



Effect of activation at elevated temperature on Li-ion batteries with flame-retarded electrolytes

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ABSTRACT

The effect of activation temperature on Li-ion batteries with flame-retarded electrolytes containing 5 wt.% dimethyl methyl phosphonate (DMMP) and trimethyl phosphate (TMP) is investigated respectively. It is found that activation at elevated temperature promotes the formation of a stable solid electrolyte interface layer on the graphite electrode, which may significantly suppress the reductive decomposition of DMMP and TMP and avoid graphite exfoliation. But fierce oxidation of the electrolytes on the LiCoO₂ electrode at elevated temperature is harmful to the cell performance. A procedure of so-called altered temperature activation (ATA) is adopted for LiCoO₂/graphite full-cells. It can compromise the contradictive effects on the separate electrodes at the elevated temperature. High capacity and good rate capability are obtained for the cells with the flame-retarded electrolytes, especially for the TMP-containing electrolyte.

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1. Introduction

It is widely considered that new energy technology will play a main role in the next round of technological revolution. And new energy vehicles are targeted in the most ambitious plan in China for stimulating economic development. Lithium-ion batteries are very attractive for electric vehicles (EV), hybrid electric vehicle (HEV) and plug-in hybrid electric vehicle (PHEV) applications, owing to their high energy density and long lifetime. However, safety concern is one of the biggest barriers for the development of lithium-ion batteries because of usage of the flammable electrolytes. Thus, the flame-retarded electrolytes have interested the battery industry and research communities [1–7]. Among the various flame-retardant additives/cosolvents, trimethyl phosphate (TMP) and dimethyl methyl phosphonate (DMMP) are highly promising for the battery industry. Both of them have high phosphonic content, low cost and excellent physicochemical characteristics, including low viscosity, high dielectric constant, low melting point and high boiling point. The high phosphonic content results in high flame-retardant efficiency so that only 5% content of additive would have distinct improvement to the safety characteristic of the electrolyte. However, similar to propylene carbonate

(PC), the flame-retarded electrolytes usually have the bad compatibility with the commonly used graphite anode because exfoliation will be caused by the decomposition products with unidentified compositions from the reduction of DMMP and TMP, that occurs at a higher potential than that to form a stable solid electrolyte interface (SEI) layer [1,8]. Although the surface-modified graphite with the amorphous carbon and film-formation additives are helpful in this regard, there are still some questions [2,8,9]. For example, the surface-modified graphite has such a high price that it has not been used widely in the industry. And the film-formation additives usually increase the impedance of cell, which becomes flagrant especially at a high current rate or in a high content of additive. In our previous work [10], the initial lithium-intercalation temperature was found to have a great impact on the extent of the graphite exfoliation in the PC-based electrolyte. At an elevated temperature (50 °C), the exfoliation can be largely suppressed and the irreversible capacity loss is reduced substantially. Since the flame-retarded electrolytes have the same problem of graphite exfoliation as the PC-based electrolyte, it is necessary to investigate the effect of temperature on the graphite exfoliation in the electrolytes containing DMMP and TMP.

In this work, the effect of activation at elevated temperature on a graphite negative electrode and LiCoO₂ positive electrode is investigated, respectively, in the flame-retarded DMMP- and TMP-containing electrolytes. Moreover, the LiCoO₂/MAG10 full-cells with the flame-retarded electrolytes are compared with those

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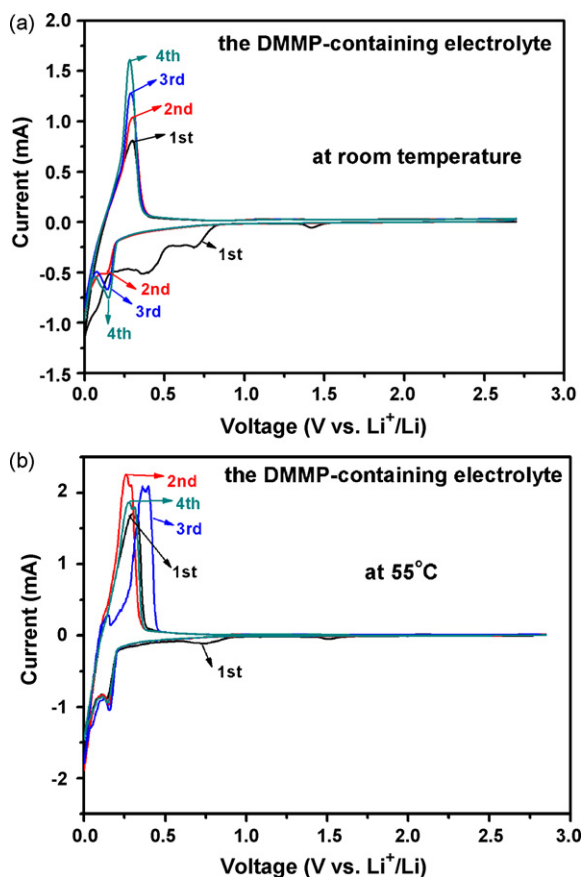


Fig. 1. Cyclic voltammograms of MAG10/Li cells with the DMMP-containing electrolyte (1 M LiPF₆/EC + DEC (1:1) + 5% DMMP) at room temperature (a) and at 55 °C (b). The potential scan rate was 0.2 mV s⁻¹.

cells with the electrolyte modified by a film-formation additive, vinyl ethylene carbonate (VEC), for the sake of DMMP and TMP applied to Li-ion batteries in an optimal way.

