer Academic Publishers, Boston, 2004.
- [3] C.W. Lee, R. Venkatchalapathy, J. Prakash, *Electrochim. Solid State Lett.* 3 (2000) 63.
- [4] J. Yamaki, I. Yamazaki, M. Egashira, S. Okada, *J. Power Sources* 102 (2001) 288.
- [5] M.S. Ding, K. Xu, T.R. Jow, *J. Electrochem. Soc.* 149 (2002) A1489.
- [6] J. Arai, *J. Power Sources* 119–121 (2003) 388.
- [7] X.M. Wang, Y. Chisa, N. Hitoshi, S. Go, K. Koichi, *J. Electrochem. Soc.* 153 (2006) A135.
- [8] E.G. Shim, T.H. Nam, J.G. Kim, H.S. Kim, S.I. Moon, *Electrochim. Acta* 53 (2007) 650.
- [9] T.H. Nam, E.G. Shim, J.G. Kim, H.S. Kim, S.I. Moon, *J. Electrochem. Soc.* 154 (2007) A957.
- [10] S. Chen, Z. Wang, H. Zhao, H. Qiao, H. Luan, L. Chen, *J. Power Sources* 187 (2009) 229.
- [11] D. Zhou, W. Li, C. Tan, X. Zuo, Y. Huang, *J. Power Sources* 184 (2008) 589.
- [12] H.F. Xiang, H.Y. Xu, Z.Z. Wang, C.H. Chen, *J. Power Sources* 173 (2007) 562.
- [13] T. Tsujikawa, K. Yabuta, T. Matsushita, T. Matsushima, K. Hayashi, M. Arakawa, *J. Power Sources* 189 (2009) 429.
- [14] H.P. Zhang, Q. Xia, B. Wang, L.C. Yang, Y.P. Wu, D.L. Sun, C.L. Gan, H.J. Luo, A.W. Bebede, T. van Ree, *Electrochem. Commun.* 11 (2009) 526.
- [15] Y. Shigematsu, M. Ue, J. Yamaki, *J. Electrochem. Soc.* 156 (2009) A176.
- [16] E.G. Shim, T.H. Nam, J.G. Kim, H.S. Kim, S.I. Moon, *Electrochim. Acta* 54 (2009) 2276.
- [17] K. Kim, S. Ahn, H.S. Kim, H.K. Liu, *Electrochim. Acta* 54 (2009) 2259.
- [18] S.I. Gonzales, W. Li, B.L. Lucht, *J. Power Sources* 135 (2004) 291.
- [19] S.M. Eo, E. Cha, D.W. Kim, *J. Power Sources* 189 (2009) 766.
- [20] K. Xu, M.S. Ding, S. Zhang, J.L. Allen, T.R. Jow, *J. Electrochem. Soc.* 149 (2002) A622.

- [21] X.L. Yao, S. Xie, C.H. Chen, Q.S. Wang, J.H. Sun, Y.L. Li, S.X. Lu, *J. Power Sources* 144 (2005) 170.
- [22] S.R. Sivakkumar, D.R. MacFarlane, M. Forsyth, D.W. Kim, *J. Electrochem. Soc.* 154 (2007) A834.
- [23] H. Zheng, K. Jiang, T. Abe, Z. Ogumi, *Carbon* 44 (2006) 203.
- [24] I.A. Profatlova, N.S. Choi, S.W. Roh, S.S. Kim, *J. Power Sources* 192 (2009) 636.
- [25] I.A. Profatlova, S.S. Kim, N.S. Choi, *Electrochim. Acta* 54 (2009) 4445.
- [26] J.A. Choi, E.G. Shim, B. Scrosati, D.W. Kim, *Bull. Korean Chem. Soc.* 31 (2010) 3190.
- [27] M. Itagaki, N. Kobari, S. Yotsuda, K. Watanabe, S. Kinoshita, M. Ue, *J. Power Sources* 148 (2005) 78.
- [28] R. Chen, F. Wu, L. Li, Y. Guan, X. Qiu, S. Chen, Y. Li, S. Wu, *J. Power Sources* 172 (2007) 395.
- [29] A. Funabiki, M. Inaba, Z. Ogumi, *J. Power Sources* 68 (1997) 227.
- [30] M.D. Levi, G. Salitra, B. Markovsky, H. Teller, D. Aurbach, U. Heider, L. Heider, *J. Electrochem. Soc.* 146 (1999) 1279.
- [31] L. Larush, V. Borgel, E. Markevich, O. Haik, E. Zinigrad, D. Aurbach, *J. Power Sources* 189 (2009) 217.
- [32] Y. Baba, S. Okada, J. Yamaki, *Solid State Ionics* 148 (2002) 311.
- [33] H. Sakabe, H. Matsumoto, K. Tatsumi, *Electrochim. Acta* 53 (2007) 1048.