

New concept of surface modification to LiCoO₂

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Abstract

As the continuance of our series study on LiCoO₂ surface modification, the complicated traditional surface coating method is replaced with simple addition of amorphous YPO₄ and Al₂O₃ in commercial LiCoO₂ or in commercial electrolyte based on our understanding to the improvement mechanism of surface modification. Comprehensive studies by X-ray photoelectron spectroscopy (XPS), gas chromatography and mass spectroscopy (GC–MS), inductively coupled plasma (ICP) and Fourier transformed infrared (FTIR) indicate that the products of spontaneous reaction between the additive and the LiPF₆ based electrolyte are responsible for the performance improvements.

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1. Introduction

Lithium ion batteries are regarded as one of the best rechargeable batteries because of their long cycle life and high energy density [1]. In the past decades, LiCoO₂ has been used as the dominant positive electrode material in most lithium ion batteries due to its ease of preparation, good rate performance and high structural reversibility below 4.2 V *versus* Li⁺/Li. Further increasing the charge cutoff voltage results in the structural damage and severe capacity decay. Many efforts have been paid to improve the electrochemical performances of LiCoO₂ at high voltages. An effective strategy developed in recent years is to coat the surface of the materials with various metal oxides, including Al₂O₃ [2], MgO [3], ZrO₂ [4,5], TiO₂ [4], ZnO [6] and metal phosphates such as AlPO₄, FePO₄, CePO₄ and SrPO₄ [7,8]. A common feature of these methods is that the authors tried every effort to coat the active material compactly, based on the assumption that the coating layer separates the electrolyte and the active material to avoid any reactions between them.

Recently we reported that surface coating cannot hinder the spontaneous reactions between LiCoO₂ and the LiPF₆-based commercial electrolytes [9]. Effective performance improvement of the LiCoO₂ material does not require the coating layer to be compact nor even needs a coating layer at all. We proposed that the spontaneous reaction products between the coating material and the electrolyte take a series of roles on the performance improvement of LiCoO₂ [10]. The roles include at least: (1) the corrosive effect of the formed Lewis acids on the surface impurities of commercial LiCoO₂, (2) migration of alien metal ions into the lattice of the corroded or charged LiCoO₂ to form a surface solid solution and (3) the formed Lewis acids are beneficial for improving the ionic conduction and ion transference in the solid electrolyte interphase (SEI) film.

This paper is to extend the coating material from metal oxides to more stable metal phosphates, compare the improvement effects of surface coating and simple addition of coating material, and provide new evidence to support our previous assumption.

2. Experimental

Amorphous YPO₄ was prepared via the replacement reaction between Y(NO₃)₃·6H₂O (99.99%, Zibo, China) and

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$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (98%, Beijing Yili Fine Chemicals) at room temperature. After repeated rinsing with distilled water, YPO_4 was dried in an oven at 120°C for 12 h. Then it was directly mixed with commercial LiCoO_2 (Nippon Chemicals, battery grade; $5\ \mu\text{m}$ in diameter) at a mass ratio of 3.64% in a mortar upon electrode sheet preparation. This mass ratio is chosen because our previous study indicated that the 3.64% YPO_4 -coated LiCoO_2 showed the best improvement effect on the electrochemical performance of the commercial LiCoO_2 [11]. The process for the preparation of electrode sheets and the assembly of button cells has been described in Ref. [11]. Nanoscaled $\gamma\text{-Al}_2\text{O}_3$ (Nanjing Hitech Nano-Materials Co. Ltd.) with average diameter of 30 nm was also used as an additive in the cathode sheet in this study.

The nano- LiCoO_2 used in this paper was prepared by calcinating the mixture of nano- Co_3O_4 , $\text{LiOH} \cdot \text{H}_2\text{O}$ and KNO_3 at 600°C for 8 h in air. KNO_3 was used as a molten salt and was removed later by repeatedly rinsing the product with distilled water and ethanol.

The morphology of the samples was observed on a Hitachi S-4000 scanning electron microscope (SEM). Differential scanning calorimetry (DSC) analysis was carried out on NETSCH STA 449C in air by sealing the charged cathode sheet in an Al crucible in dry Ar and heated from 25°C to 500°C at a rate of 5°C min^{-1} . The inductively coupled plasma (ICP) analysis was performed on Shimadzu ICP-8000.

The additives were dried at 120°C for 12 h before added into the commercial electrolyte ($1.0\ \text{mol L}^{-1}$ LiPF_6 dissolved in EC/DMC (1:1, v/v; EC for ethylene carbonate and DMC for dimethyl carbonate)) or commercial LiCoO_2 for elemental analysis. One gram of YPO_4 was soaked in 50 ml commercial electrolyte. The mixtures were sealed into a poly(tetrafluoroethylene) (PTFE) container in an Ar-filled glove box. More details for the PTFE container and sample treatments can be found in Refs. [9,10]. After 7–30 days, the rubber window of the PTFE container was penetrated through with an injector and the gas in the container was injected into the column of a gas chromatography and mass spectroscopy (GC–MS) instrument. GC was carried out on Trance 2000 series GC instrument (Finnigan, Inc.). The instrument parameters and the sampling method are the same as described in Ref. [10]. Then, the upper liquid of the mixture was centrifugally separated from the solid and used as the *new electrolyte* or for other analysis. The determination of the acidity of the new electrolyte and the commercial electrolyte has been described in Ref. [10]. The solid was repeatedly rinsed with DMC and then dried under vacuum in the mini-chamber of the glove box.

