

Review article

# Cathode materials modified by surface coating for lithium ion batteries

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## Abstract

Recent research results confirm the importance of structural surface features of cathode materials for their electrochemical performance. Modification by coating is an important method to achieve improved electrochemical performance, and the latest progress was reviewed here. When the surface of cathode materials including LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub> and LiMnO<sub>2</sub> is coated with oxides such as MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZnO, SnO<sub>2</sub>, ZrO<sub>2</sub>, Li<sub>2</sub>O·2B<sub>2</sub>O<sub>3</sub>-glass and other materials, the coatings prevent the direct contact with the electrolyte solution, suppress phase transition, improve the structural stability, and decrease the disorder of cations in crystal sites. As a result, side reactions and heat generation during cycling are decreased. Accompanying actions such as suppression of Mn<sup>2+</sup> dissolution, increase in conductivity and removal of HF in electrolyte solutions have been observed. Consequently, marked improvement of electrochemical performance of electrode materials including reversible capacity, coulomb efficiency in the first cycle, cycling behavior, rate capability and overcharge tolerance has been achieved. In conclusion, further directions are suggested for the surface modification of electrode materials. With further understanding of the effects of the surface structure of cathode materials on lithium intercalation and de-intercalation, better and/or cheaper cathode materials from surface modification will come up in the near future.

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**Keywords:** Lithium ion battery; Surface modification; Cathode materials; Coating

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Since the birth of the lithium ion battery in the late 1980s its development starting in the early 1990s has been very fast [1]. Research and development of new electrode materials with improved electrochemical performance and/or low cost has always been a focus, and methods such as sol–gel [2], non-classical ones including mechano-chemical, hydrothermal, template, pulsed laser deposition, plasma-enhanced chemical vapor deposition, radio-frequency magnetron sputtering [3], mechano-chemical method [4] and incorporation of heteroatoms [5] have been widely applied. With progress of knowledge of electrode materials it has been found that their surface structures are of great importance to the electrochemical performance of anode materials [6]. In the case of cathode materials this is also true. It has been found that surface coating was a good method to improve electrochemical performance of cathode materials. Here we reviewed the recent progress on this aspect and future directions were pointed out.

Cathode materials including lithium cobalt oxide (LiCoO<sub>2</sub>), lithium nickel oxide (LiNiO<sub>2</sub>), spinel lithium manganese oxide (LiMn<sub>2</sub>O<sub>4</sub>) and layered LiMnO<sub>2</sub> were considered in this review.

## 1. LiCoO<sub>2</sub>

LiCoO<sub>2</sub> is presently the most widely used cathode material on the market due to its typical stable layered structure [1]. The reversible amount of lithium  $x$  in Li<sub>1-x</sub>CoO<sub>2</sub> is usually below 0.5. Over-delithiation will result in a phase transition from monoclinic to hexagonal phase in the voltage range between 4.15 and 4.2 V. This transition leads to an abrupt shrinkage along the  $c$ -axis direction, corresponding to about 9% volume change; the accompanying cation disorder causes a fraction of Li ions to enter 3b sites of Co instead of normal 3a sites, leading to fracture of particles and deterioration of electrochemical performance [1]. The degradation of LiCoO<sub>2</sub> structure is partly related to the dissolution of Co<sup>4+</sup> when  $x > 0.5$ . In order to improve structural stability, coating is a preferred method.

Various metal oxide coatings such as Li<sub>2</sub>CO<sub>3</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, AlPO<sub>4</sub>, SiO<sub>2</sub>, SnO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, ZrO<sub>2</sub>, SnO<sub>2</sub> carbon and other compounds have been shown to improve both the cycle life (especially at high-voltage charging) and the rate capability of the LiCoO<sub>2</sub> cathode.

### 1.1. Li<sub>2</sub>CO<sub>3</sub>

Li<sub>2</sub>CO<sub>3</sub> coating can be done via the following process. The pristine LiCoO<sub>2</sub> powder was soaked in a mixed aqueous solution of 1 M LiOH and 0.25 M LiNO<sub>3</sub> for 30 min, then filtered and dried. The filtered LiCoO<sub>2</sub> powder was kept at 250 °C in CO<sub>2</sub> for 4 h to form a Li<sub>2</sub>CO<sub>3</sub> coating on the powder particles. Li<sub>2</sub>CO<sub>3</sub> coating reduces the interfacial resistance and suppresses the impedance rise during cycling. It significantly improves the 3.6 V-plateau efficiency from 95% to 97% [7].

### 1.2. MgO

Coating MgO can be carried out in several ways: depositing Mg(OH)<sub>2</sub> from a solution followed by a heat-treatment [8], a sol–gel method [9–12] and pulsed laser deposition (PLD) [13]. The first way is more convenient from the viewpoint of practical application.

The MgO modification acts in the following ways: (1) the surface coating itself acts as a protective layer to prevent the active core material from direct contact with the electrolytes and the dissolution of Co<sup>4+</sup> ions, and thus the phase transition is suppressed [14]. (2) Mg<sup>2+</sup> in coatings will diffuse into LiO<sub>2</sub>-layers of LiCoO<sub>2</sub> during the heat treatment after coating and charge/discharge process, which does not cause any detectable shift in positions of X-ray diffraction (XRD) peaks, but does impact the XRD peak intensity due to the aberrance of the 003 plane. Mg<sup>2+</sup> ions existing in LiO<sub>2</sub>-layers stabilize the lattice structure of LiCoO<sub>2</sub> [10]. Mg<sup>2+</sup> ions from MgO coating can diffuse into the interior space of the lattice, which also suppresses

the phase transition by occupying the left vacant  $\text{Li}^+$  sites (3a) and preventing the vacancy disordering at high charge potentials. (3)  $\text{MgO}$  coating suppresses the increase of resistances caused by repeated insertion—extraction of lithium ions while being charged up to 4.2 V versus  $\text{Li}/\text{Li}^+$ . (4) The coating decreases the activation energy of lithium ion transfer reaction at the  $\text{LiCoO}_2$  thin film electrode–electrolyte interface, indicating that the modification by  $\text{MgO}$  affects the kinetics of lithium ion transfer reaction at the  $\text{LiCoO}_2$ –electrolyte interface [13].

As a result,  $\text{MgO}$  coating significantly improves the cycling stability of  $\text{LiCoO}_2$ . For example, after 40 cycles a discharge capacity of more than 120 mAh/g remained for 1 mol%  $\text{MgO}$ -coated  $\text{LiCoO}_2$ , while only 13 mAh/g for pristine  $\text{LiCoO}_2$  remained when cycled between 3.3 and 4.7 V [10]. When the charge voltages are 4.3, 4.5, and 4.7 V (versus  $\text{Li}^+/\text{Li}$ ), respectively, the coated  $\text{LiCoO}_2$  presents available specific capacity of 145, 175, and 210 mAh/g, respectively [9]. However, it should be remembered that more  $\text{MgO}$  coating is detrimental to the electrochemical properties of  $\text{LiCoO}_2$  cathode probably due to the electrochemical inactivity of  $\text{MgO}$  particles [10].

### 1.3. $\text{Al}_2\text{O}_3$

Coating  $\text{Al}_2\text{O}_3$  can be performed in several ways: sol–gel method following heat-treatment [15–19], deposition [20], and gas-suspension spray [21].

