

Short communication

Electrochemical performance of lithium-ion batteries with triphenylphosphate as a flame-retardant additive

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Abstract

Safety concerns have been the key problem in the practical application of lithium-ion batteries. In the present study, triphenylphosphate (TPP) is used as an electrolyte additive to improve the thermal safety and electrochemical performance of lithium-ion cells. Cyclic voltammetric measurements and thermal stability measurements by means of differential scanning calorimetry are undertaken. Rate capability and cycling performance are evaluated. The flame-retarding additive TPP is electrochemically stable up to 4.9 V. The TPP-containing electrolytes display improved thermal stability compared with TPP-free electrolytes. The addition of 3% TPP to the ionic electrolyte is an optimum content for improvement of cell performance and suppression of electrolyte flammability.

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1. Introduction

Lithium-ion batteries are the most suitable power supply for portable applications because of their long cycle-life, high-specific energy and high-specific power. On the other hand, safety concerns remain an important issue in developing large-scale Li-ion batteries as power sources for spacecraft, electric vehicles and hybrid electric vehicles as fire and explosion accidents have been recorded [1]. Accordingly, much effort has been devoted to improving the safety characteristics of Li-ion cells [2]. Because of these safety limitations and the tendency towards thermal runaway, the use of Li-ion batteries in the marketplace has been limited to small cells of capacity 2–5 Ah [3]. Therefore, finding an effective approach to retard the fire and explosion risk of Li-ion batteries has become important.

To improve the safety of Li-ion batteries, considerable effort has been focused on the development of low flammability electrolytes [4]. A series of studies of flame retardants (FRs) based on phosphate or phosphorus compounds have been patented or published, and the presence of these FRs in electrolyte has been shown to suppress the flame propagation at the expense of cell performance. By contrast, few investigations have thus far been conducted on the effect of these phosphorus-based additives/co-solvents on the performance of Li-ion cells [5–7].

Trimethylphosphate (TMP) has been used as a FR additive in plastics production, and is being employed as an additive/co-solvent for Li-ion cells. Despite the expectation that TMP-containing electrolytes will have a FR ability, some authors [5] have concluded that the goal of a TMP-containing non-flammable electrolyte is impractical due to its poor cathodic stability. Nevertheless, there is very little available data on the application of TMP-based electrolytes in Li-ion batteries [2]. Promising results have been reported for triphenylphosphate (TPP) [3] and tris(2,2,2-trifluoroethyl) phosphate [4] in reducing the flammability of electrolytes without introducing any nega-

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tive effect on the cycling of Li-ion cells. By contrast, Doughty et al. [8] reported that the onset and runaway temperature of Li-ion cells was not improved by tris (trifluoroethyl) phosphate and TPP additives.

In this study, a low-flammability additive, TPP, was selected from a group of organic phosphate compounds. The aim is to establish a correlation between the thermal stability and electrochemical performance of TPP-containing electrolytes. Cyclic voltammetric and differential scanning calorimetry measurements are performed together with rate capability and cycle behaviour tests that included impedance studies.

2. Experimental

2.1. Coin-cell assembly

The positive electrode was fabricated with $\text{LiNi}_{0.3}\text{Mn}_{0.3}\text{Co}_{0.3}\text{O}_2$ as the active material, polyvinylidene difluoride (PVDF, Aldrich) as the binder and Super-p carbon black (SPB) as the conductive agent. The negative electrode consisted of graphite, PVDF and SPB. The PVDF was dissolved in *N*-methylpyrrolidinone (NMP, Kanto) and the active material and conducting mixture were added. The slurry was then coated on a thin foil (aluminum and copper) and dried for 12 h at 110 °C. A solution of 1 M LiPF_6 dissolved in ethylene carbonate and diethylene carbonate (EC:DEC; 1:1 by v/v) was used as a pristine electrolyte. The TPP as a FR was added directly to the electrolyte at 0, 3, 5 and 7 wt.%. Polypropylene was used for the separators. The electrochemical cells were prepared as 2032-type coin-cells and assembled in a dry room.