The X-ray photoelectron spectroscopy (XPS) analysis was carried out on PHI Quantera SXM using an Al X-ray source and the binding energies (BE) were calibrated with that of C1s at 284.8 eV as the reference. Each Fourier transformed infrared (FTIR) spectrum was the average of 400 scans on a BIO-RAD FTS-60 spectrometer. The samples were thoroughly mixed with KBr powder and pressed to pellets. The AC impedance measurements were performed using an IM6e (Zahner Electric) impedance analyzer over a frequency range from 100 kHz to 5 mHz.

3. Results and discussion

Some researchers believed that the coating layer separates the active material from the moisture-containing electrolyte and scavenges traces of HF in the electrolyte [12–14]. Clearly physical separation requires that the coating layer be very compact. However, some recent reports claimed that loose [15] or incomplete [16,17] coating can still improve the performance of the cathode materials. Based on our assumption listed in Section 1, it is not necessary to coat the active cathode material compactly as long as the coating material can have a good contact with the electrolyte, and therefore insures the spontaneous reaction between the coating material and the electrolyte.

Fig. 1 shows the capacity retention of commercial LiCoO_2 in the commercial electrolyte in which nano- Al_2O_3 had been soaked. The reversibility of LiCoO_2 is significantly improved in the Al_2O_3 -modified electrolyte. The initial discharge capacity of LiCoO_2 in the new electrolyte reaches $192\ \text{mAh g}^{-1}$, 85% of which is remained after 100 cycles. In contrast, only half the initial capacity is retained after 40 cycles when the commercial electrolyte is used. The improved capacity retention in Fig. 1 demonstrates that the performance improvement of the LiCoO_2 material does not require compact coating or even does not need a coating layer at all.

Another two methods more practical in operation are used to improve the structural stability of commercial LiCoO_2 . Nanoscaled $\gamma\text{-Al}_2\text{O}_3$ is mixed with the commercial LiCoO_2 upon cathode sheet preparation (Fig. 2) and added into the commercial electrolyte (Fig. 3), respectively. Clearly both ways can improve the cycling stability of commercial LiCoO_2 at high voltages. Therefore, more lithium can be extracted out of the lattice of LiCoO_2 without damaging its structure. In comparison to surface coating, using the new electrolyte by removing the soaked nano- Al_2O_3 and the other two methods described above, adding nano- Al_2O_3 into the active material during sheet preparation is easier to operate and therefore, has advantages in industrial production.

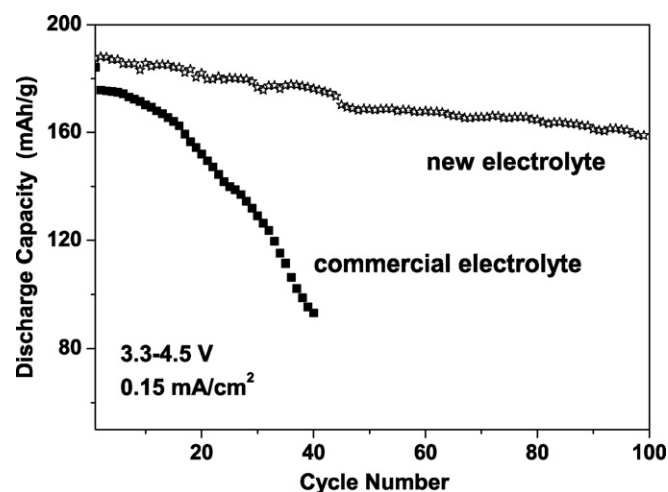


Fig. 1. Comparison of the discharge capacity retention of commercial LiCoO_2 in different electrolytes.

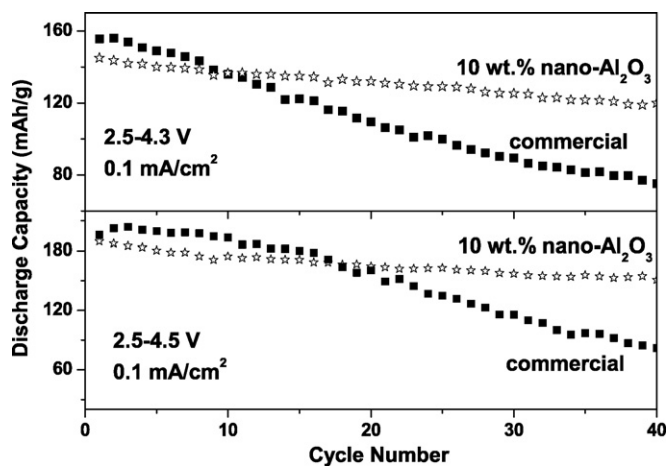


Fig. 2. Comparison of the cyclability of commercial LiCoO_2 with and without nano- Al_2O_3 additive and cycled in different voltage ranges.

Any of the above three methods should indicate clearly that compact coating is not really essential though the battery performance is strongly dependent on the surface chemistry of the active material. Therefore, the traditional view is challenged that the coating layer separates the electrode and electrolyte, suppresses the decomposition of the electrolyte and protect the active material.

