

## A positive-temperature-coefficient electrode with thermal protection mechanism for rechargeable lithium batteries

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A new positive-temperature-coefficient (PTC) material was prepared simply by blending of conductive Super P carbon black (CB) with insulating poly(methyl methacrylate) (PMMA) polymer matrix, which was employed as a coating layer on the aluminium foil substrate to fabricate a sandwiched Al/PTC/LiCoO<sub>2</sub> cathode. The experimental results from cyclic voltammetry, charge-discharge measurements and impedance spectroscopy demonstrated that the PTC electrode has a normal electrochemical performance at ambient temperature, but shows an enormous increase in the resistance at the temperature range of 80–120°C. This PTC behavior greatly restrains the reaction current passing through the electrode at elevated temperatures, capable of acting as a self-actuating safety mechanism to prevent the battery from thermal runaway.

**lithium ion batteries, positive temperature coefficient, safety, poly(methyl methacrylate), thermal runaway**

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The pressures coming from environmental concerns and oil resources exhaustion have motivated the development of hybrid electric vehicles (HEV) and electric vehicles (EV). With the advantages of high energy density and excellent cycle life, lithium ion batteries are considered as a preferable power source for these applications [1–4]. However, the safety concern, originated from poor thermal-abuse tolerance of the electrode materials, severely hinders the developments and applications of large capacity or high power lithium ion batteries in EV and HEV [5–7]. Apart from the fact that lithium ion batteries are composed of a highly oxidative cathode, a strongly reductive anode, and a flammable organic-electrolyte, their safety is also associated with the inherent poor heat dissipation of non-aqueous cell [8]. Once lithium ion batteries are subjected to abuse, such as overcharging, external or internal short-circuiting, and high-temperature impact [9], a number of exothermic reactions [10–12], including thermal decomposition of the solid electrolyte interphase (SEI), reduction of the electrolyte on the

highly reactive anode, and decomposition of the cathode material, may be triggered to produce excessive heat and flammable gas spontaneously. The accumulation of evolved heat from these side reactions could cause a rapid increase in the internal temperature of the batteries, which accelerate, in turn, the chemical and electrochemical side reactions, possibly leading to thermal runaway, cell cracking, fire or even explosion [13].

For this reason, the positive temperature coefficient resistors (PTC) are usually equipped as a safety device on the crust of commercial lithium ion batteries to restrict or even prevent current flow through the cell under abusive conditions. However, this external device could not promptly sense the inner temperature changes and therefore may fail to response to the hazardous reactions occurring at very high rates in cells [14,15]. To seek for a better safety control, much effort has been focused on the development of internal and self-actuating safety mechanisms for Li-ion batteries. Several strategies, including redox shuttles [16,17], polymerizable monomers [18], and potential-sensitive separators [19], have been devised to improve safety under overcharge condition,

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but they work only at high charging voltages and actually do not respond to heat generation in batteries. Although the polyolefin microporous separator membranes commonly used in Li-ion batteries have thermal shutdown characteristics [20], they cannot retain mechanical integrity above their shutdown temperature generally. Due to thermal inertia, the temperature can continue to rise even after shutdown. Then, the separator would melt, leading to the short-circuiting of the electrodes. Therefore, this type of separator cannot really ensure safety of the cell under abusive conditions.

Based on the strong PTC effects of the plastics-carbon composites at elevated temperature [21–23], we developed previously a PTC electrode by coating a thin PTC layer of epoxy-carbon composite in-between the cathode-active  $\text{LiCoO}_2$  layer and the cathode substrate [24]. Our previous study demonstrated that the resistance of this PTC electrode increases suddenly and enormously in the temperature range of 100–130°C, which can greatly inhibit or cut off the current passing through the electrode at elevated temperatures. Therefore, the PTC electrode of this type could provide a safety protection for rechargeable lithium batteries from thermal runaway. However, the PTC material reported therein is composed of a blend of carbon black and epoxy resin, since the preparation for PTC coating layer involves complicated solidifying process of epoxy, this type of PTC electrode is difficult for industrial production and commercial applications.

