TOPICAL REVIEW — Fundamental physics research in lithium batteries

Surface structure evolution of cathode materials for Li-ion batteries*

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Lithium ion batteries are important electrochemical energy storage devices for consumer electronics and the most promising candidates for electrical/hybrid vehicles. The surface chemistry influences the performance of the batteries significantly. In this short review, the evolution of the surface structure of the cathode materials at different states of the pristine, storage and electrochemical reactions are summarized. The main methods for the surface modification are also introduced.

Keywords: structure evolution, surface, cathode, Li-ion batteries

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1. Introduction

Since lithium ion batteries were first commercialized in 1991 by Sony, they have been widely used in many fields such as consumer electronics, for their high energy density and high safety performance.[1,2] During the last 24 years, the performance of lithium ion batteries has significantly improved. The energy density has increased from 100 Wh·kg^{-1} to 260 Wh·kg^{-1}. Now, with emerging energy storage applications including electric vehicles (EVs), hybrid electric vehicles (HEVs) and grid, higher requirements are proposed for Li-ion batteries.[3,4]

Figure 1 shows a typical lithium ion battery. Batteries are complex multiphase systems including electrodes (active materials, conductive additives, current collector and polymeric binders), electrolyte, separators, and additional phases (such as solid electrolyte interphase, SEI) usually formed during the electrochemical process.[5] Much work has been done to study bulk structure change, but the structure change of the interface and the surface are equally important. During the electrochemical process, the transport of lithium ions through/along interfaces and surfaces, including the electrode-electrolyte interface, SEI, the interfaces among active material particles, binders, and conductive additives and current collectors in the electrode. The migration of Li-ions at the interfaces above have been discussed by Jamnik *et al.*[5] During the researching and developing for Li-ion batteries, it has been realized that the surface chemistry of the cathode plays an important role in the performance of the electrode during cycling. This review summarizes the surface structure evolution of cathode materials for Li-ion batteries.

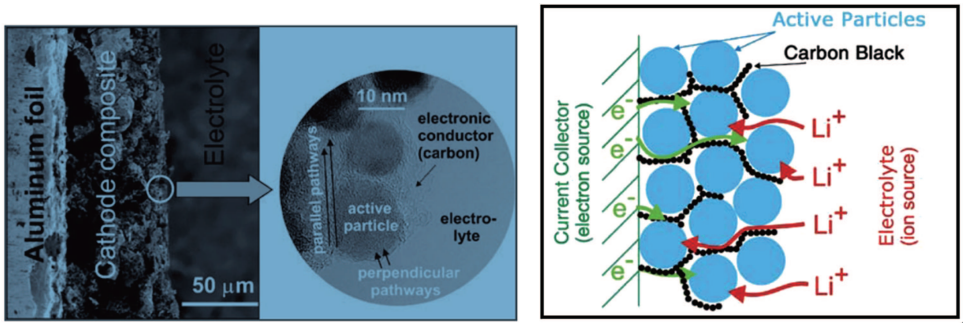


Fig. 1. Typical Li-ion battery electrodes. (a) Low magnification (on left) and high magnification (inset on the right). (b) Schematics showing the main phases constituting a modern insertion cathode and their roles in transport. The polymeric binder is not shown.[5]

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2. Surface structure of pristine material

A stable surface is a basic requirement for a perfect cathode. Film technologies offer good model electrodes to understand the influence of orientation, strain and stress on the electrochemical performance. In layered materials, the (001) plane exhibits higher discharge capacities than the (010) plane. An irreversible phase change occurs at the (010) surface, during the first (de)intercalation process, whereas reversible structural changes take place at the (001) surface.[6]

Actual surfaces usually contain defects, such as antisites, size effects, surface coating layers, gradient structure and core-shell structure. They may influence the surface structure, and introduce point defects and grain boundaries etc. to the structure. The types of defects and the concentration of the defects are controlled by thermodynamics. They are influenced by the components, crystal structure, and the synthesis methods. The defects may influence the transfer and storage of electrons and ions at the bulk, interface and surface. Defects can also offer extra sites for lithium storage.[7–9] The storage of lithium at the defects can be either reversible or irreversible. Among the cases, underpotential deposition mechanism, interfacial charging mechanism and surface charging mechanism are reversible.[10] The dangling bonds and impurity phase at the surface are irreversible.[10] Understanding the surface defect chemistry and control the surface defects enables regulating and controlling the transport, storage and reaction performance of the cathode.