Myung et al. [14] confirmed by ToF-SIMS analysis the formation of AlF_3 on the Al_2O_3 coating layer. They believed that the Al_2O_3 coating layer acted as an HF scavenger. Based on Myung's work, Sun et al. coated AlF_3 on LiCoO_2 [12] and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [18] and enhanced the cycling performance and rate capability of the cathode materials between 3.0 and 4.5 V. They attributed the improved electrochemical performances to the suppression of Co dissolution by the AlF_3 coating layer. AlF_3 was also recognized in the SEI layer on LiCoO_2 soaked in Al_2O_3 -soaked electrolyte in our recent study [10]. However, the presence of AlF_3 enhanced the acidity of the electrolyte (with or without removing the Al_2O_3 later). In another test, it is found that addition of nano- AlF_3 (5 wt.%) into the commercial electrolyte increased its acidity from 20 ppm to

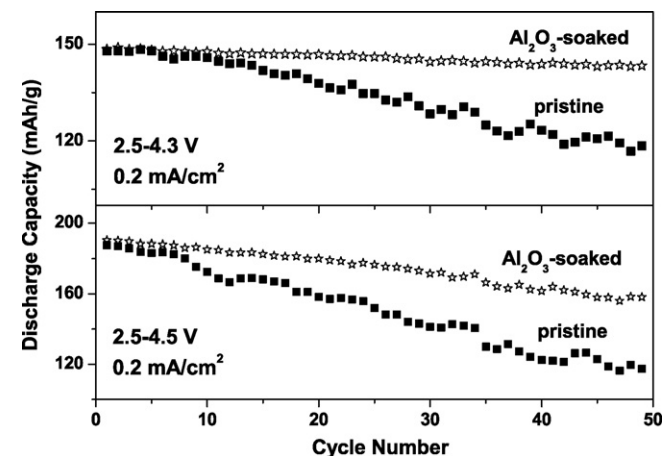


Fig. 3. Comparison of the cyclability of commercial LiCoO_2 cycled in different voltage ranges in commercial and the Al_2O_3 -soaked new electrolytes.

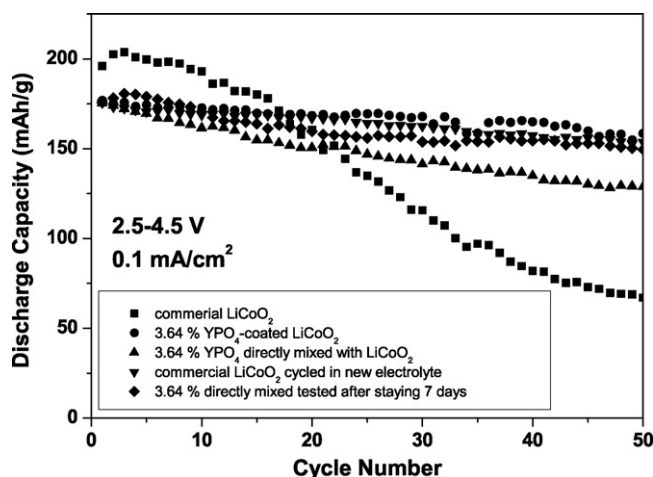


Fig. 4. Cyclability of commercial LiCoO_2 and YPO_4 -involved in different forms.

3500 ppm in 24 h at room temperature. The enhanced acidity of the electrolyte reinforces the corrosion of LiCoO_2 as well as other impurities on its surface such as Li_2CO_3 and LiOH . Actually our previous experiments showed that coating LiCoO_2 with Al_2O_3 promotes the dissolution of Li and Co from the lattice [9]. Similar phenomenon is observed in the $\text{YPO}_4/\text{LiCoO}_2$ system as shown in the following of this paper. Therefore, suppression of Co dissolution is not, at least, the main effect of the coating material.

In order to prove the assumptions listed in Section 1, the coating material is extended to YPO_4 . Fig. 4 compares the effects of different ways of LiCoO_2 performance improvement at high cutoff voltages. It seems that the presence of YPO_4 in any form in the cell, coated or mixed, in the electrolyte or in the cathode sheet, can improve the electrochemical performance of LiCoO_2 . These effects agree well to that of the Al_2O_3 addition.

Similar to the effects of Al_2O_3 addition in the commercial electrolyte, NaOH titration analysis at 0°C with bromthymol blue as indicator indicates that the acidity of the commercial electrolyte increases from 17.38 ppm to 2397.69 ppm after YPO_4 is soaked in it for 7 days. Actually the acidity of the electrolyte containing YPO_4 in any form is stronger than that of the YPO_4 -free samples (Table 1). These results are consistent with our previous tests where Al_2O_3 and SiO_2 were added in the commercial electrolyte [10].