There are several kinds of actions for the  $\text{Al}_2\text{O}_3$  coating: (1) it provides the interface with a chemically stable but highly  $\text{Li}^+$ -ion conducting barrier layer that effectively reduces the chemical reaction between the charged active material and the electrolyte. The barrier layer might be in the form of a composite of nanoparticles of  $\text{Al}_2\text{O}_3$  and organic products of reactions between the electrolyte and charged active material [17]. (2) It may form some type of protection layer to cover the active centers that serve as catalyst sites for the electrolyte decomposition and reduces the decomposition [20]. (3) The coating can endure larger variation of lattice parameters [18–20]. (4) It increases both the surface area and the electrical conductivity of  $\text{LiCoO}_2$  and induces higher thermal stability [21].

Consequently, after coating with  $\text{Al}_2\text{O}_3$ , the charge–discharge voltage characteristics, rate capability, capacity retention on cycling and thermal stability of the  $\text{LiCoO}_2$  cathodes are improved. For example, specific capacity of 190 mAh/g was obtained in  $\text{Li}/(\text{Al}_2\text{O}_3\text{-coated LiCoO}_2)$  experimental cells when charged to 4.5 V [20].

There are several factors affecting the electrochemical performance of the  $\text{Al}_2\text{O}_3$ -coated  $\text{LiCoO}_2$ . Different coating amounts (i.e. surface coverage of  $\text{Al}_2\text{O}_3$ ) cause different capacity retention after 50 cycles. The optimum  $\text{Al}_2\text{O}_3$ -coating amount for the highest capacity retention is 0.2 wt.%. This corresponds to 13.7% of surface coverage [21]. Heat-treatment temperature after coating also affects the nature of the coating. For example, heat-treating at  $T = 700^\circ\text{C}$  resulted in the presence of solid solution  $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$  in particle above 50 nm, and there was no effect of coating. When  $T < 700^\circ\text{C}$ , the solid solution of Al mainly existed on the surface of  $\text{LiCoO}_2$  particles within

50 nm [15,16]. The high concentration of Al atoms at the particle surface region led to the enhancement of structural stability during cycling, causing the disappearance of the phase transition from a hexagonal to monoclinic phase [16]. When it was heated at  $600^\circ\text{C}$  for 3 h, the  $\text{Al}_2\text{O}_3$ -coated cathode exhibited no decrease in its original specific capacity of 174 mAh/g and excellent capacity retention (97% of its initial capacity) between 4.4 and 2.75 V after 50 cycles [15].

### 1.4. $\text{AlPO}_4$

Coating  $\text{AlPO}_4$  on  $\text{LiCoO}_2$  was mainly done by direct dispersing  $\text{LiCoO}_2$  in the  $\text{AlPO}_4$  slurry [22–28]. After mixing and drying, the mixture was annealed at high temperature. The coating thickness on  $\text{LiCoO}_2$  cathodes was controlled by changing the  $\text{AlPO}_4$ -nanoparticle concentration in the coating solution [22].

The coating layer acts in the following ways: (1) it suppresses both Co dissolution and the lattice distortion. Dissolution of cobalt during cycling with a charge cut-off voltage of 4.6 V will lead to structural degradation and induce a non-uniform distribution of local strain in the cathodes [26]. (2) It behaves as a protective layer and is quite effective to prohibit the chemical reactions between the electrolyte and the cathode [23]. (3) It prevents structural degradation of  $\text{LiCoO}_2$  during cycling and shows much smaller changes in the  $c/a$  ratio than the uncoated one [25]. In the meanwhile, a suitable amount of this coating does not hinder Li diffusion and can keep appropriate electronic conductivity [22,26]. As a result, the  $\text{AlPO}_4$  coated  $\text{LiCoO}_2$  does not exhibit thermal runaway, which controls the overall safety of the Li-ion cells, and is quite effective in improving the capacity retention over the bare cathodes [24,26].

The specific capacity, cycling performance and overcharge behavior of the coated cathodes have a strong correlation with the  $\text{AlPO}_4$  coating concentration. The cycling performance of the 1.0 wt.%  $\text{AlPO}_4$ -coated cathodes was the best, showing 149 mAh/g capacity retention with 4.8 V charge cut-off by 50 cycles at 1 C after precycles. However, the bare cathode showed zero capacity retention at the same condition after only 20 cycles. As the coating thickness increases, the transportation of lithium may become slower and less efficient due to the limited electronic conduction among the particles. There is an optimum condition (1.0 wt.%  $\text{AlPO}_4$ -coated) that shows the most enhanced electrochemical properties because the appropriate coating layer can suppress both Co dissolution and the lattice distortion and does not hinder Li diffusion much with the appropriate electronic conduction [22].

When the lithium ion cells assembled with  $\text{LiCoO}_2$  cathodes were overcharged to 12 V at 1 C rate, the 5 V plateau region, which is indicative of both electrolyte oxidation and an exothermic reaction between the electrolyte and the cathode, decreased with increasing  $\text{AlPO}_4$  coating thickness or concentration. Therefore, a Li-ion cell containing a P100-coated  $\text{LiCoO}_2$  cathode ( $\text{AlPO}_4$  coating thickness was estimated as 100 nm) did not show the 5 V plateau, and displayed the lowest cell external temperature of  $60^\circ\text{C}$ , even at 12 V. When a higher current was applied (2 C), cells with bare or P10-coated ( $\text{AlPO}_4$

coating thickness was estimated as 10 nm) LiCoO<sub>2</sub> cathodes either burst or exploded, and reached external temperatures of over 275 °C. In contrast, the cell temperatures increased much slower in cells with the P30 (AlPO<sub>4</sub> coating thickness was estimated at 30 nm) and P100-coated cathodes than that of both the bare and P10-coated cathodes, and the corresponding cells did not show any short-circuit. Only a coating thickness over 20 nm could block thermal runaway [23].

The annealing temperature also influences the electrochemical performance of the coated LiCoO<sub>2</sub>. The 600 and 700 °C annealed cathodes effectively prevented the degradation of Li diffusivities during the cycles, in comparison to the bare and 400 °C annealed cathode. The 700 °C annealed cathode with better crystallinity showed an excellent rate capability up to 2 C, the 400 °C annealed cathode exhibited an inferior rate capability to the bare one. As the cut-off voltage (4.3, 4.6, and 4.8 V) increases, the coated cathodes exhibited excellent capacity retention, but the bare cathode degraded rapidly [25].

### 1.5. Silica

Coating silica on LiCoO<sub>2</sub> can be done by a simple, economical and convenient mechano-thermal coating procedure. A weighed amount of fumed silica of particle size 18 nm was dispersed in ethanol by a 1 h sonication followed by vigorous stirring. LiCoO<sub>2</sub> was added to this dispersion. The mixture was sonicated and stirred. A subsequent slow evaporation of the solvent at 50 °C resulted in a black dry mass of fumed silica-coated LiCoO<sub>2</sub> particles. To ensure complete adhesion of the coated particles with the core material the coated particles were calcined at 450 °C. The silica species can partially diffuse into the bulk of the cathode material. After coating, the lattice parameter *c* diminishes, indicating that a substitute compound of LiSi<sub>y</sub>Co<sub>1-y</sub>O<sub>2+0.5y</sub> might form upon calcination. A coating level of 1.0 wt.% or less is sufficient to impart a uniform coating on the cathode powder and good structural stability. At the optimum coating level (1.0 wt.%), the cathode material showed nearly a three-fold increase in the cycle life. However, at higher coating levels, small and loosely held agglomerates of the coating material were glued to the surface, suggesting that at the 3.0 and 5.0 wt.% coating levels, the amount of fumed silica was more than what was required to form a uniform coating on the cathode powder, and that the excess silica agglomerated into small globules on the surface. Since the conductivity of silica is very poor, the electrochemical performance becomes worse when the coating amount is too high [23].