2. Experimental

As-purchased DMMP and TMP were purified with a distillation step under vacuum and dried before use over molecular sieves (4A). The flame-retarded electrolytes were prepared by adding 5 wt.% DMMP and TMP into the baseline electrolyte of 1 M LiPF₆ in the mixture of ethylene carbonate (EC) + diethyl carbonate (DEC) (1:1, w/w), respectively, in an Argon-filled glove box (MBraun Labmaster 130). A graphite electrode consisting of 80 wt.% MAG10 (Hitachi Powdered Metals Co. Ltd.) and 20 wt.% poly(vinylidene fluoride) (PVDF) and a positive electrode consisting of 84 wt.% LiCoO₂, 8 wt.% acetylene black and 8 wt.% PVDF were made on copper foils and aluminum foils, respectively. The mass of MAG10 and LiCoO₂ in the composite electrodes above was controlled at about 2.3 mg and 5 mg, respectively.

CR2032 coin cells were assembled in the glove box and then cycled on a multi-channel battery cyler (Neware BTS2300, Shenzhen). The MAG10/Li half-cells were galvanostatically cycled between 0 V and 2.0 V at a current density of 0.2 mA cm⁻² at room temperature and 55 °C, respectively. The internal resistance of the cells was also measured by a current interruption technique. This was done by cutting off the current intermittently for 1 min through the process of charge (Li intercalation in the graphite) and recording the voltage change after interruption. Thus, the dc impedance of a cell (R_{dc}) can be calculated as $R_{dc} = \Delta U / \Delta I$, where ΔU is the difference between the voltage of before and after the 1-min interruption,

and ΔI is approximately equal to the value of constant current for cycling [11]. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) (CHI604 Electrochemical Workstation) were also used to study the electrochemical stability of the electrolyte at a scan rate of 0.2 mV s⁻¹, and the scan ranges were set at 3.0–0 V for the MAG10/Li cells and at 3.0–4.2 V for the LiCoO₂/Li cells, respectively. The LiCoO₂/Li half-cells and LiCoO₂/MAG10 full-cells were galvanostatically cycled between 2.8 V and 4.2 V at a current density of 0.2 mA cm⁻² (equivalent to about 1/3C). For comparison, other electrolytes modified by VEC were prepared by adding 2 wt.% VEC into the flame-retarded electrolytes with 5 wt.% DMMP or TMP.

3. Results and discussion

CV measurement (Figs. 1 and 2) has confirmed the suppression effect on the reductive decomposition of the flame-retarded electrolytes on the graphite at elevated temperature (55 °C). Fig. 1 shows CV results of the DMMP-containing electrolyte (5 wt.% DMMP added in the baseline electrolyte) at room temperature and 55 °C. At room temperature (Fig. 1a), during the first cathodic scan, a large cathodic band from 0.84 V to 0.25 V suggests the reductive decomposition of DMMP on the graphite, which consists of two parts with the peaks at about 0.7 V and 0.4 V. At the lower potential range (0.25–0 V), the cathodic peak is corresponding to lithium intercalation into the graphite, and the reverse scan (lithium deintercalation) gives rise to a sharp anodic peak at about 0.3 V. In the following scans, the anodic peaks gradually rise, which might suggest that an unstable solid electrolyte interface (SEI) layer is formed. In contrast to the room temperature cycling, an obvious cathodic peak from 0.95 V to 0.6 V is believed as a symbol of