The corrosion effect of the spontaneous reaction products between YPO_4 and the commercial electrolyte is obvious. Fig. 5

Table 1
Acidity variation of the electrolyte determined by NaOH titration

Sample	Acid content as HF (ppm)
Commercial electrolyte	17.38
Commercial LiCoO_2 soaked in electrolyte for 7 days	978.44
3.64% YPO_4 -coated LiCoO_2 soaked in electrolyte for 7 days	1307.85
3.64% YPO_4 mixed with LiCoO_2 soaked in electrolyte for 7 days	1210.73
YPO_4 soaked in electrolyte for 7 days	2397.69

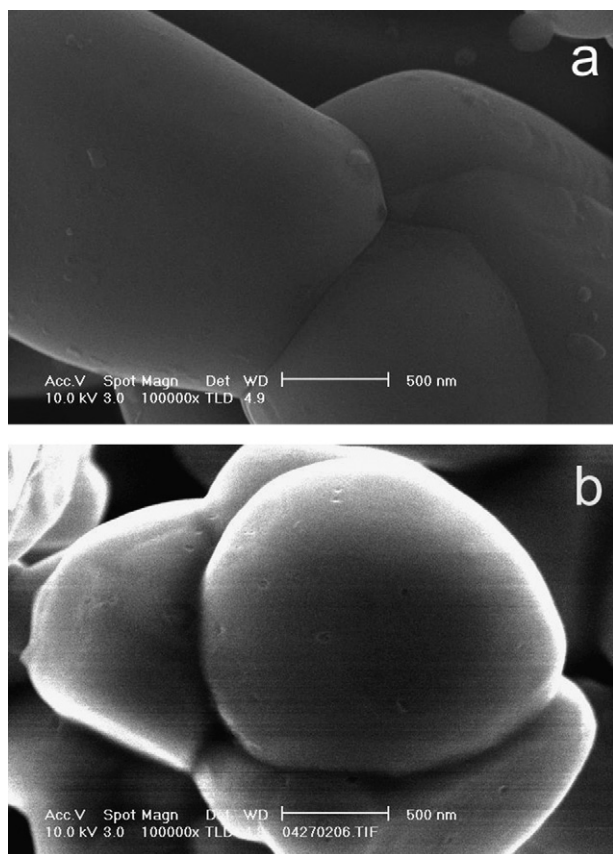


Fig. 5. Surface morphology of commercial LiCoO_2 soaked in commercial (a) and new electrolyte (b) for 7 days.

compares the surface morphology of commercial LiCoO_2 stored in commercial electrolyte and in the above YPO_4 -added new electrolyte (acidity: 2397.69 ppm). It is seen that the surface of commercial LiCoO_2 becomes very rough after being stored in the new electrolyte. Some corrosion pits are distributed on the surface. Therefore, YPO_4 enhances rather than suppresses the dissolution of commercial LiCoO_2 .

Chen and Dahn [5] attributed the improved capacity retention of LiCoO_2 charged to 4.5 V to the removal of the surface impurities during the essential heating process of surface coating. They believed that the fresh LiCoO_2 surface suppresses the side reactions between LiCoO_2 and the electrolyte. However, none of the samples in Fig. 4 involves a heating process. Therefore, surface impurities still exist on LiCoO_2 long-term stored in air before it meets YPO_4 in the electrolyte. It should be the enhanced acidity of the electrolyte that is responsible for the removal of these impurities.

YPO_4 has a tetragonal symmetry and belongs to space group I_1/amd . Chains parallel to the c axis of corner-sharing structural units built of a (YO_8) dodecahedron and a (PO_4) tetrahedron are linked together by an edge. These chains are further linked together by edge sharing. These features guarantee the structural stability of YPO_4 . Takita et al. [19] even reported that AlPO_4 is a suitable catalyst support in reactions involving HF. However, the above experimental results indicate that YPO_4 is not inert in the LiPF_6 -based commercial electrolyte.

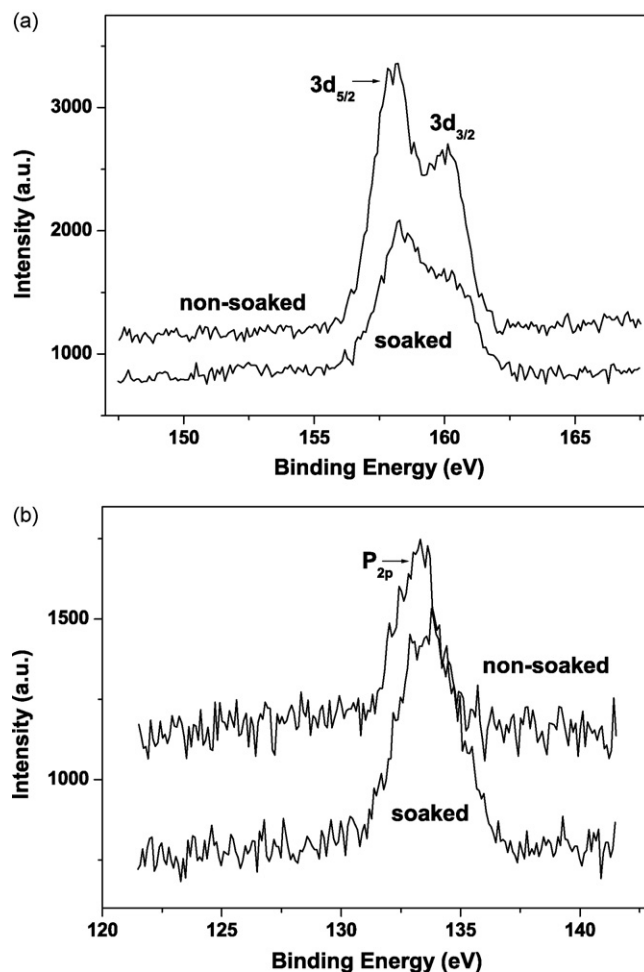


Fig. 6. Binding energies of Y_{3d} (a) and P_{2p} (b) in 12% YPO_4 -coated nano- LiCoO_2 before and after soaked in commercial electrolyte.