2.2. Cyclic voltammetric measurements

The stability of the TPP-based electrolytes was measured by cyclic voltammetry (CV). The measurements were conducted using a three-electrode cell. The potential was scanned between 0 and 5.5 V versus Li/Li^+ at a scan rate of 1 mV s^{-1} . CV measurements were made using a VMP2 system (EG&G).

2.3. Thermal stability

The thermal stability of the electrolytes was determined by means of differential scanning calorimeter (DSC) at a heating rate of 5°C min^{-1} , from 25 to 400 °C. The DSC measurements were performed with a DSC6200 system from SEICO Instruments Inc., Japan.

2.4. Charge/discharge tests

Charge–discharge tests were performed on graphite/ $\text{LiNi}_{0.3}\text{Mn}_{0.3}\text{Co}_{0.3}\text{O}_2$ coin-cells. The rate capability of the cells was evaluated via a constant current (CC) discharge at the following current drains: 0.30 mA (0.2C), 0.75 mA (0.5C), 1.50 mA (1C) and 3.0 mA (2C). The tests were conducted with steps of CC/constant-voltage (CC/CV) charging (at 0.3 mA, 4.2 V charging voltage) and CC discharging (at 0.3 mA, end-of-discharge voltage of 3.0 V). Cycle-life tests were carried out by repeated

charging (0.75 mA) and discharging (0.75 mA). The rate capability tests and cycling tests were with a VMP2 system at room temperature.

2.5. Impedance measurements

The characteristics of the 2032-type coin-cells were examined by means of ac impedance. The cells underwent electrochemical impedance spectroscopy (EIS) measurements using a VMP2 system. The frequency was varied from 100 kHz to 0.01 Hz and the amplitude was set at 10 mV. The impedance data were analyzed using ZSimpWin Version 3.00 software (EG&G).

2.6. SEM analysis

To investigate the morphology of the electrode surface, scanning electron microscopy (SEM) observation of the samples was performed before and after 40 cycles. The SEM images of samples were obtained with Hitachi S-3500H and S-4800 scanning electron microscopes.

3. Results and discussion

To measure the electrochemical stability of the electrolyte-containing FR additives, cyclic voltammetric behaviour, was examined, as shown in Fig. 1. The electrolyte is stable up to approximately 5.0 V versus Li/Li^+ in a TPP-free solution. There is no decomposition of the FR additive up to 4.9 V. This suggests that it is safe to use over the operating voltage range of 2.5–4.3 V, which covers the majority of Li-ion battery applications [3].

The DSC scans of the 1 M $\text{LiPF}_6/\text{EC}:\text{DEC}$ (1:1 by v/v) electrolyte with and without TPP as the FR additive are given in Fig. 2. An endothermic peak is observed at about 205 °C in the electrolyte without FR. All TPP-containing electrolytes display two peaks. The reaction temperature of the first peak

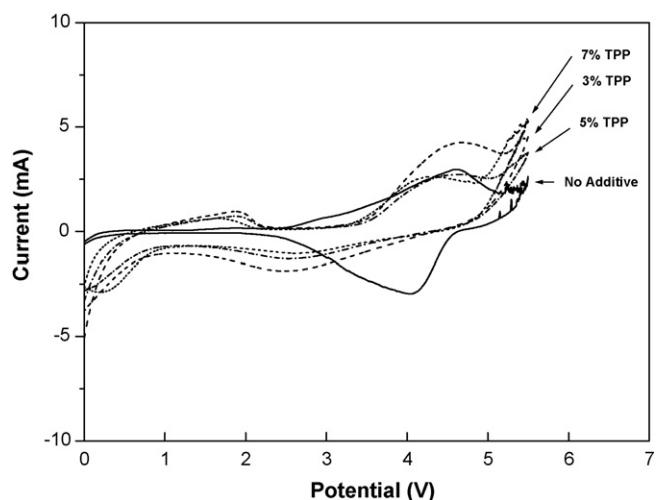


Fig. 1. Cyclic voltammograms of samples with TPP as a flame retardant additive at various contents in 1 M $\text{LiPF}_6/\text{EC}:\text{DEC}$ (1:1) electrolyte. Scan rate: 1 mV s^{-1} .