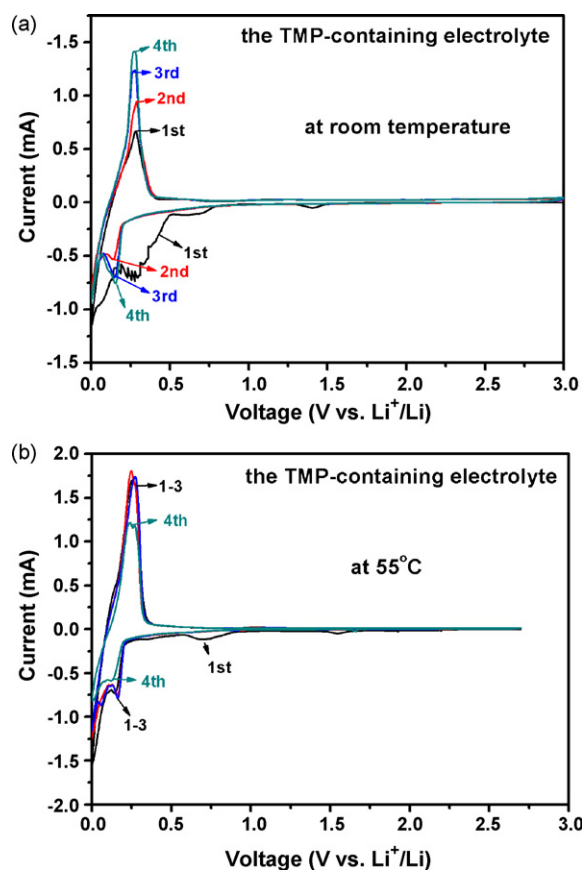


Fig. 2. Cyclic voltammograms of MAG10/Li cells with the TMP-containing electrolyte (1 M LiPF₆/EC + DEC (1:1) + 5% TMP) at room temperature (a) and at 55 °C (b). The potential scan rate was 0.2 mV s⁻¹.

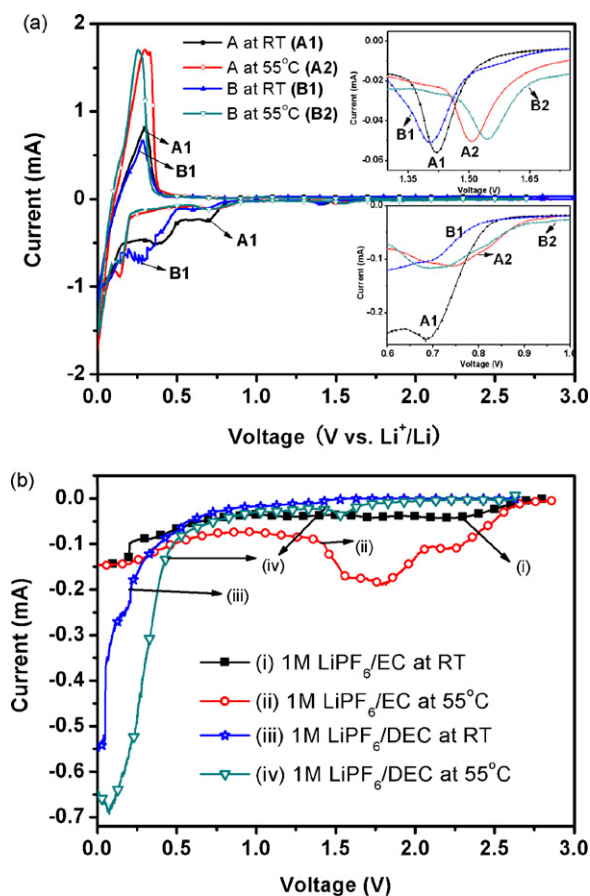


Fig. 3. Comparison of CV results (a) between the DMMP-containing electrolyte (A) and the TMP-containing electrolyte (B) in the MAG10/Li cells at room temperature and 55 °C. (A1) The DMMP-containing electrolyte at room temperature; (A2) the DMMP-containing electrolyte at 55 °C; (B1) the TMP-containing electrolyte at room temperature; (B2) the TMP-containing electrolyte at 55 °C. LSV results (b) of 1 M LiPF₆/EC electrolyte and 1 M LiPF₆/DEC electrolyte in the MAG10/Li cells at room temperature and 55 °C.

an SEI layer at 55 °C (Fig. 1b). Moreover, in the following scans, the observed rather stable peak intensities suggest that the SEI layer formed is quite stable. Such a stable SEI layer can effectively suppress the reductive decomposition of DMMP and graphite exfoliation, and the higher reversibility and capacity (peak area) of intercalation–deintercalation for Li⁺ can be concluded from the much stronger intercalation–deintercalation peaks (Fig. 1b) than those in Fig. 1a.

As far as the TMP-containing electrolyte (5 wt.% TMP added in the baseline electrolyte) is concerned, similar results have been obtained as shown in Fig. 2. Comparing Fig. 2b with a, it can be concluded that reductive decomposition of TMP and graphite exfoliation is also suppressed by a stable SEI layer formed at 55 °C. By comparing the first cathodic scans of the two electrolytes at room temperature and 55 °C in Fig. 3a, we can easily find that at 55 °C, each cathodic peak at around 1.5 V at room temperature shifts to higher cathodic potential when at 55 °C. Also, the cathodic process starting from about 0.9 V shifts to higher potential. As a result, the reductive decomposition of DMMP or TMP and graphite exfoliation have been suppressed and even avoided completely. To find out the reason, two electrolytes have been prepared, i.e. 1 M LiPF₆/EC and 1 M LiPF₆/DEC, in order to identify which solvent component plays the main role for the stable SEI layer. From Fig. 3b, it can be concluded that EC has the better performance of film-formation at elevated temperature with the cathodic reduction potential obviously higher than that of the flame-retardant additives. Hence it

plays a critical role as a film-formation additive at elevated temperature to prevent the flame-retardant additives from reduction and to suppress the graphite exfoliation.