Antisite defect is the most common defect in cathode materials. It has different influences on cathode materials based on the lithium diffusion channels. In materials with the one-dimensional (1D) channel, such as LiMPO$_4$ (M = Fe, Co, Mn), the antisite defects strongly affect the electrochemical performance of the cathode material, since it will block the well-known one-dimensional lithium diffusion channel.[11–16] Controlling the antisite defects has been suggested as an effective way to improve the electrochemical performance of the olivine-type phosphates.[17–19] In materials with three-dimensional (3D) lithium diffusion channels, the antisite defects in spinel $LiMn_2O_4$ increase the charge transfer impedance.[20] While antisite defects in triplite $(Li_{0.5}Fe_{0.5})_2SO_4F$ does not block the Li^+ diffusion, it still exhibits an excellent electrochemical activity.[21,22]

In layered cathode materials, with 2D channel, antisite defect is the origin of the poor reactivity of $LiNiO_2$ and $LiCrO_2$.[23–27] Our recent investigation of well-crystallized $LiCrO_2$ cathode indicates that Cr ions can migrate into the Li layers in the surface regions, leading to irreversible phase transformation from the layered to the rock-salt structure. The existence of the rock-salt phase in the surface blocks the extraction of lithium in the material.[27] $LiNi_{1/2}Mn_{1/2}O_2$ with fewer antisite defects can perform a much better property during cycle process.[25,28] Jinhyuk Lee *et al.* recently reported a Li-rich layered material which has a certain cation mixing but exhibits excellent performance.[29,30] In this layered material, Li diffuses from site to site by hopping through intermediate tetrahedral sites. Studies of $Li_{1.2}Cr_{0.4}Mn_{0.4}O_2$ also show that cation mixing in lithium rich layered cathode does not affect the lithium storage capacity but stabilizes the structure.[31] Moreover, Li_3NbO_4-based system with cation-disordered rock-salt structure also shows a high capacity of approximately 300 mAh·g^{-1}, but the cycle performance is not acceptable.[32]

Size effects are also important. Nano-sized materials usually have a high rate performance, since the lithium ion diffusion path is much shorter in the nano materials. Micro-sized $LiCrO_2$ shows almost no signs of reversible lithium intercalation.[33,34] Feng *et al.* have found that the electrochemical cycling performance of $LiCrO_2$ is dependent on its particle size. If the grain size is reduced to nano-size, e.g. less than 20 nm, up to 0.7–0.9 lithium can be de-intercalated from the cathode and 0.5 lithium can be intercalated back into the cathode in the first cycle.[35] But nano-materials have a bigger specific surface area with more surface defect density, with higher surface energy. This usually causes serious side reaction during cycle.[36,37]

Other kinds of surface defects are lithium-deficiency, element enrichment, inhomogeneity and amorphousness. For example, $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ prepared by the hydrothermally assisted method have minimal Ni-rich surfaces and demonstrate much better capacity retention and much smaller voltage fade during cycling, compared to samples synthesized by coprecipitation or sol–gel methods.[38,39] The surface coating layers and gradient structures will be discussed in detail below.

3. Surface structure of the material after storage in air

The storage characteristics have very significant impacts on their structure and electrochemical performance.[40–46] Xia *et al.*[44] reported that commercial $LiFePO_4$ could be oxidized in humid and/or hot air and become α-Fe_2O_3 and $FePO_4$ at the surface. A $Li3PO_4$ layer has been found at the $LiFePO_4$ grains' surface after immersion in water.[40] Martin *et al.*[47] reported that the performance of $LiFePO_4$/C nano-composites exposed to atmosphere at 120 °C decreases due to oxidation, involves H_2O and the formation of disordered ferric lithium phosphate phase.

Li_2CO_3 is commonly found on the surfaces of cathode materials that have been exposed to air. During storage, a thin layer forms on the particle surface and becomes thicker. Using $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ as an example, the formation of Li_2CO_3 is presumed to take place via reaction

$$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 + x/2\ CO_2 + x/4\ O_2$$

$$\rightarrow Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2 + x/2\, Li_2CO_3. \quad (1)$$

Figures 2(a) and 2(b) show the fresh and air exposed $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ samples. The excessive formation of Li_2CO_3 on the particle surface consumes a mass of Li^+. The presence of Li_2CO_3 in the electrode will limit the rate performance (Figs. 2(c) and 2(d)) and result in capacity and power losses during cycling.[41] Zhao *et al.*[45] reported that the capacity of the $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ cathode materials decays due to formation of Li_2CO_3 on the particle surface. Ma *et al.*[46] reported that the surface of Li_2MoO_3 reacts with CO_2 and O_2 in air. It is partially oxidized/decomposed to amorphous Li_2MoO_4, Li_2CO_3, and MoO_3 after long-term storage. Therefore air exposure should try to be avoided in the fabrication and application of lithium-containing cathode materials. Fortunately, the detrimental chemical species can apparently be removed by a heat-treatment to a high temperature. The electrodes made with heat-treated $LiCoO_2$ show excellent capacity retention even when cycled to 4.5 V.[48,49]