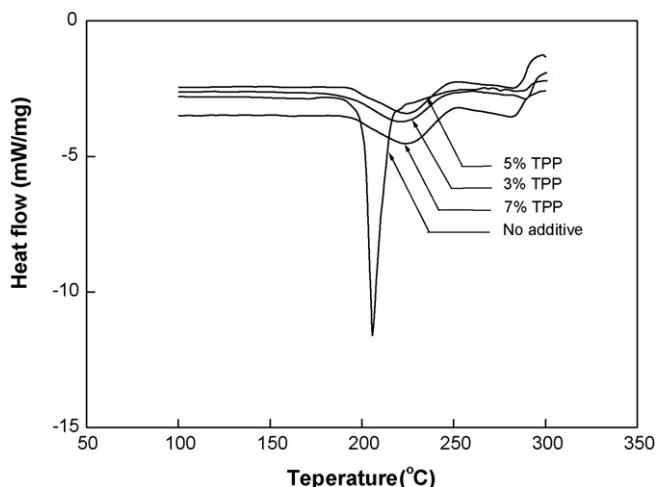


Fig. 2. DSC profiles for 1 M LiPF₆/EC:DEC (1:1 by v/v) electrolyte with and without TPP as a flame-retardant additive.

is 221, 224 and 223 °C at 3, 5 and 7 wt.% TPP, respectively. The reaction temperature did not vary significantly in the three TPP-containing electrolytes. The thermal stability of Li-ion cells is improved by using TPP-containing electrolytes. Phosphate compounds are known as FRs that function in the vapour phase by a radical mechanism. Phosphorus can also function in the condensed phase, promoting char formation on the surface that shields the substrate from heat and oxygen and interferes with the loss of decomposition products to the flame zone [3].

The effect of TPP addition in the electrolyte on the electrochemical cell performance was evaluated galvanostatically at various FR contents. In order to satisfy the demands of high-power applications, commercial Li-ion cells must deliver good performance at high-current drains. The rate capability of cells was evaluated via a CC discharge at the following current drains: 0.30 mA (0.2C), 0.75 mA (0.5C), 1.50 mA (1C) and 3.00 mA (2C). The resulting data are shown in Fig. 3. Among the FR

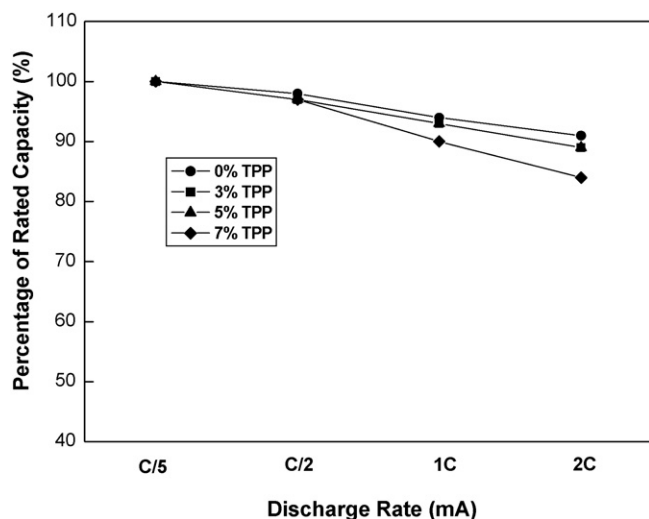


Fig. 3. Rate capability of 0, 3, 5 and 7 wt.% TPP-containing electrolytes in graphite/LiNi_{0.3}Mn_{0.3}Co_{0.3}O₂ cells.