### 1.6. LiMn<sub>2</sub>O<sub>4</sub>

LiMn<sub>2</sub>O<sub>4</sub> can be coated onto LiCoO<sub>2</sub> and the main consideration is to improve the safety problem of lithium ion batteries because among the cathode materials LiCoO<sub>2</sub>, LiNiO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub>, LiMn<sub>2</sub>O<sub>4</sub> is the thermally most stable one, exhibiting the highest onset temperature of about 240 °C for exothermal processes and emitting a minimum level of exothermal heat when charged up to 4.3 V [29]. Since the LiMn<sub>2</sub>O<sub>4</sub> coating is effective in retarding the decomposition reaction of LiCoO<sub>2</sub> with

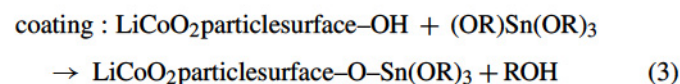
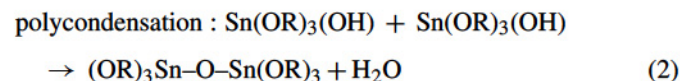
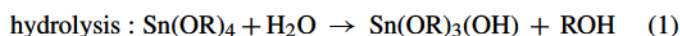
the electrolytes as well as sustaining its structural stability during cycling, the onset temperature for thermal decomposition of the LiMn<sub>2</sub>O<sub>4</sub>-coated LiCoO<sub>2</sub> prepared by heating at 800 °C is 225 °C, whereas that of the bare LiCoO<sub>2</sub> is only 185 °C. In addition, the coating also improves significantly the capacity retention on cycling at a charge cut-off voltage of 4.3 V [29].

### 1.7. ZrO<sub>2</sub>

A sol-gel coating of ZrO<sub>2</sub>, which has the highest fracture toughness, formed a fracture-toughened thin-film solid solution (tens of nm thick) near the particle surface. This film significantly improves the structural stability of the cathode material by suppressing *c*-axis expansion (or phase transition), thereby preventing capacity fading during electrochemical cycling. The lattice constant *c* of the ZrO<sub>2</sub>-coated Li<sub>1-x</sub>CoO<sub>2</sub> exhibits negligible shift in the range 0 < *x* < 0.7, indicating that the original hexagonal symmetry is unaffected by delithiation. The sample does not show any noticeable capacity fading over 70 cycles, thereby retaining its original capacity. In contrast, bare LiCoO<sub>2</sub> keeps ~60% of its original capacity after only 30 cycles [14,27,30].

### 1.8. SnO<sub>2</sub>

SnO<sub>2</sub> coating can be performed by a sol-gel method, and this procedure is shown as follows [31]:



where OR is an alkoxy group.

After coating, the properties of the coated LiCoO<sub>2</sub> depend on the subsequent heat-treatment. When *T* < 600 °C, tin is preferably distributed on the surface, and the coated LiCoO<sub>2</sub> exhibits excellent structural stability since the phase transitions of the monoclinic phase at 4.15 and 4.2 V disappear. As a result, >80% of the capacity is retained after 47 cycles between 4.4 and 2.75 V at the 0.5 C rate as shown in Fig. 1. In contrast, when *T* = 600 °C, tin distributes uniformly throughout the coated LiCoO<sub>2</sub> particles, a capacity loss of 51% after 47 cycles (Fig. 1, curve d) is observed since tin cannot prevent the contact of LiCoO<sub>2</sub> with the electrolyte, phase transition and the resulting cation disorder during cycling [31].

### 1.9. Carbon

Carbon coating on LiCoO<sub>2</sub> by spark-plasma-sintering has been attempted to improve the rate performance of an all-solid-state battery using oxysulfide glass. 2.5 wt.% of AB (acetylene black) would be an optimal amount to balance the enhancement of the electronic conductivity and the suppression of electrode

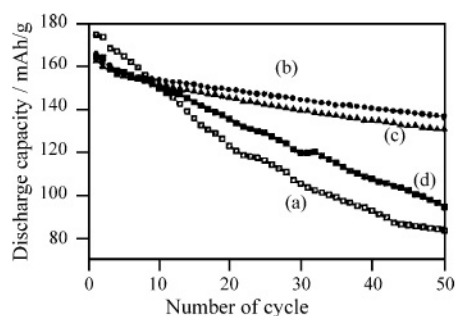


Fig. 1. Cycling behavior of uncoated (a) and  $\text{LiCoO}_2$  coated with  $\text{SnO}_2$  from sol-gel method prepared at  $400^\circ\text{C}$  (b),  $500^\circ\text{C}$  (c) and  $600^\circ\text{C}$  (d) at 0.5 C rate (70 mA/g) between 4.4 and 2.75 V (from Ref. [31]).

reaction at the lower rate. On the other hand, the higher discharge capacity of above 100 mAh/g is exhibited even at the higher current density. Carbon coating on the active material  $\text{LiCoO}_2$ , rather than merely mixing or adding, is effective for improving rate performance in all-solid-state batteries [32].

#### 1.10. Other compounds

The above results show that oxide coatings are effective to improve electrochemical performance of  $\text{LiCoO}_2$ . When composite oxides from the above oxides such as  $\text{MgAl}_2\text{O}_4$ ,  $\text{ZrTiO}_4$  and phosphates were used as coating, they showed superior electrochemical performance to the single coating [19,27]. Of course, other kinds of metal oxides or nonmetal oxides such as  $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$  glass can also be used, which is one future direction for research.

In summary, it is evident that coating is a good method to improve the electrochemical behavior of  $\text{LiCoO}_2$  cathode in terms of reversible capacity, cycling, rate capability, overcharge tolerance and safety problem associated with heat production during cycling. The main reasons for these improvements were raised by Cho et al., i.e. the coating can prevent the direct contact between electrolyte and inner body of  $\text{LiCoO}_2$ . As a result, the dissolution of cobalt and the side chemical reactions are decreased, and structural and thermal stabilities are increased. Based on these explanations, the toughness of the coating affects evidently the coating effect. When the oxide is tough, then better electrochemical performance will be achieved. For example, the cycling performance increases with the following order:  $\text{B}_2\text{O}_3 < \text{TiO}_2 < \text{Al}_2\text{O}_3 < \text{ZrO}_2$ , which is consistent with the toughness [18]. However, as to the specific actions, there are other kinds of saying. It was reported that the main action was from the suppression of impedance growth in the cell associated with repeated charging to 4.5 V. Good capacity retention cannot be attained for cycling  $\text{LiCoO}_2$  above 4.5 V with respect to Li metal, presumably because of the structural changes occurring near 4.55 V [33]. It was also observed that the coating caused a slight degradation in rate capability instead of enhancement. The heat-treatment step applied during the process of coating metal oxide was mainly responsible for the improvement of cycle life [34]. Others reported that surface coating could not prevent the dissolution of lithium from  $\text{LiCoO}_2$  in the electrolyte solvent and its structural degradation at room temperature. Rather, modify-

ing the surface of commercial  $\text{LiCoO}_2$  particles can suppress the formation of oxygen with higher oxidizing power and alleviate the electrolyte decomposition at charged states [35]. Perhaps all of the above reported mechanisms just noted one or some aspects and ignored others. Of course, depending on the preparation process the obtained results will also be different. These different opinions remain to be solved.