The binding energies of Y_{3d} and P_{2p} in 12% YPO_4 -coated nano- LiCoO_2 and in YPO_4 before and after being soaked in commercial electrolyte are characterized by XPS. Figs. 6 and 7 indicate that the binding energies of Y_{3d} and P_{2p} obviously increase about 0.5 eV after soakage. This implies that some Y–F bond is formed and the P–F bond becomes stronger. The former might probably represent the formation of YF_3 while the latter have complicated sources, including the decomposition products of LiPF_6 . Combining the previous XPS results, we presume that the YPO_4 herein reacts with the electrolyte and forms certain Lewis acid(s), YF_3 for example.

Based on the above analysis, the improved capacity retention in Fig. 4 can be understood as follows. YPO_4 tends to react with the LiPF_6 based electrolyte and converts to Lewis acid YF_3 . As a Lewis acid, YF_3 corrodes the surface alkaline impurities on LiCoO_2 in commercial electrolyte with traces of water. For the YPO_4 -coated LiCoO_2 , the distribution of YF_3 becomes homogeneous short after the contact with the electrolyte because the coating layer has been homogeneous before being assembled into the cell. For the sample that 3.64% YPO_4 is directly mixed with LiCoO_2 , the additive does not take its effect right after cycling because it takes some time to form YF_3 on LiCoO_2 . After some time (e.g. 7 days), sufficient YF_3 is distributed uni-

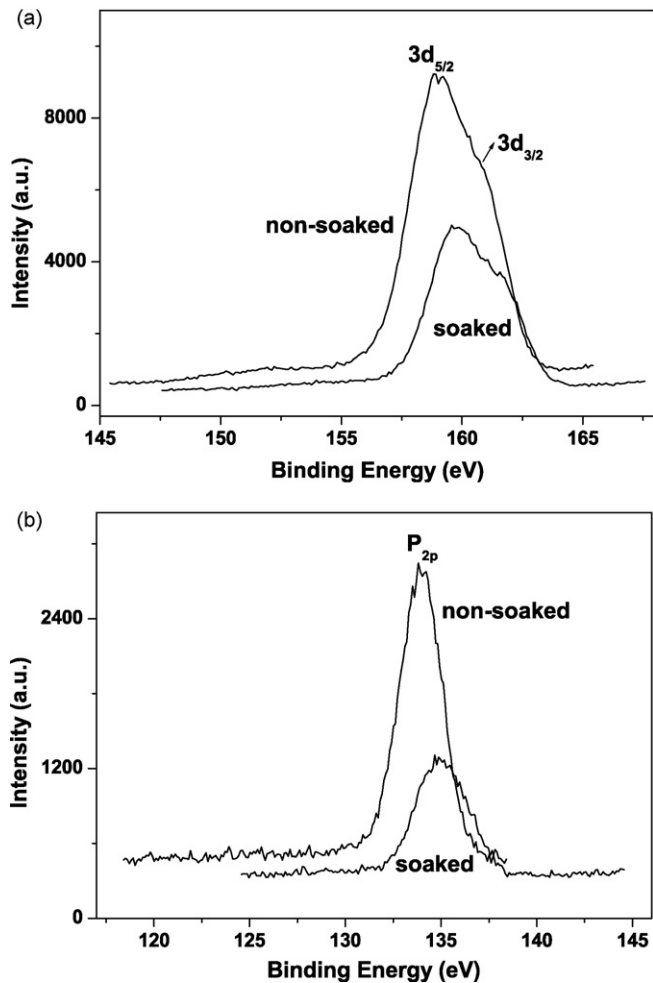


Fig. 7. Binding energies of Y_{3d} (a) and P_{2p} (b) of YPO_4 before and after soaked in commercial electrolyte.

formly on $LiCoO_2$. Thereafter, the Lewis acid begins to take its effects and the capacity retention of $LiCoO_2$ becomes better. Similar is the case for the cell using the new electrolyte. The YF_3 formed in the new electrolyte during soakage of YPO_4 adheres to the surface of $LiCoO_2$ as soon as the new electrolyte is injected in to the lithium cell. Therefore, the $LiCoO_2$ cell using the new electrolyte can have similarly improved performances as the cell that is stored for 7 days before cycling and the cell that YPO_4 -coated $LiCoO_2$ is used.

The exothermic reaction between the electrode materials and the flammable organic solvent in the electrolyte brings about safety concerns to the battery. The temperature of the exothermic reaction of charged cathode becomes lower as the charge cut-off voltage rises. This problem has been harassing the scientists and engineers since the birth of lithium ion batteries. Fig. 8 compares the DSC traces of the cathode sheets of commercial $LiCoO_2$ processed by different methods and charged to 4.7 V. It is seen that adding YPO_4 in the cathode sheet or in the electrolyte delays the exothermic reaction by at least 6 °C and decreases the exothermic amount significantly. Therefore, addition of YPO_4 in whatever method, coated on $LiCoO_2$, directly mixed with $LiCoO_2$ or soaked in the electrolyte is effective in improving