The cell performances of the DMMP-containing electrolyte in the MAG10/Li cells are shown in Fig. 4. The first-cycle voltage profiles of the cells at room temperature (Fig. 4a) indicate that substantial reductive decomposition of DMMP accompanied with graphite exfoliation takes place in the first charge step from 0.8 V to 0.25 V, which leads to an irreversible capacity loss of about 270 mAh g⁻¹, even though the reversible charge capacity of the cell between 0 V and 2 V still reaches about 300 mAh g⁻¹. And the coulombic efficiency of the 1st cycle is only about 52%. Obviously, the addition of only 5 wt.% DMMP has a detrimental influence on the cell performance, and the flame-retarded electrolyte has bad compatibility with the graphite. However, at 55 °C the voltage plateau corresponding to the reductive decomposition of DMMP and graphite exfoliation basically disappears. Moreover, the reversible capacity rises to 352 mAh g⁻¹, and the coulombic efficiency reaches 82%. From Fig. 4b, the cells at 55 °C retain higher reversible capacity and better cycling performance, which indicates that the SEI layer formed at 55 °C is stable enough to protect the graphite and DMMP. That is, the compatibility between the graphite and the DMMP-containing electrolyte could be significantly improved by activation at elevated temperature. The resistance measurements (Fig. 4c and d) show that the cells cycled at 55 °C have the lower area-specific-impedance (ASI) either in the 1st cycle or in the 10th cycle. The reductive decomposition of DMMP could definitely destroy the structure of graphite, and the so-called exfoliation makes it difficult for graphite particles to contact with each other, which will cause higher ASI. When a stable SEI layer formed at 55 °C protects the graphite from exfoliation, the cells will have lower ASI. Thus, the cells cycled at 55 °C have higher reversible capacity and better capacity retention.

For the TMP-containing electrolyte, the similar results can be obtained (Fig. 5). At 55 °C, the reversible capacity rises to 354 mAh g⁻¹ from 330 mAh g⁻¹ at room temperature, with the higher coulombic efficiency of 81% from 55% (Fig. 5a). Owing to the stable SEI layer formed at 55 °C, reductive decomposition of TMP and graphite exfoliation are avoided so that the cycling performance is much better than that of the cells cycled at room temperature (Fig. 5b). The stable SEI layer that contributes to a lower impedance of the cell cycled at 55 °C has been validated by the ASI results of the 1st cycle and the 10th cycle (Fig. 5c and d).

Based on the results above and our previous work on PC-based electrolyte [10], it is definitely proved that activation at elevated temperature is beneficial for these electrolytes which have bad compatibility with the graphite electrode. However, we should also investigate the electrochemical behavior of electrolyte at elevated temperature on positive electrodes such as LiCoO₂. Fig. 6a shows the first voltage profiles at 55 °C of LiCoO₂/Li cells with three kinds of electrolytes: the baseline electrolyte, the DMMP- and the TMP-containing electrolyte. It is obvious that all the cells have low coulombic efficiencies of about 60%. Compared with the cells cycled at room temperature, the cells cycled at 55 °C all have higher charge capacity and lower discharge capacity. From the CV results shown in Fig. 6b, it can be found that the baseline electrolyte has a lower anodic onset potential in the LiCoO₂/Li cell at 55 °C than at room temperature. So it can be concluded that the electrolytes in the LiCoO₂/Li cells at 55 °C experience violent oxidative decomposition which leads to much higher apparent charge capacity than the theoretical capacity of LiCoO₂. More oxidation products formed on the surface of LiCoO₂ electrode result in higher impedance at 55 °C, which is the reason for the lower discharge capacity than at room temperature. Although unfortunate results come from the LiCoO₂/Li cells at elevated temperature, we surmise that ruinous oxidation of the electrolyte should mainly occur at relatively high