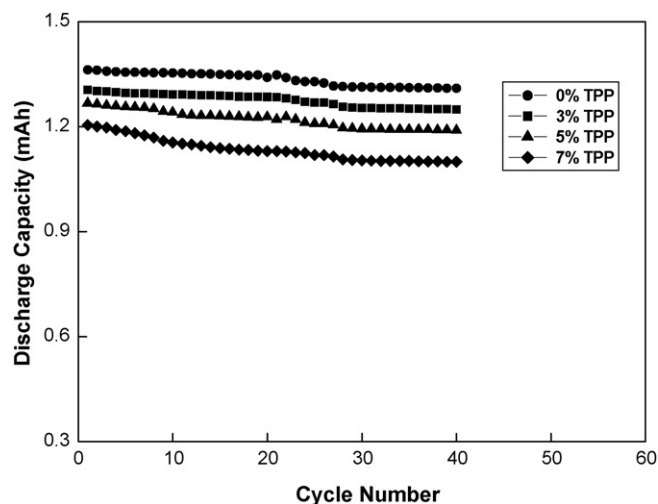


Fig. 4. Discharge capacity of 2032-type cells with charge–discharge cycling at C/2 rate.

additives, the rate capability is identical for the electrolyte with 3 and 5 wt.% added TPP (89% of rated capacity at 2C rate). By contrast, the solvent with 7 wt.% TPP does not give satisfactory results in terms of rate capability (84% of rated capacity at 2C rate). At high-current rates, the Li-ion cell can be normally discharged but it cannot, or at least only with great difficulty, be charged back from a fully discharged state. This is because the substantially high resistance of charge-transfer produces high-resistance polarization as soon as a high current is applied to fully discharged Li-ion cells [9].

Cycle-life tests were carried out by repeatedly charging and discharging. The electrochemical cycling performance of Li-ion coin-cells with electrolytes that contain various TPP concentrations is shown in Fig. 4. The initial discharge capacity is reduced with increasing TPP concentration. The TPP-containing cells experience more capacity loss on cycling than the cell with no additive, probably due to increased cell impedance. The reduced cell performance is caused either by electrochemical instability (which leads to capacity fading) or by increased viscosity of the additive (which affects capacity utilization and power) [10]. These results suggest that 1 M LiPF₆/EC:DEC (1:1)+3 wt.% TPP electrolyte gives the best cycling performance among the three TPP-additive levels examined.

In addition to the cycling data, impedance measurements were also performed on the Li-ion cells during 40 cycles. The ac impedance spectra of graphite/LiNi_{0.3}Mn_{0.3}Co_{0.3}O₂ cells containing 0, 3, 5 and 7 wt.% TPP are presented in Fig. 5. The R_{ct} values obtained in the discharged state (3.0 V) of the cells on cycling are shown in Fig. 6. A typical electrochemical impedance spectrum (EIS) of the Li-ion cells is shown in Fig. 7. In general, R_s is the electrolyte resistance of the cell, R_{sei} and C_{sei} are the resistance and capacitance, respectively, of the solid-electrolyte interface layer formed on the surface of the electrodes, which corresponds to the semicircle at high frequencies. R_{ct} and C_{dl} are the charge-transfer resistance and its relative double-layer capacitance, respectively, which correspond to the semicircle at medium frequencies. W is the Warburg impedance related to the combined effect of the diffusion of