## 2. $\text{LiNiO}_2$

$\text{LiNiO}_2$  has a layered structure similar to  $\text{LiCoO}_2$  and is cheaper than  $\text{LiCoO}_2$  [1]. Its reversible capacity is higher than that of  $\text{LiCoO}_2$  and it is a promising candidate as cathode material for lithium ion batteries though it is not easy to prepare on a large scale due to the difficult oxidation of  $\text{Ni}^{2+}$  to  $\text{Ni}^{3+}$  and easy decomposition of  $\text{LiNiO}_2$  into Li-deficient compounds  $\text{Li}_d\text{NiO}_{2-d}$  ( $0 < d < 1$ ) during high temperature synthesis. These problems can be overcome by incorporation of heteroatoms [4] and sol-gel methods [2]. However, during cycling it is similar to  $\text{LiCoO}_2$ , and there are phase transitions when  $x$  (in  $\text{Li}_{1-x}\text{NiO}_2$ )  $> 0.5$ , for example from the original hexagonal phase (H1) to the monoclinic one (M), from M to another hexagonal phase (H2), and from H2 to the third hexagonal phase H3. The latter two phase transitions are especially serious leading to detrimental effects. As a result, microcracks are formed in each particle induced by anisotropic lattice changes along  $a$  and  $c$ -axis in the initial hexagonal phase, and new hexagonal (H2 and H3) and dominant monoclinic phases appear; capacity fades markedly with cycling. In order to circumvent this problem it has been found that coating is a good method. In the case of doped  $\text{LiNiO}_2$ , there are still some possible improvements. For example,  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  is a very promising cathode material with high capacity and medium cost for lithium ion secondary cells. Its cycle performance and thermal stability still needs further improvement and surface coating is a useful way. The coating materials include  $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$  glass (LBO),  $\text{MgO}$ ,  $\text{AlPO}_4$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$ .

### 2.1. $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glass (LBO)

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powders were coated with  $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$  glass through mixing  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ ,  $\text{LiOH} \cdot \text{H}_2\text{O}$  and  $\text{H}_3\text{BO}_3$  and heating the mixture at  $500^\circ\text{C}$  for 10 h. The formed  $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$  glass has high  $\text{Li}^+$  conductivity and stability, prevents direct contact between  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  with liquid electrolyte, and minimizes the side reactions within the battery. As a result, the coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathode material presents enhanced reversible capacity, decreased irreversible capacity, stable cycling performance, reduced self-discharge, and especially improved performance at elevated temperature [36].

### 2.2. $\text{MgO}$

When  $\text{MgO}$  is coated on the surface of semi-crystalline  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$  with magnesia xerogel, the cycling behavior is also improved though the initial discharge capacity is decreased. A minor phase of  $\text{Mg}_{1-x}\text{Ni}_x\text{O}$  forms presumably near

the surface. This layer lowers the initial discharge capacity of the battery. However, the cycling behavior is greatly improved [37,38].

In the case of  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ , further doping can be performed. When the surface of  $\text{LiSr}_{0.002}\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_2$  is coated with MgO, the onset temperature of thermal dissociation increases by about  $10^\circ\text{C}$ , and heat dissipation during thermal decomposition diminishes considerably. As a result, tendency toward explosion in the cylindrical battery is largely alleviated by the surface treatment. In addition, it exhibits improved electrochemical performance especially at the demanding rate of 1 C [39]. The detailed action of the MgO coating is still not understood and needs further study. It is suggested that protection is one reason for the improvement.

### 2.3. $\text{AlPO}_4$

$\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  cathode material has a larger specific capacity than  $\text{LiCoO}_2$ , but its thermal instability hinders its practical use in Li-ion cells. Coating  $\text{AlPO}_4$  is considered as a good method to improve its performance. The  $\text{AlPO}_4$  coating noticeably diminishes the violent exothermic reaction of the cathode material with the electrolyte, without sacrificing the specific capacity of the bare  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  (188 mAh/g at cut-off voltage of 4.3 V). The results are consistent with the thermal abuse tests using Li-ion cells. The cells assembled with the  $\text{AlPO}_4$ -coated  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  cathode do not exhibit thermal runaway of smoke and explosion, in contrast to those with the bare cathode. In addition, the  $\text{AlPO}_4$ -coated  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  cathode shows a superior cycling performance compared to the bare  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  [40]. By the way, it presents excellent overcharge performance. In comparison with  $\text{AlPO}_4$ -coated  $\text{Li}_x\text{CoO}_2$  cathodes, the  $\text{AlPO}_4$ -coated  $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  exhibits less heat generation than the latter as the charge voltage increases. As the C rate increases from 1 to 3 C, the cell-surface temperature with the  $\text{AlPO}_4$ -coated  $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  cathode does not exceed  $125^\circ\text{C}$ , and that of the coated  $\text{Li}_x\text{CoO}_2$  exceeded  $170^\circ\text{C}$  [24].

### 2.4. Silica

Coating a thin layer of  $\text{SiO}_x$  on  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  particles can be performed via chemical vapor deposition (CVD). Though it was said to be very reproducible [41], it is not easy in comparison with the above used methods such as mechanochemical one [23]. The aim is to enable lithium ions to intercalate into the cathode material through the coating layer while preventing the surface of the cathode to contact directly with the electrolyte media. The structure of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  is only slightly modified by the CVD process. The deposited film around the cathode particles consists of an amorphous layer of under-stoichiometric silicon dioxide  $\text{SiO}_x$  ( $x < 2$ ) which is 3–5 nm thick. The initial charge capacity of the starting material is not affected by the protective coating; nevertheless, the capacity fade was slightly larger upon cycling compared to the uncoated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder. In the meanwhile, the  $\text{SiO}_x$  coating is efficient to decrease by 50% the

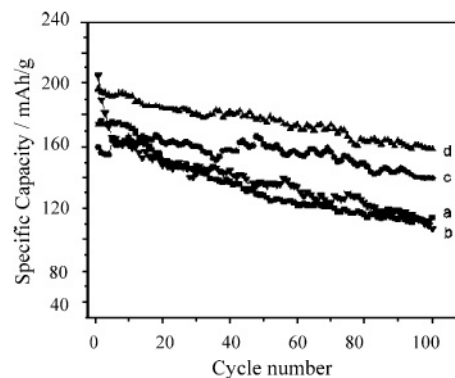


Fig. 2. Comparison of the cycling stability of uncoated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  and  $\text{TiO}_2$ -coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathodes in different voltage ranges at C/5 rate: (a) uncoated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  (3.0–4.3 V), (b) uncoated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  (3.0–4.6 V), (c)  $\text{TiO}_2$ -coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  (3.0–4.3 V), (d)  $\text{TiO}_2$ -coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  (3.0–4.6 V) (from Ref. [42]).

exothermic reaction occurring at around  $210^\circ\text{C}$  in the charged state [41].

### 2.5. $\text{TiO}_2$

$\text{TiO}_2$  can be coated on  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powders by hydroxylation of tetra-*n*-butyl titanate (TBT) in air or precipitation from alcohol solution following a heat-treatment [42–44].

There is almost no change of bulk structure for  $\text{TiO}_2$ -coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ . Electrochemical impedance spectroscopy (EIS) experiments implied that the interface stability is improved during cycling [43]. The different electrolyte decomposition products on the coated and uncoated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  surface also demonstrate the improved interface stability. On the coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  there are mainly  $\text{HCOO}_2^-$ ,  $(\text{CH}_3)_2\text{CHCOO}_2^-$  beside  $\text{POF}_x^-$  salt, whereas on the uncoated one there are not only  $\text{HCOO}_2^-$  and  $(\text{CH}_3)_2\text{CHCOO}_2^-$  but also carboxyl salts of shorter carbon chains such as  $\text{CH}_3\text{COO}_2^-$  and  $\text{CH}_3\text{CH}_2\text{COO}_2^-$  [44]. Consequently, the  $\text{TiO}_2$  coating can enhance the cycling stability by suppressing the decomposition reaction of the electrolyte [42,43]. For example, the  $\text{TiO}_2$ -coated electrodes exhibited good cycle stability no matter whether the upper cut-off potential is 4.3 or 4.6 V as shown in Fig. 2b and d. In comparison, the uncoated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  showed a poor stability during cycling as shown in Fig. 2a and c.