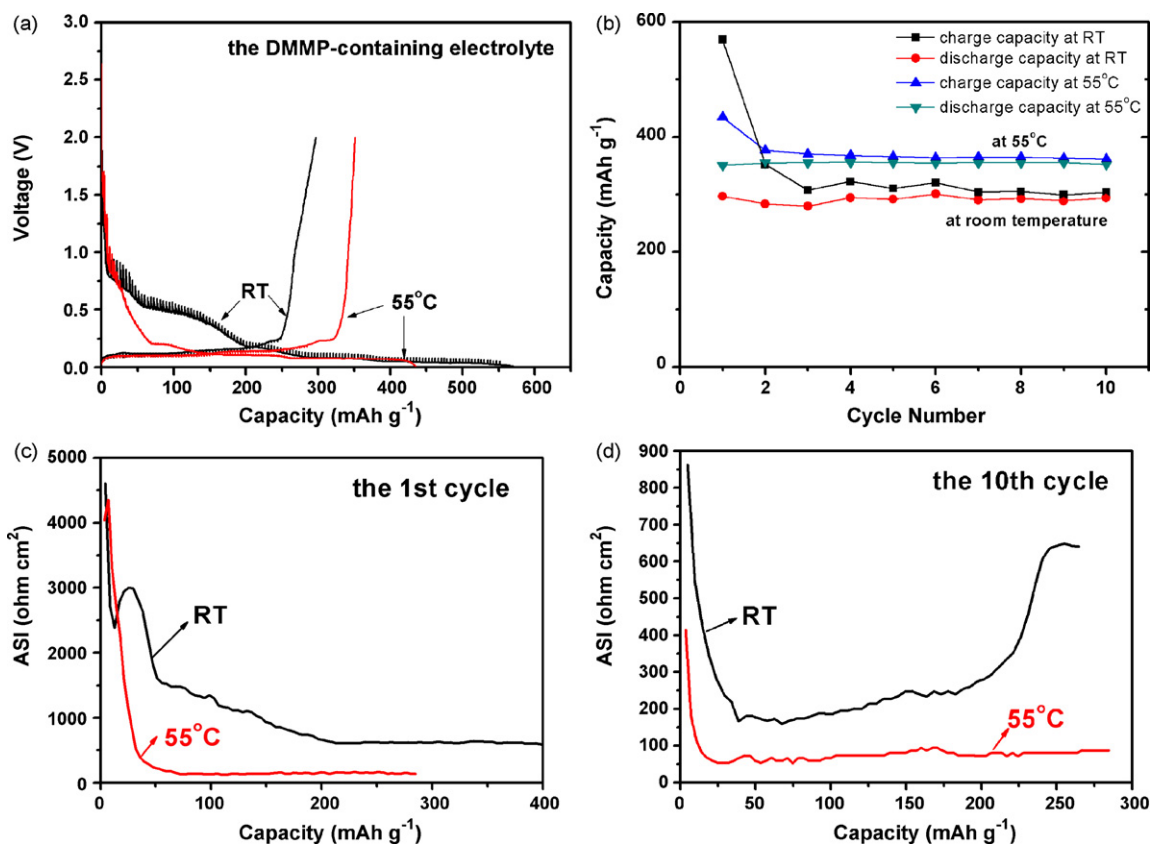


Fig. 4. First-cycle voltage profiles (a) and the cycling performance (b) of MAG10/Li cells with the DMMP-containing electrolyte at room temperature and 55 °C. The current density was 0.2 mA cm⁻². And the area-specific-impedance (ASI) at the 1st cycle (c) and the 10th cycle (d) is shown.