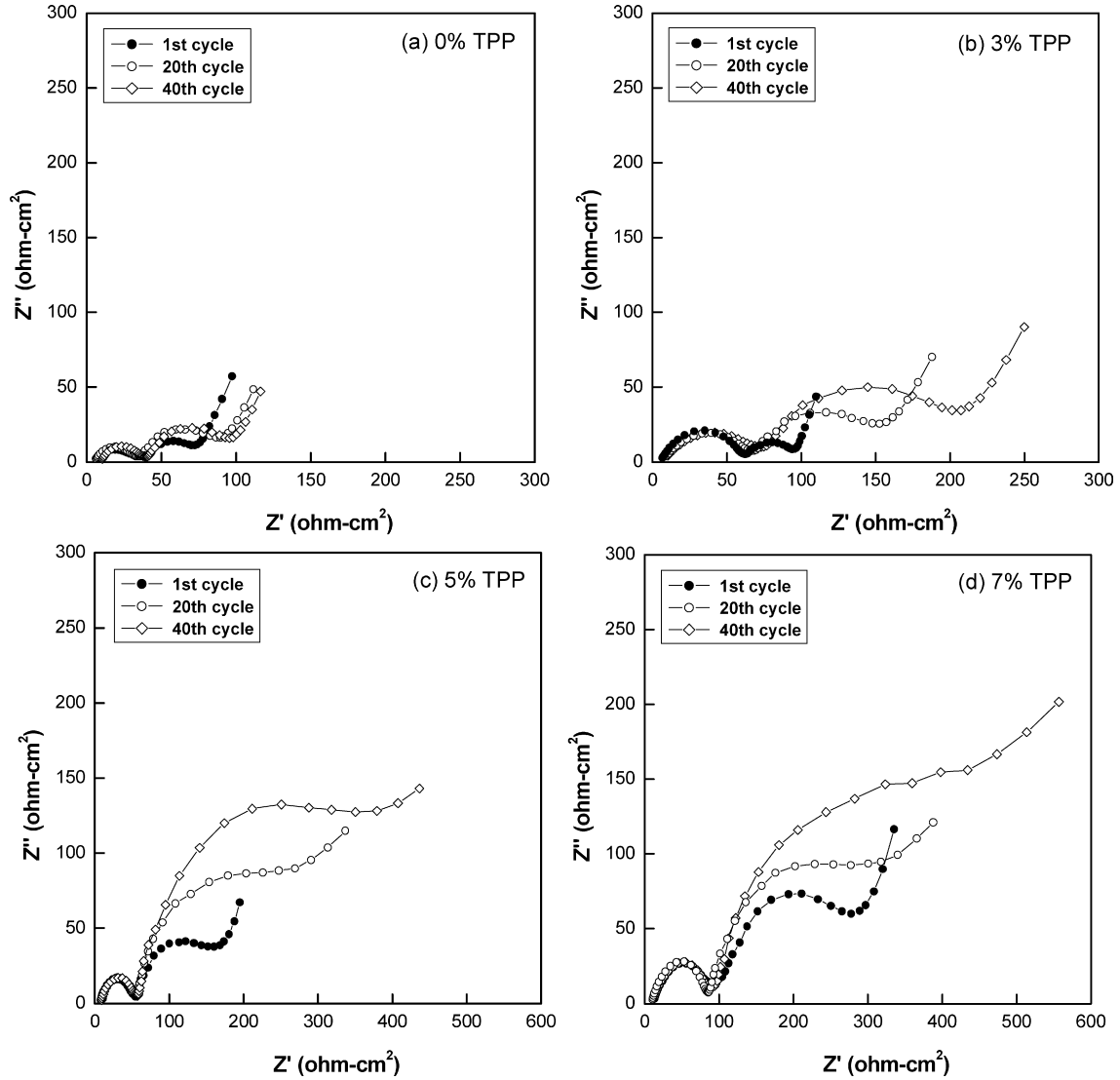


Fig. 5. Electrochemical impedance spectra in 1 M LiPF₆ EC:DEC + x wt.% TPP: (a) x = 0, (b) x = 3, (c) x = 5 and (d) x = 7.

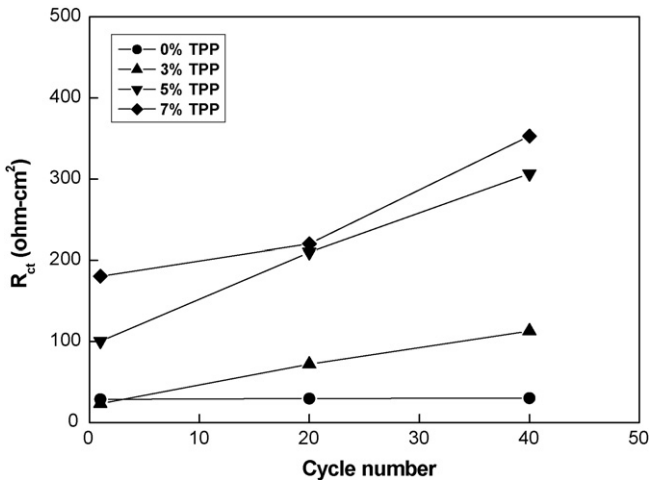


Fig. 6. Variation of R_{ct} with cycle number for 2032-type cells in four different electrolytes.