To simplify the fabrication procedure for the PTC electrode, we propose a novel PTC compound (C-PMMA) prepared by simply blending of conductive Super-P carbon black (CB) with insulating poly(methyl methacrylate) (PMMA) matrix, and use this PTC compound as a coating layer on the substrate to fabricate a sandwiched  $\text{LiCoO}_2$ -PTC cathode. In this paper, we report the electrical properties of the C-PMMA compound and the fabrication method of a sandwiched  $\text{LiCoO}_2$ -PTC cathode. Furthermore, we describe the electrochemical and thermal behaviors of the PTC electrode at various temperatures.

## 1 Experimental

### 1.1 Preparation of the PTC electrode

The C-PMMA composite used in this study was a blend of poly(methyl methacrylate) (PMMA) and super P black (SP). The PTC blending was prepared by mechanically ball-milling a mixture of 10 wt.% Super P black and 90 wt.% PMMA (Aldrich Chem. Co.,  $M_w = 996000$ ) with adaptable chloroform for 6 h in a rotation speed of 200 r/min, to form a well dispersed slurry. The PTC electrode was fabricated by firstly spreading a thin layer of PTC slurry onto aluminium foil, then blade-coating a  $\text{LiCoO}_2$  cathode slurry onto the thus-prepared PTC layer, and finally drying the electrode at 70°C for 24 h. The  $\text{LiCoO}_2$  cathode slurry is a well-dispersed mixture of 90 wt.%  $\text{LiCoO}_2$  powder, 3 wt.%

acetylene black, 7 wt.% poly(vinylidene fluoride) (PVDF) and adaptable *N*-methyl-2-pyrrolidone (NMP) solvent. The thickness of PTC electrode is ~0.1 mm.

### 1.2 Materials characterization

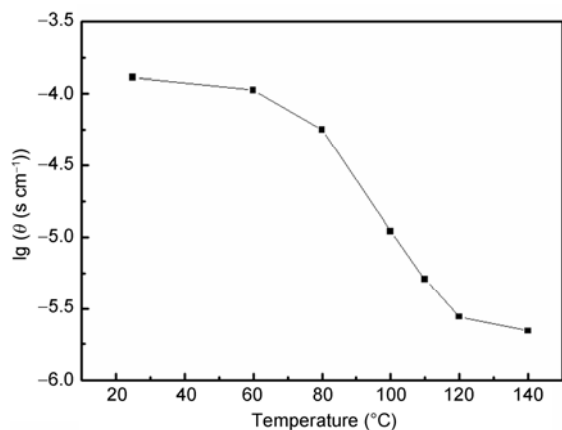
The ohmic resistance of the C-PMMA composite was measured directly by a digital multi-meter using a thin film sandwiched between two parallel Al foils at temperature range of 20–130°C.

All the electrochemical characterizations for  $\text{LiCoO}_2$ -PTC cathode were carried out using coin cells with lithium sheet as counter electrode. The electrolyte solution was 1 mol/L  $\text{LiPF}_6$  dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylene methyl carbonate (EMC) (1:1:1 by Vol.), purchased from Guotai-Huarong New Chemical Materials Co., Ltd. (Zhangjiagang, China). The cells were assembled in an argon-filled glove box. The charge and discharge measurements were performed using a programmable computer-controlled battery charger (CT2001A Land Battery Testing System, Wuhan, China) at a voltage interval of 4.30–3.0 V. Cyclic voltammetry measurements and Nyquist impedance spectra were conducted on a CHI660a electrochemical workstation (Chenhua Instrument Co., Shanghai, China).