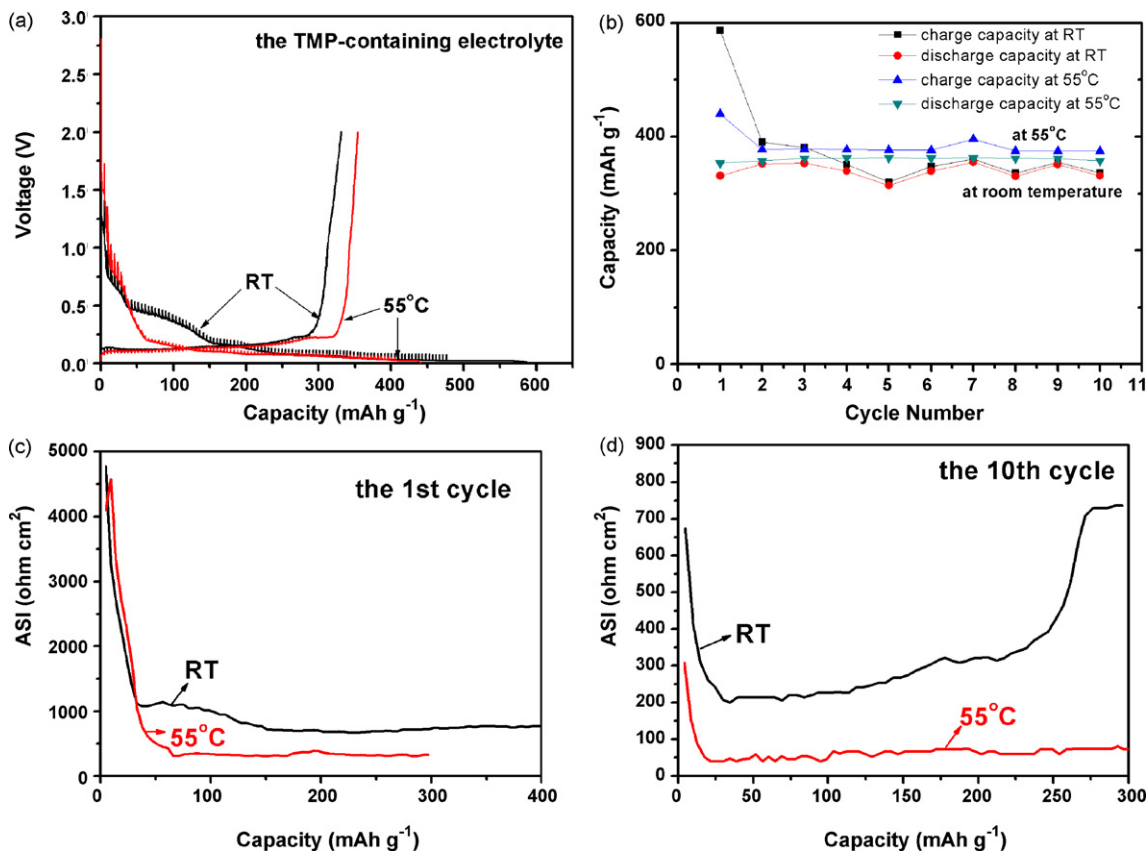


Fig. 5. First-cycle voltage profiles (a) and the cycling performance (b) of MAG10/Li cells with the TMP-containing electrolyte at room temperature and 55 °C. The current density was 0.2 mA cm⁻². And the area-specific-impedance (ASI) at the 1st cycle (c) and the 10th cycle (d) is shown.

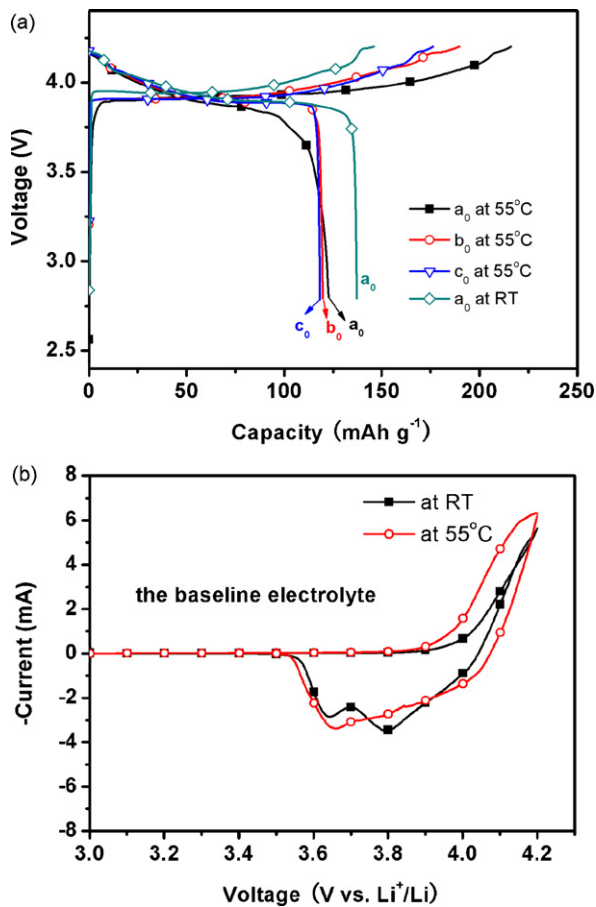


Fig. 6. First-cycle voltage profiles (a) and cyclic voltammograms (b) of LiCoO₂/Li cells with the different electrolytes at room temperature and 55 °C. (a₀) The baseline electrolyte; (b₀) the DMMP-containing electrolyte; (c₀) the TMP-containing electrolyte. The current density was 0.2 mA cm⁻².

electrode potentials. Perhaps it is not too bad at the beginning of the charge process, where the SEI layer at the negative electrode is usually formed. Therefore, the contradictory effects of activation at elevated temperature on the positive and negative electrodes in the flame-retarded electrolytes could be compromised if only the film-formation process was activated at elevated temperature and the following Li-intercalation process into the graphitic layers was performed at room temperature.

LiCoO₂/MAG10 full-cells were assembled into the CR2032 coin cells with 2.3 mg MAG10 and 5.0 mg LiCoO₂ for each cell, to make the capacity of the cells limited by the positive electrode. An altered temperature activation (ATA) procedure, i.e. a cell was charged to 3.6 V first at 55 °C followed by charged to 4.2 V continuously and discharged at room temperature, was adopted for the full-cells. The 3.6 V is considered roughly as the end point for the film-formation process and the beginning for the Li-intercalation process. Fig. 7a shows the first voltage profiles of LiCoO₂/MAG10 full-cells with the DMMP-containing electrolyte under the three different activation conditions, which is compared with the effect of the film-formation additive (VEC) on the compatibility between the DMMP-containing electrolyte and the graphite electrode. When the cell is activated at room temperature, there is a charge plateau at 3.4 V, which is corresponding to reductive decomposition of DMMP at around 0.5 V at the MAG10 negative electrode. The voltage of 3.4 V here is the difference between 3.9 V charge plateau for LiCoO₂ and the 0.5 V plateau for DMMP reduction. As the result of the reductive decomposition of DMMP and graphite exfoliation (Fig. 4a), the discharge capacity is only 50 mAh g⁻¹ (curve a). When the cell was cycled at 55 °C, the