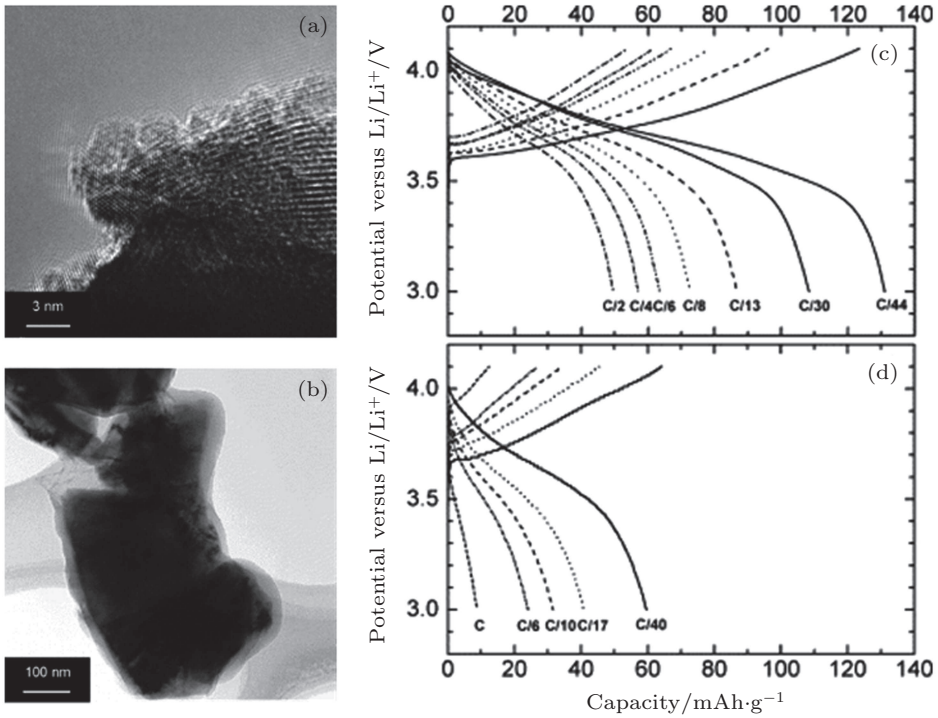


Fig. 2. TEM images of (a) fresh $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ powder and (b) $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ grain from air-exposed electrode. Charge and discharge profiles for (c) fresh cathode and (d) air-exposed cathode.[41]

4. Surface structure evolution: chemical and electrochemical reactions

An ideal surface should be stable while soaked in the electrolyte and during the electrochemical process. But the actual surfaces of electrodes usually suffer from oxygen loss, transition metal dissolution and migration. Authors have reported that charged cathode electrode materials tend to react with the non-aqueous electrolyte violently at elevated temperatures or high voltage. Here we focus on the surface structure evolution of classical cathode materials, including layered, spinel, and olivine $LiFePO_4$.

4.1. Surface evolution of layered materials

Layered cathode materials, such as $LiCoO_2$, $LiNi_{1-x-y}Co_xMn_yO_2$ ($0 < x < 1$, $0 < y < 1$), $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and lithium-rich manganese layered oxide are the most promising candidates for high energy-density lithium-ion batteries used in EVs or HEVs. A change in surface structure may destroy the two-dimensional Li^+ diffusion channels in these materials. Our recent investigation of well-crystallized $LiCrO_2$ cathode indicates that Cr ions can migrate into the Li layers in the surface regions, leading to an irreversible phase transformation from the layered to the rock-salt structure. The existence of the rock-salt phase in the surface blocks the extraction of lithium from the material.[27] Research has shown that during cycling, transition metal ions in both $LiNi_{1-x-y}Co_xMn_yO_2$ and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ migrate irreversibly and lead the surface structure to change from layered to spinel and rock-salt, resulting in capacity fade.[50–54] The oxygen loss from the surface of the material is the main reason.[54]

Lithium-rich manganese layered oxides materials, which have a high discharge capacity exceeding 250 mAh·g^{-1}, suffer many practical issues such as oxygen release,[55] volt-

age fade,[56,57] poor rate performance[58] and low coulomb efficiency.[59–61] Among these, oxygen release and voltage fade are believed to be related to changes of the materials' surface structure. The high charge capacity of Li-rich layered cathode materials at high voltage arises mainly from the oxygen reduction reaction at the electrode surface. The proposed reaction schemes are summarized in Fig. 3 by Yabuuchi *et al.*[62] During the initial activation process, which is oxygen release from the surface of the structure, a large number of oxygen vacancies are formed by the end of the charge. As a result, the transition metal ions coordinated with reduced oxygen ions are destabilized and prone to migrate to the vacant octahedral sites in Li layers via the adjacent tetrahedral sites. This phase transformation initiates from the crystal surface, leading to the formation of a surface reconstruction layer and gradual voltage fade during cycling. Oxygen removal associated with the initial charge on the high voltage plateau causes oxygen molecule generation in the electrochemical cells. The oxygen molecules in the cell are electrochemically reduced in the subsequent discharge below 3.0 V, leading to the extra capacity. In addition to the conventional transition metal redox reactions, at least some of the reversible capacity for the lithium-rich manganese layered oxides originates from the electrochemical redox reaction of the oxygen molecules at the electrode surface. It has been concluded that suppression of the lithium carbonate formation is necessary to improve the cycle performance of the surface redox reaction.