## 2 Results and discussion

The PTC effects of the C-PMMA composite are usually considered to result from the variation of inter-particles distance of conductive reagent at elevated temperature. At normal operating temperatures, the conductive particles embedded in a crystalline polymer matrix provide a low resistance path for current flow. At elevated temperatures, the polymer's structure changes to an amorphous state, leading to a volume expansion of the polymer matrix. This thermal expansion breaks the conductive pathway between the embedded particles, resulting in a significant increase in resistivity [25,26]. In this work, we chose PMMA polymer as an insulating matrix because of its good processability to dissolve in commonly used organic solvents, which could greatly simplify the fabrication procedure for a PTC electrode.

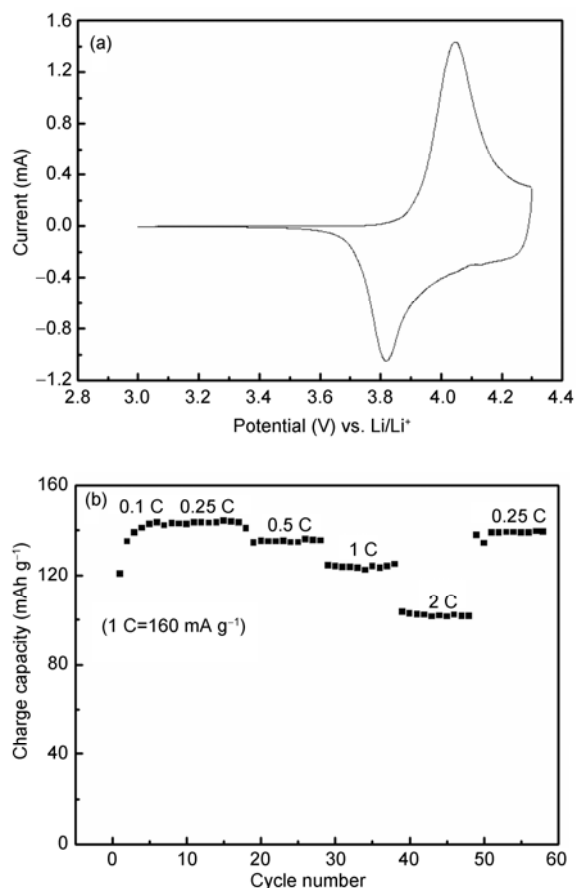
The PTC behavior of the C-PMMA composite prepared in this work can be visualized from the temperature dependence of the DC conductivity as shown in Figure 1. It can be seen that in the temperature region of 40–80°C, the conductivity of the PTC material shows only a slow decrease. When the temperature exceeds 80°C, the conductivity decreases suddenly by two orders of magnitude, showing a remarkable PTC effect. In general, Li-ion batteries are strictly prohibited to work at the temperature higher than 100°C, at which the safety of the batteries are thought to be in uncertainty. Obviously, the C-PMMA composite is suitable to serve as a PTC material to provide thermal cut off



**Figure 1** Logarithmic conductivity as a function of temperature for the C-PMMA composite. Super P: 10 wt.%, PMMA: 90 wt.%.

mechanism for safety control of the rechargeable Li batteries.

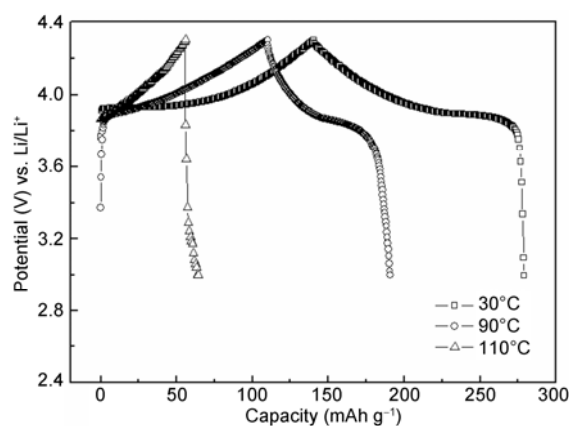
The electrochemical performances of the LiCoO<sub>2</sub>-PTC electrode were investigated by cyclic voltammetry (CV) and charge-discharge cycling at room temperature. The data are given in Figure 2. As displayed in Figure 2(a), the LiCoO<sub>2</sub>-PTC electrode shows a pair of reversible bands with its