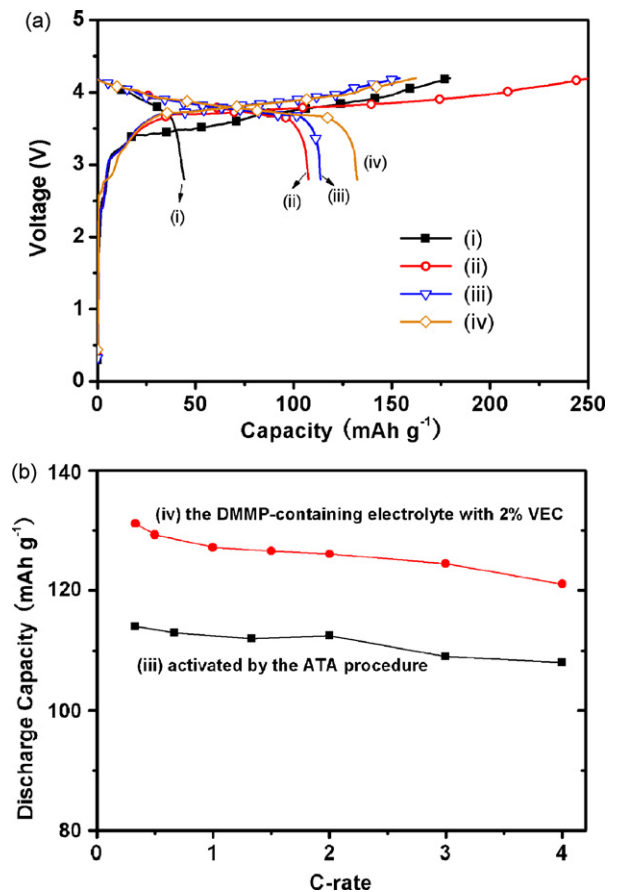


Fig. 7. First-cycle voltage profiles (a) and rate capability (b) of LiCoO₂/MAG10 full-cells with the DMMP-containing electrolytes by different activation procedures. (i) Activated at room temperature; (ii) activated at 55 °C; (iii) activated by the ATA procedure; (iv) the DMMP-containing electrolyte with 2% VEC activated at room temperature. All the cells was charged at a current density of 0.2 mA cm⁻², which is equivalent to a current rate of 1/3C.

discharge capacity is distinctly improved to 107 mAh g⁻¹ (curve b), but a high charge capacity of 251 mAh g⁻¹ is also measured, which suggests that the violent oxidation of the electrolyte on the LiCoO₂ positive electrode could cause a sharp rise of the cell impedance. When ATA is adopted, the discharge capacity is further improved to 114 mAh g⁻¹ (curve c). More importantly, the oxidation of the electrolyte on the LiCoO₂ positive electrode is suppressed significantly in addition to the improvement on the MAG10 negative electrode. However, the film-formation additive, VEC, seems to be more suitable for the DMMP-containing electrolyte, because the full-cell gives a higher discharge capacity of 132 mAh g⁻¹ when 2% VEC is introduced in the electrolyte (curve d). The rate capability of the cell activated by ATA method as well as modified by VEC is shown in Fig. 7b. It can be found that the full-cell activated by ATA method has good rate capability, the discharge capacity at the rate of 4C is 97 mAh g⁻¹ that is 85% of the discharge capacity at the 1/3C rate, and the full-cell with the electrolyte modified by VEC also exhibits excellent rate capability. Moreover, the latter always maintains higher discharge capacity at the same current rate. So it can be concluded that the LiCoO₂/MAG10 full-cell with the DMMP-containing electrolyte exhibits acceptable capacity and excellent rate capability by the ATA procedure, although it is not as good as that with the electrolyte modified by VEC.

Fig. 8a shows the first voltage profiles of LiCoO₂/MAG10 full-cells with the TMP-containing electrolyte under the same conditions above as the DMMP-containing electrolyte. Similarly, the ATA procedure is more suitable for the cells with the TMP-containing