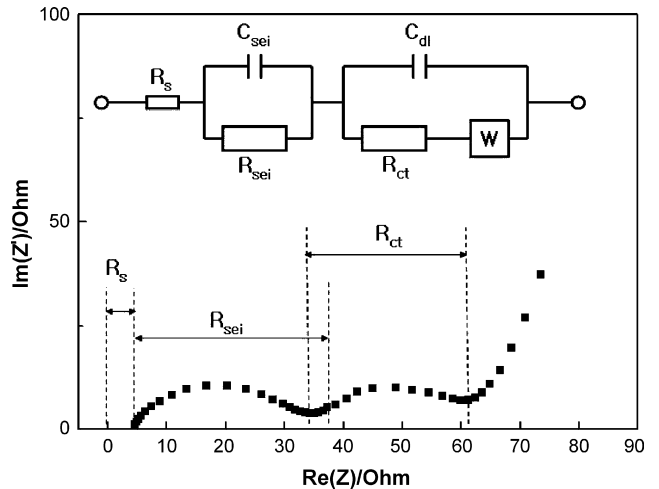


Fig. 7. Typical EIS spectrum of the Li-ion cell and equivalent circuit used to fit EIS.

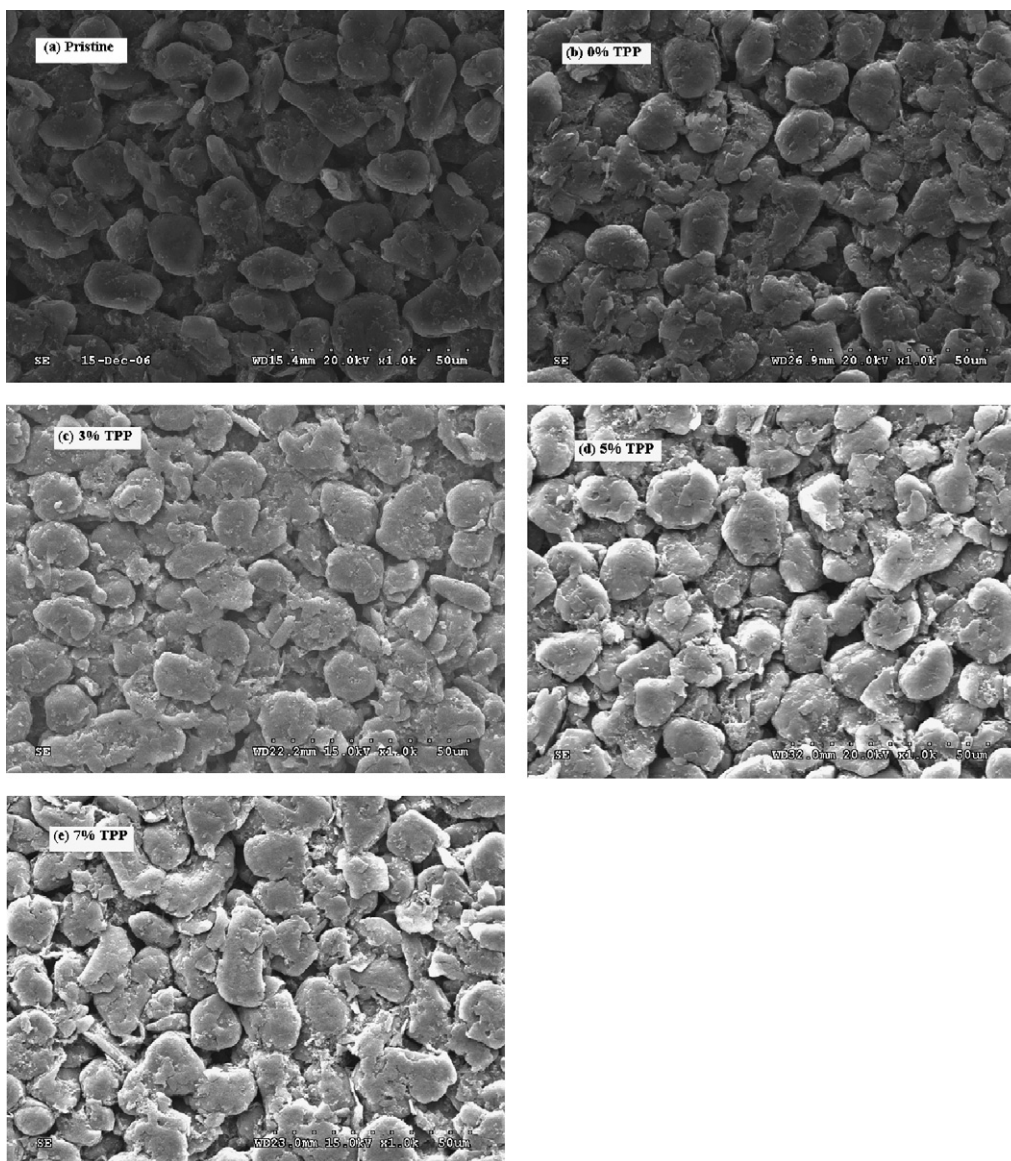


Fig. 8. SEM images of (a) pristine graphite electrode surface and of electrodes after 40 cycles with (b) 0 wt.% TPP, (c) 3 wt.% TPP, (d) 5 wt.% TPP and (e) 7 wt.% TPP.

lithium-ions at the interface between the active material particles and electrolyte, which corresponds to the straight sloping line at the low-frequency end. Since R_s and R_{sei} are ohmic in nature, their combination is called an ‘ohmic impedance’. The combination of R_{ct} and W is called a ‘faradic impedance’, which reflects the kinetics of the cell reactions. During the cycling process, R_s and R_{sei} remain relatively unchanged, while the R_{ct} varies significantly. The greatest contribution to the increase in impedance comes from the second semicircle, R_{ct} [9,11–13]. In Figs. 5 and 6, these results show an increase in resistance during the cycling process. The R_{ct} values in the TPP-free electrolyte are almost the same up to the 40 cycles. However, the R_{ct} values of the cell with 7 wt.% TPP-containing electrolyte displays an increase in its R_{ct} values from $181 \Omega \text{ cm}^2$ on the first cycle to $353 \Omega \text{ cm}^2$ after 40 cycles. Among the four electrolytes, the base electrolyte exhibits the lowest impedance. These results are similar to the cycle performance tests.