**Figure 2** Electrochemical performances of the LiCoO<sub>2</sub>-PTC composite electrode at room temperatures. (a) CV curves measured in 1 mol L<sup>-1</sup> LiPF<sub>6</sub> in EC+DMC+EMC at a scan rate of 0.1 mV s<sup>-1</sup>; (b) cycling stability at varied C-rates.

anodic branch at 4.10 V and cathodic branch at 3.80 V, agreeing well with those observed from the bare-LiCoO<sub>2</sub> electrode. These CV features suggest that the PTC coating layer do not affect the intercalation kinetics of lithium ions on LiCoO<sub>2</sub> at ambient temperature. Figure 2(b) shows the cycling performance of the PTC electrode at ambient temperature at various C-rates from 0.1 to 2 C. It can be found in Figure 2(b) that the PTC electrode can deliver a specific capacity of 140 mAh g<sup>-1</sup> LiCoO<sub>2</sub> at 0.25 C rate. As the C-rate increasing from 0.5 to 1 C, the specific capacity of the PTC electrode gradually decreased from 135 to 123 mAh g<sup>-1</sup>. Even cycled at 2 C rate, this electrode can still deliver a steady capacity of ~100 mAh g<sup>-1</sup>, showing a satisfactory C-rate capability. These data suggest that the detrimental impact of the ohmic polarization arising from the PTC layer on the electrochemical performances of the LiCoO<sub>2</sub> electrode is insignificant at normal operating temperature. Furthermore, the PTC electrode of this type also exhibited an excellent cycling performance at ambient temperature. After 50 cycles in a scheduling C-rate order of 0.1, 0.25, 0.5, 1, and 2 C, the electrode still could give a discharge capacity of 137 mAh g<sup>-1</sup> as the cycling rate returned to 0.25 C.

To evidence the thermal cut off function of the PTC electrode, laboratory coin cells were assembled with the LiCoO<sub>2</sub>-PTC composite electrode and tested at various temperatures. Figure 3 shows the charge-discharge curves of the cells at a controlled voltage range of 4.3–3.0 V. As demonstrated in Figure 3, the cells show a reversible charge-discharge capacity of about 140 mAh g<sup>-1</sup> LiCoO<sub>2</sub> at 30°C and similar charge-discharge voltage plateaus as observed in bare LiCoO<sub>2</sub> electrode, suggesting that the thin PTC layer in the electrode does not affect the electrochemical behaviors of the electrode. When the cell was cycled at 90°C, the charging voltage was ca. 100 mV higher and the discharging voltage was ca. 200 mV lower than the corresponding values observed at 30°C. In the meantime, the reversible discharge capacities was greatly decreased to ca.



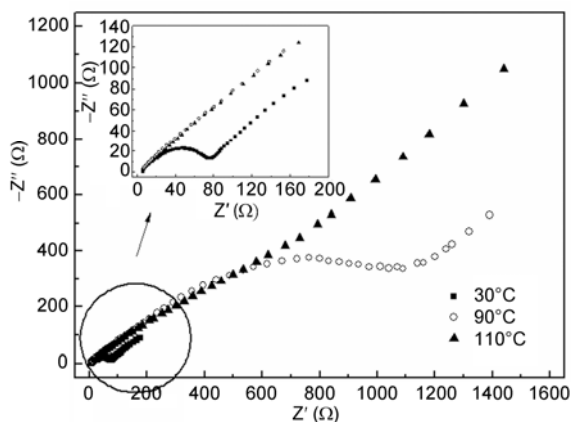
**Figure 3** The charge-discharge curves of the C-PMMA based PTC electrode at a constant current density of 40 mA g<sup>-1</sup> (0.25 C) at the temperatures of 30, 90, and 110°C, respectively.