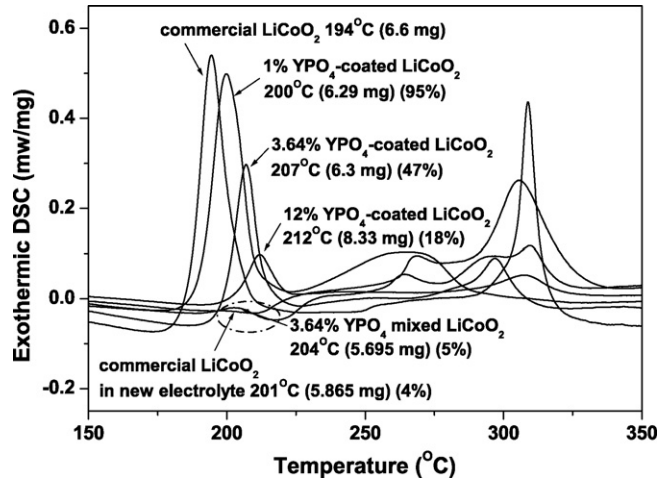


Fig. 8. Comparison of the exothermic reaction temperature of commercial $LiCoO_2$ charged to 4.7 V and with YPO_4 added in different ways.

the thermal safety of the charged cathode material. The effects of the added YPO_4 are similar to that of nano- Al_2O_3 on the thermal performance improvement of $LiCoO_2$ [10]. The improved thermal stability is attributed to the formation of surface solid solution $Li_xM_yCo_{1-y}O_2$ ($M = Al$ or Y) on $LiCoO_2$, considering the corrosion of the additive (or its reaction products) to $LiCoO_2$ (Fig. 5).

Resistance increase of the SEI layer is an important reason for the capacity fading of the cells [5]. Our previous work indicated that the resistance of the SEI layer on YPO_4 -coated $LiCoO_2$ increases much slower with electrochemical cycling than that on commercial $LiCoO_2$ [11]. In order to further study the impact of the addition of YPO_4 on the resistance of the SEI layer, the AC impedance spectra of commercial $LiCoO_2$ and nano- $LiCoO_2$ containing YPO_4 in some form are recorded (only those of the commercial $LiCoO_2$ are shown). The semicircle in the high-frequency region of the Nyquist plot is mainly the contribution of the SEI film on the electrode. Fig. 9 indicates that the presence of YPO_4 in whatever form in the cathode material suppresses the increase of the SEI resistance with storage time. The resistance of the commercial $LiCoO_2$ increases sharply, while those of the YPO_4 -coated and YPO_4 -added $LiCoO_2$ still keep rather stable after two weeks. Within 5 weeks, the resistance of the SEI layer on commercial $LiCoO_2$ increases by 25 times, while that for the 3.64% YPO_4 coated sample and the 3.64% YPO_4 added samples are only 7 and 4 times of the new cell. Suppression of resistance increase is favourable for elongating the lifetime of a cell. Addition of YPO_4 into nano- $LiCoO_2$ shows similar effects as in commercial $LiCoO_2$.

The suppression of the resistance of the SEI layer may have two reasons: increase of the conductivity of the SEI layer or the decrease of the thickness of the layer. As the addition of the coating material promotes the decomposition of the electrolyte, the SEI layer on $LiCoO_2$ should be thicker than on $LiCoO_2$ free of coating material. Our previous study [9] has shown the enhanced growth of the SEI layer and the presence of short-chain PEO-like species on Al_2O_3 -coated $LiCoO_2$ while Xi et al. [20] reported that addition of solid superacid SO_4^{2-}/ZrO_2 enhances

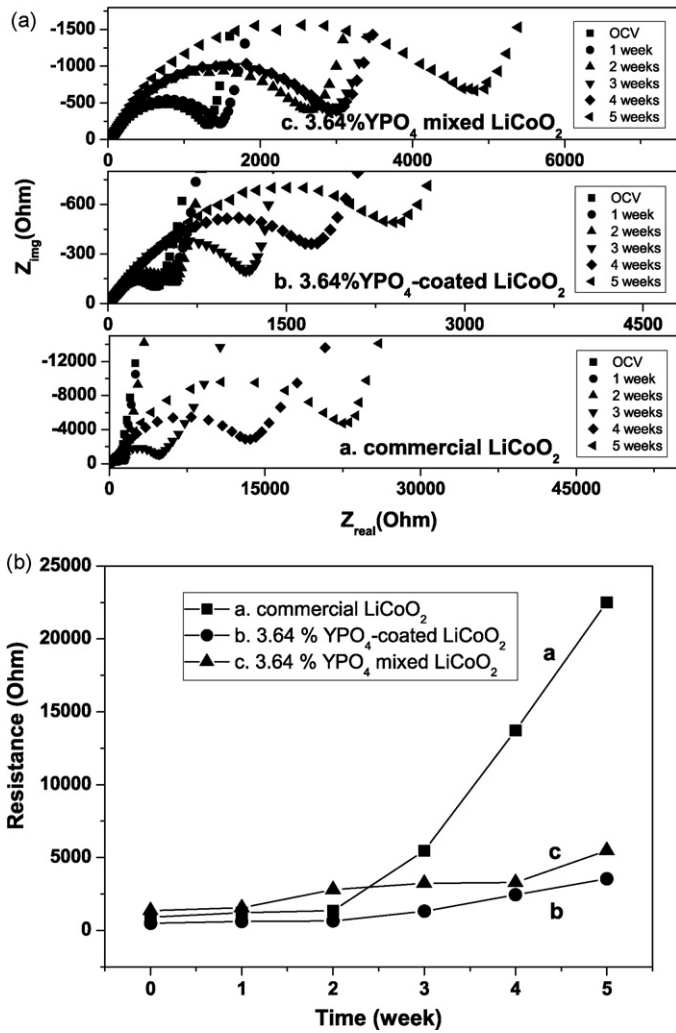


Fig. 9. Comparison of time-dependent resistance evolution of the SEI layer on commercial LiCoO₂ with and without YPO₄ added/coated.

the conductivity of PEO-based polymer electrolytes. Therefore, the suppression of the SEI resistance is attributed to the increase of the conductivity of the SEI layer.