### 2.6. $\text{ZrO}_2$

After coating with  $\text{ZrO}_2$  by a sol–gel method, each  $\text{LiNiO}_2$  particle was covered with a thin coating layer. This coating layer reduces significantly the lattice distortion, and the coated  $\text{LiNiO}_2$  shows several times lower changes in the lattice constants during charging in comparison with the bare sample. When the concentration of Zr at the particle surface within  $\sim 1\ \mu\text{m}$  is high, effective suppression of the lattice distortion and thereby phase transitions especially the above mentioned ones from M to H2 and H2 to H3 have been achieved. As a result, the coated  $\text{LiNiO}_2$  shows great improvement in the Li intercalation stability over many cycles. For example, only 2% capacity loss in the

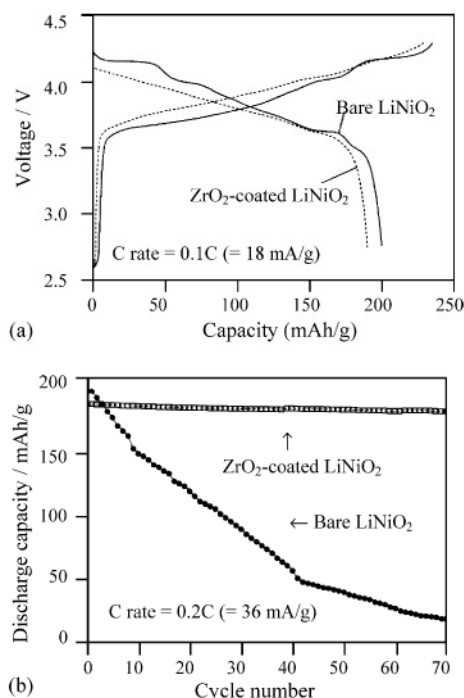


Fig. 3. Charge and discharge profiles of bare and ZrO<sub>2</sub>-coated LiNiO<sub>2</sub> in the first cycle between 4.3 and 2.75 V at the rate of 0.1 C (18 mA/g) (a) and their cycling behavior at the rate of 0.2 C (36 mA/g) (b) (from Ref. [45]).

ZrO<sub>2</sub>-coated sample after 70 cycles between 4.3 and 2.75 V as shown in Fig. 3 have been reported [14,45].

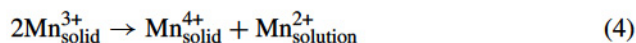
From the above discussion, it can be seen that LiNiO<sub>2</sub> coating has several effects: (1) preventing the direct contact of LiNiO<sub>2</sub> with electrolyte solution resulting in a decrease of side reactions; (2) decreasing the heat production during cycling due to improvement of surface properties; (3) suppressing phase transition and improving structural stability. As a result, the surface treatment is effective to improve the comprehensive properties of LiNiO<sub>2</sub> as cathode material for lithium secondary batteries. As to the actions of the coatings on LiNiO<sub>2</sub>, there is no different opinion so far and they are mainly based on Cho's coating mechanism [12,27]. Consequently, the oxides with tough structure present better performance [45]. Of course, other kinds of metal oxides such as those used for LiCoO<sub>2</sub> (Al<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub>) can also be used to achieve improvements.

### 3. LiMn<sub>2</sub>O<sub>4</sub>

LiMn<sub>2</sub>O<sub>4</sub> has a spinel structure, different from LiCoO<sub>2</sub> and LiNiO<sub>2</sub>. Since it has a low price, is environmentally benign, and has a good thermal behavior, which does not require additional expensive safety devices, it is fairly attractive as cathode material of lithium ion batteries for electric vehicles [1]. However, there are still some problems that should be solved prior to its commercial use: capacity fading, Mn dissolution at high temperature and poor high-rate capability. The capacity fading is mainly due to the following three factors [1,46]:

- (1) *Dissolution of Mn<sup>3+</sup>*: At the end of discharge, the concentration of Mn<sup>3+</sup> arrives at its highest level. The Mn<sup>3+</sup> at the

surface may disproportionate according to the following Eq. (4):



Mn<sup>2+</sup>-ions from this disproportionation dissolve in the electrolyte solution.

- (2) *Jahn–Teller effect*: At the end of discharge, the Jahn–Teller effect happening at first on the surface of particles may spread into the overall composition of Li<sub>1+δ</sub>[Mn<sub>2</sub>]O<sub>4</sub>. Thermodynamically speaking, this system is not really at equilibrium. The phase transition from cubic into tetragonal symmetry is a first-order process. Even though this kind of change is small, it is big enough to destroy the structure to form a tetrahedral structure, which is low in symmetry and high in disorder.
- (3) In organic solvents, the highly de-lithiated particles are not stable at the end of charge, viz. the high oxidation ability of Mn<sup>4+</sup> will lead to decomposition of solvents.

These factors may act at the same time resulting in a fading capacity. By the way, after doping with heteroatoms improvement in the cycling stability has been achieved [4]. However, this improvement is usually effective only at room temperature. At elevated temperature its cycling behavior is still poor due to severe Mn dissolution by HF produced from F-containing inorganic electrolyte salt. Furthermore, its rate capability is inferior to that of LiCoO<sub>2</sub> due to its low electric conductivity (10<sup>−6</sup> S/cm) in comparison with that of LiCoO<sub>2</sub> (10<sup>−2</sup> S/cm). In order to use LiMn<sub>2</sub>O<sub>4</sub> as a cathode material of lithium ion batteries for electric vehicles (EVs), its rate capability should be improved. To solve partially or completely the above mentioned problems, coating the surface of LiMn<sub>2</sub>O<sub>4</sub> is also a good method, and the coating materials include Li<sub>2</sub>O·2B<sub>2</sub>O<sub>3</sub> glass (LBO), MgO, Al<sub>2</sub>O<sub>3</sub>, Li<sub>1−x</sub>CoO<sub>2</sub> (x ≥ 0), LiCo<sub>x</sub>Mn<sub>2−x</sub>O<sub>4</sub>, ZnO, ZrO<sub>2</sub>, composite oxides, conductives and polymers.

#### 3.1. Li<sub>2</sub>O·2B<sub>2</sub>O<sub>3</sub> glass (LBO)

In order to prevent the dissolution of Mn<sup>2+</sup>, the surface of LiMn<sub>2</sub>O<sub>4</sub> can be coated with a thin layer of inorganic Li<sub>2</sub>O·2B<sub>2</sub>O<sub>3</sub> glass (LBO) [47]. The reason for choosing the LBO is as the follows: (1) the LBO-coated LiMn<sub>2</sub>O<sub>4</sub> exhibits good wetting properties. The combination of its good wetting properties and relatively low viscosity in the molten state allows easy processing and results in even coverage with the use of a minimal amount of material; (2) LBO-coated LiMn<sub>2</sub>O<sub>4</sub> has already been investigated as solid lithium ionic conductors which exhibits good ionic conductivity; (3) electrochemical studies have shown that these materials are stable against the high oxidation potentials of the 4 V positive electrode materials used in Li-ion batteries today; (4) such materials have processing temperatures consistent with those of LiMn<sub>2</sub>O<sub>4</sub>. This surface treatment improves the elevated temperature performance of the Li<sub>1+x</sub>Mn<sub>2−x</sub>O<sub>4</sub> spinel to some degree because the dissolution of Mn<sup>2+</sup> is decreased [47].