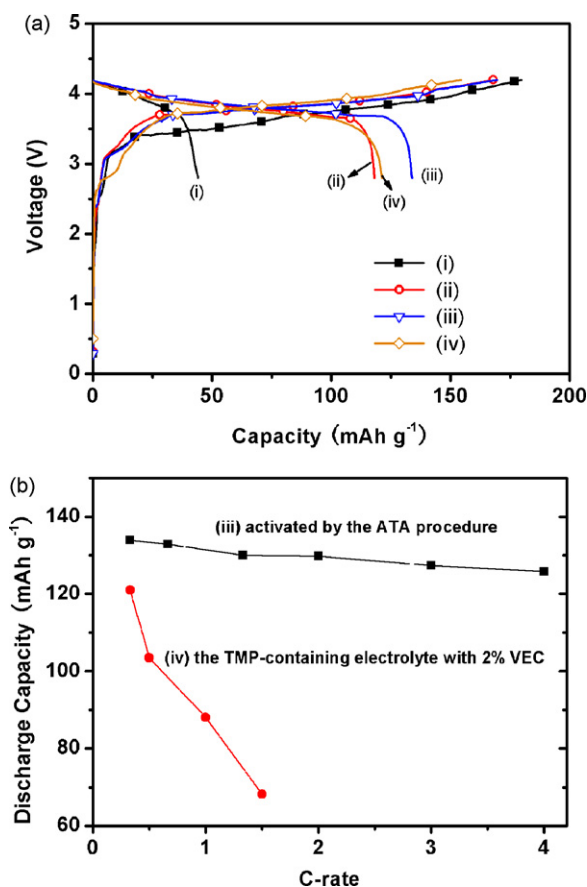


Fig. 8. First-cycle voltage profiles (a) and rate capability (b) of LiCoO₂/MAG10 full-cells with the TMP-containing electrolytes by different activation procedures. (i) Activated at room temperature; (ii) activated at 55 °C; (iii) activated by the ATA procedure; (iv) the TMP-containing electrolyte with 2% VEC activated at room temperature. All the cells was charged at a current density of 0.2 mA cm⁻², which is equivalent to a current rate of 1/3C.

electrolyte than activation at room temperature or 55 °C separately. The cell by the ATA procedure has the highest discharge capacity of 134 mAh g⁻¹ and the lowest charge capacity compared with the cells activated at room temperature and 55 °C. That is, the ATA method is also a good way to compromise the reverse effects of activation at elevated temperature on the LiCoO₂ positive electrode and the MAG10 negative electrode. When 2% VEC is added into the TMP-containing electrolyte for improving the compatibility between the electrolyte and the graphite electrode, the LiCoO₂/MAG10 cell exhibits discharge capacity of 121 mAh g⁻¹ and the first coulombic efficiency is about 80%. Therefore, it can be concluded that the film-formation additive, VEC, is also successful for the TMP-containing electrolyte. However, the discharge capacity is lower than that for the cell under the ATA condition, and higher charge plateau and lower discharge plateau suggest the cell modified by VEC has higher impedance. Fig. 8b shows the rate capability

of the cell activated by ATA method as well as modified by VEC. It is clear that the LiCoO₂/MAG10 full-cell with the electrolyte modified by VEC has the bad rate capability, which is probably owing to the higher impedance of the cell. However, the cell under the ATA condition has 126 mAh g⁻¹ discharge capacity at the 4C rate, which is 94% of the discharge capacity at the 1/3C rate. Different from the DMMP-containing electrolyte, the LiCoO₂/MAG10 full-cell with the TMP-containing electrolyte exhibit higher capacity and more excellent rate capability by the ATA procedure than that with the electrolyte modified by VEC.

4. Conclusions

Compatibility between graphite electrode and DMMP- and TMP-containing flame-retarded electrolytes can be improved by the cell activation at elevated temperature (55 °C). However, the activation at 55 °C has an adverse effect on LiCoO₂/Li half-cells. Fortunately, the contradiction can be compromised by an altered temperature activation (ATA) procedure, i.e. a cell is charged to 3.6 V first at 55 °C followed by being charged to 4.2 V and subsequently cycled at room temperature. Both DMMP- and TMP-containing flame-retarded electrolytes can be used for LiCoO₂/MAG10 full-cells directly with the ATA activation procedure above, and the cells exhibit much higher capacity than those activated only at room temperature or 55 °C. Compared with the electrolytes modified by VEC, the DMMP-containing electrolyte in a LiCoO₂/MAG10 full-cell under the ATA condition has lower discharge capacity, but the TMP-containing electrolyte leads to higher discharge capacity and much better rate capability. It is concluded that the flame-retarded electrolytes can be applied directly to the state-of-the-art Li-ion batteries by a simple activation procedure, especially for the TMP-containing electrolyte.

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References

- [1] X.M. Wang, E. Yasukawa, S. Kasuya, J. Electrochem. Soc. 148 (2001) A1058.
- [2] X.M. Wang, C. Yamada, H. Naito, G. Segami, K. Kibe, J. Electrochem. Soc. 153 (2006) A135.
- [3] K. Xu, M.S. Ding, S. Zhang, J.L. Allen, T.R. Jow, J. Electrochem. Soc. 149 (2002) A622.
- [4] Y.E. Hyung, D.R. Vissers, K. Amine, J. Power Sources 119/121 (2003) 383.
- [5] S. Zhang, K. Xu, T.R. Jow, J. Power Sources 113 (2003) 166.
- [6] 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.
- [7] H.F. Xiang, H.Y. Xu, Z.Z. Wang, C.H. Chen, J. Power Sources 173 (2007) 562.
- [8] H.F. Xiang, Q.Y. Jin, C.H. Chen, X.W. Ge, S. Guo, J.H. Sun, J. Power Sources 174 (2007) 335.
- [9] X.M. Wang, E. Yasukawa, S. Kasuya, J. Electrochem. Soc. 148 (2001) A1066.
- [10] H.F. Xiang, C.H. Chen, J. Zhang, K. Amine, J. Power Sources, accepted for publication.
- [11] H.Y. Xu, S. Xie, N. Ding, B.L. Liu, Y. Shang, C.H. Chen, Electrochim. Acta 51 (2006) 4352.