To further understand the mechanism of the remarkably improved electrochemical and thermal performances of LiCoO₂, extended analysis was carried out.

12%YPO₄ coated nano-LiCoO₂ and YPO₄ were soaked respectively in commercial electrolyte (the content of YPO₄ for the latter is therefore nine times that of the former in the electrolyte). After 30 days, the gas, the liquid and the solid in the specifically designed container are analysed by GC–MS, ICP and FTIR. GC–MS analysis indicates that more CO₂ is formed in the 12% YPO₄ coated LiCoO₂ sample. Yet less EC and DMC are detected in the liquid where YPO₄ rather than 12% YPO₄ coated LiCoO₂ was soaked.

The electrolyte becomes red after soakage of YPO₄ for 30 days. The colour variation of the electrolyte can be recognized with naked eyes. It becomes darker with soakage time, indicating the dissolution of Co³⁺ ions into the electrolyte. ICP analysis demonstrates that the dissolution of Co³⁺ becomes more severe as the content of YPO₄ increases in the electrolyte (Table 2). It

Table 2

The atomic ratio of some elements in the separated solid and liquid after soaking various materials in commercial electrolyte for 30 days

	Li	P	Y	Co
Nano-LiCoO ₂ (solid)	0.98	Too low	/	1
Nano-LiCoO ₂ (liquid)	1.03	1	/	Too low
12%YPO ₄ -coated nano-LiCoO ₂ (solid)	0.97	0.12	0.09	1
12%YPO ₄ -coated nano-LiCoO ₂ (liquid)	1.06	1	Too low	0.0016
YPO ₄ (solid)	0.21	1	0.94	/
YPO ₄ (liquid)	0.89	1	0.01	/
Nano-LiCoO ₂ soaked in new electrolyte (solid)	0.94	0.11	0.0007	1
Nano-LiCoO ₂ soaked in new electrolyte (liquid)	1.02	1	0.009	0.01

is interesting to analyse the differences of the atomic ratios in the solid and liquid of the YPO₄-soaked sample. For the solid, suppose that all the detected Y belongs to YPO₄ and the detected Li to any Li-containing species except for LiPF₆ as it is easy to be rinsed off. Then the content of the Li-containing compounds should be very high in the solid. For the liquid, suppose that all the Li ions belongs to LiPF₆, then it will be seen that much of the salt is decomposed because the P/Y atomic ratio becomes (1 – 0.89 =) 0.11:0.01 in the liquid. That is, the atomic ratio of the left P is 10 times that of Y. Clearly the high content of P in the liquid means the severe decomposition of LiPF₆ and the formation of P-containing soluble species, PF₅, for example. Although the above estimation is rather rough, it indeed indicates the severe decomposition of the electrolyte, both the solvent and the salt, on YPO₄. With this, it is easy to understand the remarkably increased acidity of the new electrolyte and the severe dissolution of LiCoO₂ (the colour of the electrolyte changes from colourless to yellow and finally to brown with time when YPO₄ alone is soaked in the commercial electrolyte).

Fig. 10 shows the FTIR spectra of YPO₄ before and after soaked in commercial electrolyte for 30 days. Table 3 listed

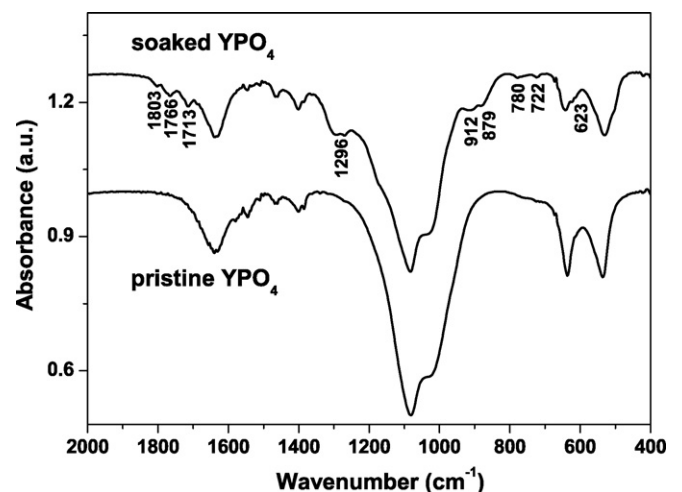


Fig. 10. FTIR spectra of YPO₄ before and after soakage in commercial electrolyte for 30 days.