To investigate the surface morphology on the pristine and cycled electrodes, SEM images of the graphite electrode are presented in Fig. 8. The electrode surface is smooth and has spherical shapes, as shown in Fig. 8(a). The morphology change of the electrodes after 40 cycles is demonstrated in Fig. 8(b)–(e). These images show the partial exfoliation of the flakes, the roughness of the particles and the phase separation of the crystalline particles during the charge–discharge cycles. The surface of the TPP-containing electrodes, especially with 5 and 7 wt.%, have poorer phases than the TPP-free electrodes, which results in lower capacities and inferior electrochemical cycling performance.

4. Conclusions

In order to solve the safety problems suffered by Li-ion cells, tests on the electrochemical and thermal properties

of TPP-based electrolytes have been performed. The results reveal that the FR solution is electrochemically stable up to 4.9 V. The thermal stability of the cells is considerably improved by using TPP-containing electrolytes compared with the non-TPP 1 M LiPF₆/EC:DEC base electrolyte. Although the TPP-based solution gives a somewhat lower electrochemical performance than the graphite/LiNi_{0.3}Mn_{0.3}Co_{0.3}O₂ cells, among the three 1 M LiPF₆/EC:DEC + TPP electrolyte compositions tested, the best cell cycling performance is observed with 3 wt.% TPP. In conclusion, electrolyte formulations involve a trade-off between the thermal stability of the electrolyte and cell performance. Considering the effect of TPP on these two features, the optimum content of TPP is 3 wt.%.

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