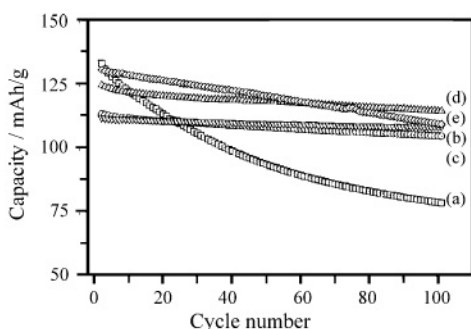


Fig. 4. Cyclability of different kinds of  $\text{LiMn}_2\text{O}_4$  at a current density of  $0.5 \text{ mA/cm}^2$  ( $C/2$  rate) at  $60^\circ\text{C}$ : (a)  $\text{LiMn}_2\text{O}_4$ , (b)  $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ -coated  $\text{LiMn}_2\text{O}_4$ , (c)  $\text{LiCoO}_2$ -coated  $\text{LiMn}_2\text{O}_4$ , (d)  $\text{Li}_{0.75}\text{CoO}_2$ -coated  $\text{LiMn}_2\text{O}_4$  and (e)  $\text{Al}_2\text{O}_3$ -coated  $\text{LiMn}_2\text{O}_4$  (from Ref. [48]).

### 3.2. MgO

Coating MgO involves the dispersion of the  $\text{LiMn}_2\text{O}_4$  spinel oxide in an aqueous solution of magnesium nitrate, precipitation of hydrous magnesium oxide over  $\text{LiMn}_2\text{O}_4$  particles through the addition of ammonium hydroxide, and heating the resultant product at  $300$  and  $600^\circ\text{C}$ , respectively, in air for 4 h. The coated  $\text{LiMn}_2\text{O}_4$  shows good electrochemical performance with initial discharge capacity of  $136.5 \text{ mAh/g}$  and fading rate of  $0.073\%/ \text{cycle}$  at room temperature. This improvement is due to the maintenance of low microstrain, better structural integrity and crystallinity during cycling from the MgO coating [48].

### 3.3. $\text{Al}_2\text{O}_3$

$\text{Al}_2\text{O}_3$  can also be used to coat on  $\text{LiMn}_2\text{O}_4$  by a chemical process, and commercially available  $\text{LiMn}_{2-x}\text{Zr}_x\text{O}_4$  by a sol-gel method following a heat-treatment at  $300$ – $800^\circ\text{C}$  [14,48,49]. After coating, polarization and the lattice parameter  $a$  increase due to the formation of a solid solution on the surface [49]. However, the coated samples show much better capacity retention at both  $25$  and  $60^\circ\text{C}$  than the uncoated  $\text{LiMn}_2\text{O}_4$  ( $41\%$  fade in 100 cycles at  $60^\circ\text{C}$ ). For example, the  $\text{Al}_2\text{O}_3$ -modified  $\text{LiMn}_2\text{O}_4$  spinel shows a higher capacity of  $130 \text{ mAh/g}$  and capacity fade of only  $16\%$  in 100 cycles at  $60^\circ\text{C}$  as shown in Fig. 4 (curve e).

### 3.4. $\text{Li}_x\text{CoO}_2$ ( $0 < x \leq 1$ )

Coating  $\text{Li}_x\text{CoO}_2$  ( $0 < x \leq 1$ ) on the surface of  $\text{LiMn}_2\text{O}_4$  is performed by sol-gel methods [48,50–52] and micro-emulsion method [53].

Concerning the nature of the coating there are different reports [50–53]. It is not  $\text{LiCoO}_2$  but a newly formed spinel phase,  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{Co}_x\text{O}_4$ , due to heat-treatment at  $800^\circ\text{C}$  [52]. Since the coating layer is situated at the surface of  $\text{LiMn}_2\text{O}_4$ , this kind of structure is also called a core-shell structure [54]. Co ions at the surface are effective in protecting the active material from  $\text{Mn}^{3+}$  dissolution into the electrolyte solution, leading to less cation disorder [48,52,54]. Electrochemical impedance spectroscopy (EIS) showed that the first and second semicircles

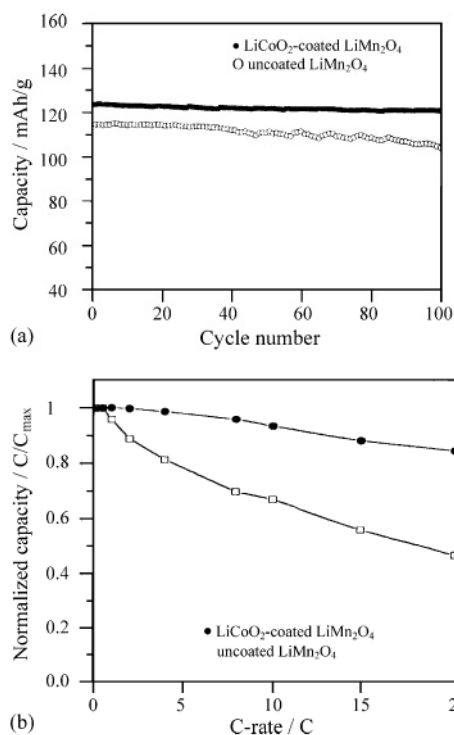


Fig. 5. Cycling behavior (a) and change of normalized discharge capacity (b) of uncoated and  $\text{LiCoO}_2$ -coated  $\text{LiMn}_2\text{O}_4$  at room temperature (from Ref. [51]).

of coated  $\text{LiMn}_2\text{O}_4$  were reduced, implying that the passivation film acting as an electronic insulating layer suppresses the inter-particle contact resistance [50,51]. By the way,  $\text{LiCoO}_2$  has a higher capacity than  $\text{LiMn}_2\text{O}_4$ . As a result, the capacity, cycling performance at room and elevated temperatures and rate capability of the coated  $\text{LiMn}_2\text{O}_4$  are greatly improved. For example, a  $\text{LiCoO}_2$ -coated  $\text{LiMn}_2\text{O}_4$  showed a higher discharge capacity of  $120 \text{ mAh/g}$  than uncoated  $\text{LiMn}_2\text{O}_4$  ( $115 \text{ mAh/g}$ ) (Fig. 5a). The latter maintained only  $50\%$  of its maximum capacity at  $20 \text{ C}$  rate ( $2400 \text{ mA/g}$ ), and the former more than  $80\%$  of maximum capacity (Fig. 5b). In addition,  $\text{LiCoO}_2$ -coated  $\text{LiMn}_2\text{O}_4$  with  $3 \text{ wt.}\%$  conducting agent (acetylene black) showed better rate capability than the uncoated  $\text{LiMn}_2\text{O}_4$  with  $20 \text{ wt.}\%$  conducting agent [50,51]. There was also marked improvement in its electrochemical performance at high temperatures such as  $55$  and  $65^\circ\text{C}$  [51,52]. The  $\text{Li}_{0.75}\text{CoO}_2$ -modified sample shows a good combination of capacity ( $124 \text{ mAh/g}$ ) and capacity retention ( $8\%$  fade in 100 cycles at  $60^\circ\text{C}$ ) (Fig. 4, curve d) [48].

### 3.5. $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ( $0 < x < 1$ )

When the surface of  $\text{LiMn}_2\text{O}_4$  is coated with  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  ( $x = 0.2$  and  $0.5$ ), this coating will suppress the decomposition of electrolyte solution and reduce Mn dissolution [48,55]. As a result, compared with pure  $\text{LiMn}_2\text{O}_4$  the coated  $\text{LiMn}_2\text{O}_4$  shows excellent capacity retention and cycling behavior at high temperature ( $65^\circ\text{C}$ ). For example, in the case of  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ -modified sample it shows superior capacity retention with only  $2.8\%$  fade in 100 cycles at  $60^\circ\text{C}$  and a capacity of about  $110 \text{ mAh/g}$  (Fig. 4, curve b) [48].