Table 3
New peaks and their assignments of YPO₄ soaked in commercial electrolyte for 30 days

Peaks	Assignments and references
623	CO ₂ asymmetric bending [21]
722	CO ₂ asymmetric bending [21]
780	CO ₂ asymmetric bending [21]
879	CO ₃ bending, Li ₂ CO ₃ [22]
912	CH ₂ wagging [21]
1296	CO ₂ symmetric stretching [22]
1713	Carbonyl stretching [23]
1766	C=O stretching [22]
1803	C=O stretching [22]

the new peaks in the spectrum of YPO₄ after soakage and their assignments. Compared to pure YPO₄, several obvious absorbance peaks are observed between 1700 cm⁻¹ and 1800 cm⁻¹, most of which can be assigned to C=O stretching, implying the formation of RCOOLi, typical species of the SEI layer. These results support the above deduction of the electrolyte decomposition by ICP analysis.

4. Conclusions

The above experiments indicate that the electrochemical and thermal performances of commercial LiCoO₂ are remarkably improved by adding YPO₄ or Al₂O₃ into LiCoO₂ or the electrolyte. A novel concept of surface modification was developed to improve the capacity retention of LiCoO₂ at high cut-off voltage. The essence of this concept is that it is not important whether the coating is compact. What is critical is that the additive/coating material must react with the LiPF₆-based commercial electrolyte and form some Lewis acids. The Lewis acids take their effects in three ways: (1) increasing the acidity of the moisture containing LiPF₆ electrolyte and purify the surface of commercial LiCoO₂; (2) enhancing the decomposition of the electrolyte but increasing the conductivity of the formed SEI layer; and (3) promoting the formation of structurally more stable surface solid solution by replacing the Co and Li ions with the metal ions of the additives. Now that the additives react with the LiPF₆ based electrolyte and form some metal fluorides, we believe that some metal fluoride as well as metal oxides and phosphates can be utilized as the additive to improve the performances of the cathode materials.

Acknowledgements

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References

- [1] J.M. Tarascon, M. Armand, *Nature* 1414 (2001) 359.
- [2] J. Cho, Y.J. Kim, B. Park, *Chem. Mater.* 12 (2000) 3788.
- [3] Z.X. Wang, C. Wu, L.L. Liu, F. Wu, L.Q. Chen, X.J. Huang, *J. Electrochem. Soc.* 149 (2002) A466.
- [4] J. Cho, Y.J. Kim, T.J. Kim, B. Park, *Angew. Chem. Int. Ed.* 40 (2001) 3367.
- [5] Z.H. Chen, J.R. Dahn, *Electrochim. Acta* 49 (2004) 1079.
- [6] T. Fang, J.G. Duh, S.R. Sheen, *J. Electrochem. Soc.* 152 (2005) A1701.
- [7] J. Cho, Y.W. Kim, B. Kim, J.G. Lee, B. Park, *Angew. Chem. Int. Ed.* 42 (2003) 1618.
- [8] J. Kim, M. Noh, J. Cho, H.M. Kim, K.B. Kim, *J. Electrochem. Soc.* 152 (2005) A1142.
- [9] Z.X. Wang, X.J. Huang, L.Q. Chen, *J. Electrochem. Soc.* 151 (2004) A1641.
- [10] J.Y. Liu, N. Liu, D.T. Liu, Y. Bai, L.H. Shi, Z.X. Wang, L.Q. Chen, V. Hennige, A. Schuch, *J. Electrochem. Soc.* 154 (2007) A55.
- [11] Y. Bai, N. Liu, J.Y. Liu, Z.X. Wang, L.Q. Chen, *Electrochem. Solid-State Lett.* 9 (2006) A552.
- [12] Y.K. Sun, J.M. Han, S.T. Myung, S.W. Lee, K. Amine, *Electrochem. Commun.* 8 (2006) 821.
- [13] J.S. Kim, C.S. Johnson, J.T. Vaughey, S.A. Hackney, K.A. Walz, W.A. Zeltner, M.A. Anderson, M.M. Thackeray, *J. Electrochem. Soc.* 151 (2004) A1755.
- [14] S.T. Myung, K. Izumi, S. Komaba, Y.K. Sun, H. Yashiro, N. Kumagai, *Chem. Mater.* 17 (2005) 3695.
- [15] A.M. Kannan, L. Rabenberg, A. Manthiram, *Electrochem. Solid-State Lett.* 6 (2003) A16.
- [16] S. Oh, J.K. Lee, D. Byun, W.I. Cho, B.W. Cho, *J. Power Sources* 132 (2004) 249.
- [17] N. van Landschoot, E.M. Kelder, P.J. Kooyman, C. Kwakemaak, J. Schoonman, *J. Power Sources* 138 (2004) 262.
- [18] Y.K. Sun, S.W. Cho, S.W. Lee, C.S. Yoon, K. Amine, *J. Electrochem. Soc.* 154 (2007) A168.
- [19] Y. Takita, T. Ohkuma, H. Nishiguchi, K. Nagaokaa, T. Nakajo, *Appl. Catal. A: Gen.* 283 (2005) 47.
- [20] J.Y. Xi, X.Z. Tang, *Chem. Phys. Lett.* 393 (2004) 271.
- [21] N.B. Colthup, L.H. Daly, S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, third ed., Academic Press, San Diego, CA, 1990.
- [22] V.W. Behrendt, G. Gattow, M. Drager, *Z. Anorg. Allg. Chem.* 397 (1973) 237.
- [23] D. Aurbach, *J. Power Sources* 89 (2000) 206.