80 mAh g<sup>-1</sup>. These phenomena are obviously originated from a serious ohmic polarization occurring in the PTC composite electrode. Because of the large increase in resistance of the PTC layer, the current flow passing in-between the substrate and active LiCoO<sub>2</sub> electrode is restrained to a great extent, which limits the charge and discharge of the PTC electrode. When the temperature was further increased to 110°C, the electrode can only deliver a discharge capacity of 8.4 mAh g<sup>-1</sup>, showing almost an effective blocking off the PTC layer to switch off the active LiCoO<sub>2</sub> electrode. Obviously, the strong PTC effects of the C-PMMA composite proposed in this work could prohibit, or even cut off the current passing through the electrode at elevated temperature, and thus to provide a thermal safety protection for rechargeable lithium batteries.

The PTC effect can also be evidenced from impedance measurements of the PTC composite electrode at various temperatures. As demonstrated in Figure 4, the impedance spectrum obtained at 30°C shows a well-defined semicircle at high frequencies and a sloping line at low frequencies, representing the interfacial charge transfer and Li<sup>+</sup> diffusion into the LiCoO<sub>2</sub> phase. At an elevated temperature of 90°C, the diameter of the semicircle is more than 15 times larger than that at 30°C. With temperature further increasing, the diameter of the semicircle increases enormously and the most part of the impedance spectrum appears to be a straight line resembling that given by a pure resistor. This enormous increase in the electrochemical impedance of the electrode indicates that the polarization of the PTC composite electrode greatly increases at high temperature. Obviously, such high impedance of the PTC composite electrode can slow down and eventually block off the electrochemical reactions occurring on the active LiCoO<sub>2</sub> particles at elevated temperatures, thereby to prevent the cell from thermal runaway.

### 3 Conclusions

In summary, we prepared a new PTC material based on C-



**Figure 4** Nyquist impedance spectra of the PTC composite electrode at various temperatures.

PMMA composite by simply blending of conductive Super P with PMMA polymer and test this PTC material as a coating layer on the substrate to fabricate a sandwiched LiCoO<sub>2</sub>-PTC cathode. The experimental results demonstrated that the resistance of the PTC electrode increases suddenly in the temperature range of 80–120°C, which can greatly restrain or even cut off the current passing through the electrode at elevated temperatures. Since the fabrication procedure for the PTC electrode is very simple for industrial production and commercial applications, this type of PTC electrode could be used conveniently as a safety mechanism to prevent the cell from thermal runaway.