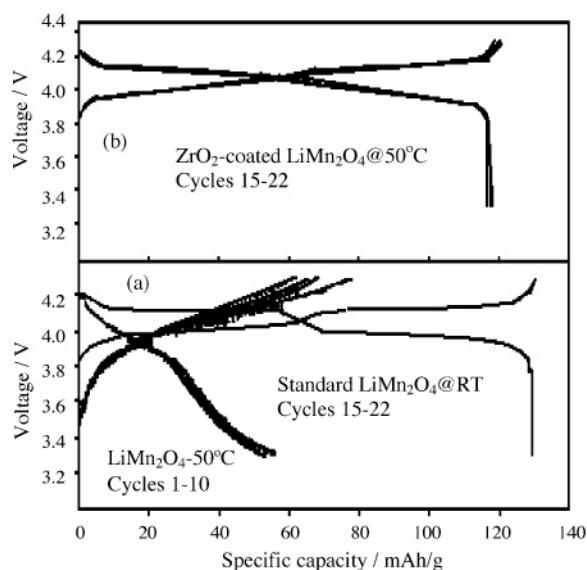


Fig. 6. Comparison of the electrochemical cycling stability of lithium cells with: (a) uncoated  $\text{LiMn}_2\text{O}_4$  electrodes at room temperature and  $50^\circ\text{C}$ , and (b)  $\text{ZrO}_2$ -coated  $\text{LiMn}_2\text{O}_4$  electrodes at  $50^\circ\text{C}$  (from Ref. [56]).

### 3.6. $\text{ZrO}_2$

Colloidal nano-particles of  $\text{ZrO}_2$  can be deposited on the surface of the spinel  $\text{LiMn}_2\text{O}_4$  electrode. They suppress the dissolution of  $\text{Mn}^{3+}$  and strong  $\text{Zr}-\text{O}$  bonds at the electrode surface decrease the oxygen activity at high potentials.  $\text{ZrO}_2$  at the surface scavenges the acidic  $\text{HF}$  species from the electrolyte solution by reaction with  $\text{HF}$ . As a result, excellent capacity retention on cycling has been achieved [56]. For example, Fig. 6 shows the comparison of the cycling stability at room temperature and  $50^\circ\text{C}$  of the standard  $\text{LiMn}_2\text{O}_4$  and  $\text{ZrO}_2$ -coated one. The data at  $50^\circ\text{C}$  confirm the well-known phenomenon that the capacity of  $\text{LiMn}_2\text{O}_4$  spinel electrode fades rapidly at this temperature, which is attributed to the dissolution of manganese at the spinel surface. In contrast, the  $\text{ZrO}_2$ -coated  $\text{LiMn}_2\text{O}_4$  shows negligible capacity loss when cycled at the same current rate [56].

### 3.7. $\text{ZnO}$

When the doped  $\text{LiMn}_2\text{O}_4$  is coated by metal oxides, for example,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  coated by  $\text{ZnO}$  using sol-gel method [57,58], great improvements have been achieved. After 50 cycles at  $55^\circ\text{C}$   $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  shows a serious capacity loss and exhibits a mixture of tetragonal phase ( $\text{Li}_2\text{Mn}_2\text{O}_4$ ), rock salt phase ( $\text{Li}_2\text{MnO}_3$ ) and cubic phase. In contrast, a 1.5 wt.%  $\text{ZnO}$ -coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode delivers an initial discharge capacity of 137 mAh/g with excellent cyclability at elevated temperature  $55^\circ\text{C}$ , almost no capacity loss, and maintains almost perfect cubic spinel structure [57]. The main reason is that the small amount of  $\text{ZnO}$  coating plays an important role in improving the cycling behavior of the Mn-based cathode materials in the 5 V region by significantly reducing  $\text{HF}$  content or removing  $\text{HF}$  from the electrolyte solution [58]. Perhaps other factors such as suppression of

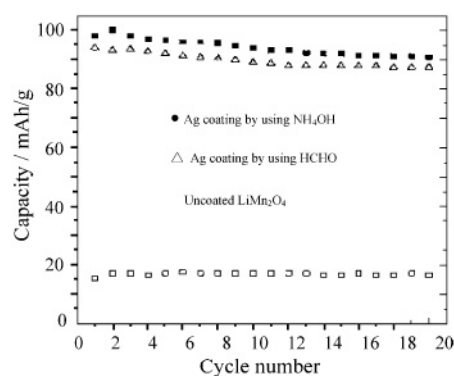


Fig. 7. Cycle efficiency of  $\text{LiMn}_2\text{O}_4$  under 2C galvanostatic conditions: (a) uncoated  $\text{LiMn}_2\text{O}_4$ , and (b) silver-coated  $\text{LiMn}_2\text{O}_4$  (from Ref. [63]).

structural change are also in action, which deserves further study.

### 3.8. Composite oxides

Composite oxides such as  $\text{Al}_2\text{O}_3/(\text{PtO}_x \text{ or } \text{CuO}_x)$  can be coated on commercial spinel powder ( $\text{LiMn}_{2-x}\text{Zr}_x\text{O}_4$ ) by a sol-gel method [59]. After testing, bare spinel showed abnormal surfaces, which were formed by decomposing the electrolyte, while  $\text{Al}_2\text{O}_3/\text{CuO}_x$ -coated spinel displayed a normal surface covered with a surface film. It was expected that the composite oxide layer coated on the spinel powder functions as a protective film, which suppresses the reaction between electrolyte solution and active material [60]. In the meanwhile, a new  $\text{Li}_2\text{Mn}_4\text{O}_9$ ,  $\text{Li}_2\text{MnO}_3$  phase, which is expected to have stability against phase transition (Jahn-Teller distortion) may be formed after the coating [59]. Consequently, the coated spinel exhibits stable cycle performance in the range from 2.5 to 4.4 V [59,60].

### 3.9. Conductive coatings

Conductive coatings have low resistance and can therefore enhance the surface intercalation reaction of lithium ions, reduce cell polarization and inter-particle resistance and contact between active electrode materials and electrolyte solution if they are coated on  $\text{LiMn}_2\text{O}_4$ . The studied conductives include acetylene black, silver and gold [61–64]. Silver coating can be performed by deposition or reduction from  $\text{AgNO}_3$  solutions [63,64]. The diameters of the silver particles are in the range of 10–100 nm. The electrochemical cycling behavior of uncoated and silver-coated electrodes is presented in Fig. 7, which shows that the silver-coated electrode has superior cycling performance and higher capacity [63]. The coated one also has better rate capability. The amount of Ag could not be excessive. If silver content is too high, the coating layer forms a barrier for the movement of Li ions, which hinders their movement into the spinel and results in low initial specific capacity [63,64].

### 3.10. Polymers

The studied polymers include poly(diallyldimethylammonium chloride) (PDDA), and electroactive polymers such

as poly(3,4-ethylenedioxy)thiophene (PEDOT) and polypyrrole (PPy).

A thin polymer film of PDDA was coated on  $\text{LiMn}_2\text{O}_4$  particles via surface adsorption. The adsorbed polymer layer inhibits surface reactions causing degradation and arrests the  $\text{Mn}^{3+}$  dissolution. The cathodes at room temperature show minor changes in surface topography during cycling. As a result, the modified  $\text{LiMn}_2\text{O}_4$ -based cathode displays an improved stability during repeated charge/discharge in organic electrolyte at room temperature and storage at elevated temperature, and the surface-modified  $\text{LiMn}_2\text{O}_4$  electrode extends the lifetime of the lithium ion battery [65]. The electrochemical performance also depends on the absorbed amount of the polymer. For example, capacity fading is the lowest for the cathodes obtained from powder coated in solutions containing 30–50 mM PDDA.