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- Armand M, Tarascon J M. Building better batteries. *Nature*, 2008, 451: 652–657
- Etacheri V, Marom R, Elazari R, et al. Challenges in the development of advanced Li-ion batteries: A review. *Energy Environ Sci*, 2011, 4: 3243–3262
- Xiong X Q, Jiang Y, Xia S A, et al. Synthesis and modification of well-ordered layered cathode oxide LiNi<sub>2/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>. *China. Chin Sci Bull*, 2010, 55: 3419–3423
- Gao X P, Yang H X. Multi-electron reaction materials for high energy density batteries. *Energy Environ Sci*, 2010, 3: 174–189
- Goodenough J B, Kim Y. Challenges for rechargeable Li batteries. *Chem Mater*, 2009, 22: 587–603
- Tarascon J M, Armand M. Issues and challenges facing rechargeable lithium batteries. *Nature*, 2001, 414: 359–367
- Scrosati B, Garche J. Lithium batteries: Status, prospects and future. *J Power Sources*, 2010, 195: 2419–2430
- Bandhauer T M, Garimella S, Fuller T F. A critical review of thermal issues in lithium-ion batteries. *J Electrochem Soc*, 2011, 158: R1–R25
- Pérès J P, Pertion F, Audry C, et al. A new method to study Li-ion cell safety: Laser beam initiated reactions on both charged negative and positive electrodes. *J Power Sources*, 2001, 97–98: 702–710
- Zhang Z, Fouchard D, Rea J R. Differential scanning calorimetry material studies: Implications for the safety of lithium-ion cells. *J Power Sources*, 1998, 70: 16–20
- Yamaki J I, Baba Y, Katayama N, et al. Thermal stability of electrolytes with Li<sub>x</sub>CoO<sub>2</sub> cathode or lithiated carbon anode. *J Power Sources*, 2003, 119–121: 789–793
- Baba Y, Okada S, Yamaki J I. Thermal stability of Li<sub>x</sub>CoO<sub>2</sub> cathode for lithium ion battery. *Solid State Ionics*, 2002, 148: 311–316
- Tobishima S I, Takei K, Sakurai Y, et al. Lithium ion cell safety. *J Power Sources*, 2000, 90: 188–195
- Leising R A, Palazzo M J, Takeuchi E S, et al. A study of the overcharge reaction of lithium-ion batteries. *J Power Sources*, 2001, 97–98: 681–683
- Balakrishnan P G, Ramesh R, Prem K T. Safety mechanisms in lithium-ion batteries. *J Power Sources*, 2006, 155: 401–414
- Zhang Z, Zhang L, Schlueter J A, et al. Understanding the redox shuttle stability of 3,5-di-tert-butyl-1,2-dimethoxybenzene for overcharge protection of lithium-ion batteries. *J Power Sources*, 2010, 195: 4957–4962
- Chen Z, Qin Y, Amine K. Redox shuttles for safer lithium-ion batteries. *Electrochim Acta*, 2009, 54: 5605–5613
- Feng J K, Cao Y L, Ai X P, et al. Tri-(4-methoxyphenyl) phosphate: A new electrolyte additive with both fire-retardancy and overcharge protection for Li-ion batteries. *Electrochim Acta*, 2008, 53: 8265–8268

- 19 Li S L, Xia L, Zhang H Y, et al. A poly(3-decyl thiophene)-modified separator with self-actuating overcharge protection mechanism for LiFePO<sub>4</sub>-based lithium ion battery. *J Power Sources*, 2011, 196: 7021–7024
- 20 Jeong H S, Lee S Y. Closely packed SiO<sub>2</sub> nanoparticles/poly (vinylidene fluoride-hexafluoropropylene) layers-coated polyethylene separators for lithium-ion batteries. *J Power Sources*, 2011, 196: 6716–6722
- 21 Shen L, Lou Z D, Qian Y J. Effects of thermal volume expansion on positive temperature coefficient effect for carbon black filled polymer composites. *J Polym Sci Part A: Polym phys*, 2007, 45: 3078–3083
- 22 Zheng W, Wong S C. Electrical conductivity and dielectric properties of PMMA/expanded graphite composites. *Compos Sci Technol*, 2003, 63: 225–235
- 23 Dang Z M, Li W K, Xu H P. Origin of remarkable positive temperature coefficient effect in the modified carbon black and carbon fiber cofilled polymer composites. *J Appl Phys*, 2009, 106: 024913
- 24 Feng X M, Ai X P, Yang H X. A positive-temperature-coefficient electrode with thermal cut-off mechanism for use in rechargeable lithium batteries. *Electrochem Commun*, 2004, 6: 1021–1024
- 25 Li Q, Siddaramaiah K N H, Yoo G H, et al. Positive temperature coefficient characteristic and structure of graphite nanofibers reinforced high density polyethylene/carbon black nanocomposites. *Compos Part B: Eng*, 2009, 40: 218–224
- 26 Jiang S L, Yu Y, Xie J J, et al. Positive temperature coefficient properties of multiwall carbon nanotubes/poly(vinylidene fluoride) nanocomposites. *J Appl Polym Sci*, 2010, 116: 838–842

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