When PEDOT and PPy are coated on the surface of cathode oxides  $\text{Li}_{1.03}\text{Mn}_{1.97}\text{O}_4$ , the polymers can function as an electronic conductor and substitute the carbon usually mixed with the inorganic oxide-based electrodes to improve their electronic conductivity. In the meanwhile, these polymer coatings can also act as a protection layer to decrease  $\text{Mn}^{3+}$  dissolution. Furthermore, these polymers are electroactive in the same potential range of  $\text{LiMn}_2\text{O}_4$ . As a result, reversible capacity and capacity retention are increased [66,67].

In summary, the coating layer on the surface of  $\text{LiMn}_2\text{O}_4$  can lead to the following effects: (1) suppressing the dissolution of  $\text{Mn}^{3+}$ , (2) decreasing the disorder of cations in crystal sites, (3) providing high conductivity, (4) removing HF from electrolyte solutions with F-containing inorganic electrolyte salts, and (5) keeping good structural stability. The above improvements lead to improvement of electrochemical performance of  $\text{LiMn}_2\text{O}_4$  such as capacity retention and high rate capability, and therefore the surface coated  $\text{LiMn}_2\text{O}_4$  will be attractive particularly for electric vehicles due to its lower cost coupled with high rate capability and excellent cycling behavior. From the presented results, it seems that  $\text{Li}_{1-x}\text{CoO}_2$  coating is more advantageous than the other coatings from the viewpoint of cycling performance and reversible capacity. As to specific reasons for this difference, there is still no perfect explanation and further studies are needed.

#### 4. Layered $\text{LiMnO}_2$

Spinel  $\text{LiMn}_2\text{O}_4$  is a promising cathode material due to its high voltage, low cost, abundance and nontoxicity. However, its discharge capacity is low due to its inherent structure. Since it has a high theoretical discharge capacity (285 mAh/g) – about twice that of  $\text{LiMn}_2\text{O}_4$  – and low cost compared to  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$ ,  $\text{LiMnO}_2$  has been intensively investigated as a new layered cathode material.  $\text{LiMnO}_2$  is mainly present in two structural forms: orthorhombic  $\text{LiMnO}_2$  with an ordered rock salt structure of the space group  $Pmnm$ , and monoclinic  $\text{LiMnO}_2$  with space group  $C2/m$ . However, both of them have the cation ordering of the layered  $\alpha\text{-NaFeO}_2$  structure. They are generally not differentiated and referred to as layered  $\text{LiMnO}_2$ . Here we use this terminology though it is not completely accurate.

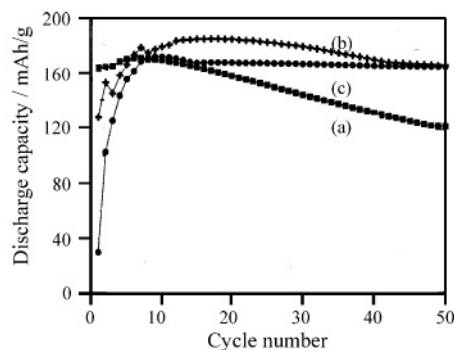


Fig. 8. Plots of the discharge capacity vs. cycle number in: (a) bare, (b) CoO-coated, and (c)  $\text{Al}_2\text{O}_3$ -coated  $\text{LiMnO}_2$  electrodes at the rate of 0.2 C ( $\approx 36$  mA/g) between 4.5 and 2 V at 55 °C (from the Ref. [69]).

When both 3 and 4 V plateaus are used for cycling at room temperature, orthorhombic  $\text{LiMnO}_2$  shows better cycle life performance than  $\text{LiMn}_2\text{O}_4$ . However, the capacity loss increases apparently when cycling at 55 °C, showing that its capacity fades from the maximum 180 to 80 mAh/g after 100 cycles between 4.4 and 2 V. Improving the structural stability by coating is one way to minimize the capacity fading [54,68].

##### 4.1. $\text{Al}_2\text{O}_3$

$\text{Al}_2\text{O}_3$  is coated on  $\text{LiMnO}_2$  by a sol–gel method following a heat-treatment at high temperature [68,69]. Different temperature results in different distribution of Al element. At low temperature  $\text{Al}_2\text{O}_3$  exists almost completely at the surface. When the heat-treatment temperature is above 400 °C, Al atoms diffuse into the inner part of  $\text{LiMnO}_2$  particles and act as doping instead of coating. The  $\text{Al}_2\text{O}_3$  coating stabilizes the layer structure of  $\text{LiMnO}_2$  [68]. As a result, the capacity retention of the  $\text{Al}_2\text{O}_3$ -coated electrodes is excellent, showing only 2% capacity loss after 50 cycles as shown in Fig. 8 [69]. If Al acts as doping and diffuses deeply (uniformly) into the particle ( $\text{LiMn}_{1-x}\text{Al}_x\text{O}_2$ ), capacity retention will deteriorate. After cycling, the peak broadening of the coated sample increases, and this is associated with the formation of nanosize crystallites and/or lattice strains [68].

##### 4.2. $\text{CoO}$

Coating CoO can be performed by a sol–gel method followed by a heat-treatment at 400 °C, and it changes to  $\text{LiMn}_{1-x}\text{Co}_x\text{O}_2$  thin-film layer, which acts as a protection from the direct contact of electrodes with electrolytes. After coating,  $\text{Li}_2\text{MnO}_3$  impurity phase disappears. As a result, the capacity fading of bare  $\text{LiMnO}_2$ , which originates from Mn dissolution, is greatly reduced. By the way, the discharge capacity of the CoO-coated electrode is higher than that of the bare ones, showing 179 mAh/g after 10 cycles, which is due to the additional voltage plateau (near 2 V) at the end of discharge [69].

#### 5. Concluding remarks

From the above illustrations, it is clear that the surface structures are of great importance to electrochemical performance of

cathode materials. Surface coatings such as  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and other compounds/composites on  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMnO}_2$  can prevent the direct contact of electrolyte solutions with cathode materials, improve structural stability and suppress phase transitions. Of course, other kinds of improvement such as increase of conductivity can also be achieved dependent on the specific coating. Consequently, marked improvement can be achieved such as capacity retention, rate capability and electrochemical behavior at high temperature.

As to practical applications, perhaps mechano-thermal treatment is one promising one since this process is much cheap and easily performed [28]. However, as to whether it can ensure good uniformity of the products, it is still a question. sol–gel methods are a little more expensive, but they can be widely applied to coating a lot of oxides homogenously on the surface of cathodes. Since the amount of oxides coating is not much, the cost is not a problem due to marked improved performance [12]. Other methods such as chemical vapor deposition can be applied in special cases, for example thin film batteries, because the production process itself requires special equipments.

Different oxides present different influence and results. The main reason is not clear, but in most cases such as lithium cobalt oxides, lithium nickel oxides and lithium manganese oxides the improvement in electrochemical performance is consistent with the toughness. Of course, besides this, other factors should be considered since different results have been observed [33–35].

On the basis of the above studies, other kinds of cathode materials can also be modified by coating such as aerogel  $\text{V}_2\text{O}_5$ , and considerable improvements in electrochemical performance have been achieved [70]. It is sure that the surface structure of cathode materials will play an more and more important role in their electrochemical performance with a better understanding of their actions during lithium intercalation and de-intercalation, and better and/or cheaper cathode materials from surface modification will come up in the near future [71–75].

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