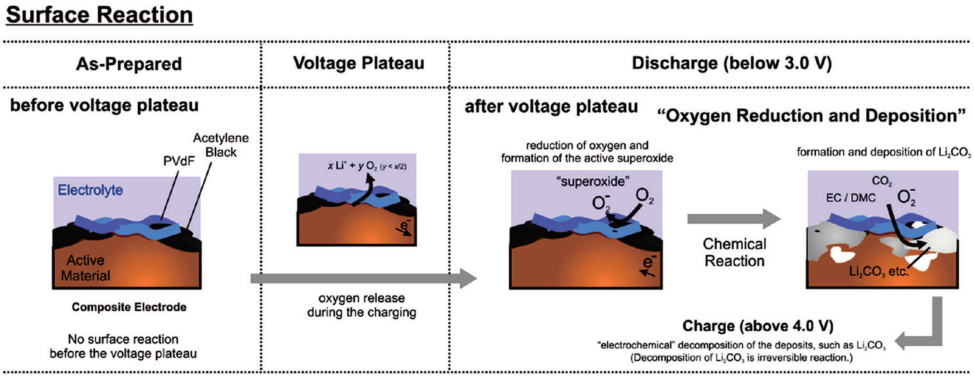


Fig. 3. Scheme of surface reaction mechanism in the Li-rich layered electrode.[62] Reprinted from Ref. [62]. Copyright 2011 American Chemical Society.

The voltage fade mechanism is also related to the surface structure evolution during cycles. Zhang *et al.* systematically researched the phase transformation pathway in detail.[63–65] During the cycle, a phase transformation from the layered structure (initial $C2/m$ phase transforms to R-3m phase after activation) to a LT-$LiCoO_2$ type defect spinel-like structure (with the Fd-3m space group) and then to a disordered rock-salt structure (with the Fm-3m space group). The voltage fade can be well correlated with lithium-ion insertion into octahedral sites rather than tetrahedral sites, in both defect spinel-like and disordered rock-salt structures. Note that the transformation pathway of the Li-rich cathode is closely correlated to its initial structure and preparation conditions, and for a certain electrode, different direction may have different surface structure change.[53,66,67]

4.2. Surface evolution of spinel materials

Surface dissolution of manganese is a long-standing issue for spinel cathode materials such as $LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$. It is generally believed to be the main cause of their capacity fade, especially when cycling at high temperature. Our recent studies gained direct observation of the formation of a M_3O_4 phase and rock-salt in spinel $LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$.[20,68] Figure 4 shows a scanning transmission electron microscope (STEM) image of the surface and subsurface regions of the initially charged $LiNi_{0.5}Mn_{1.5}O_4$ sample, with schematic lattice structures of M_3O_4 phase at the surface and rock-salt phase at the sub-surface. This matches well with the study by soft x-ray absorption spectroscopic (s-XAS), in Fig. 5. The gradient Mn^{2+} evolution at charged states in $LiNi_{0.5}Mn_{1.5}O_4$ electrodes is directly observed,

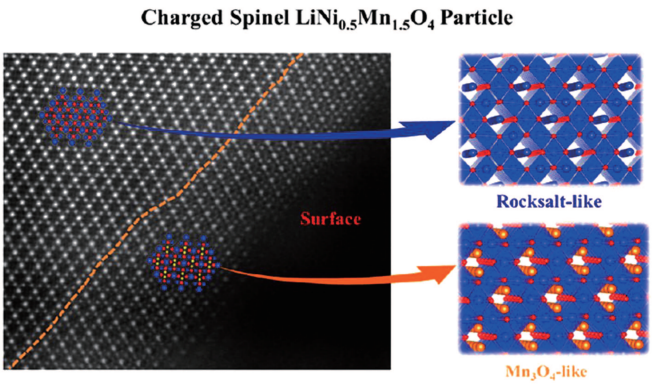


Fig. 4. A typical STEM image and schematic lattice structures, showing the surface and subsurface regions of the initially charged $LiNi_{0.5}Mn_{1.5}O_4$ sample.[68]Reprinted from Ref. [68]. Copyright 2014 American Chemical Society.

and the charged state contains the largest percent of Mn^{2+}.[69] The soluble Mn^{2+} leads to the loss of active material and gradual capacity fading.

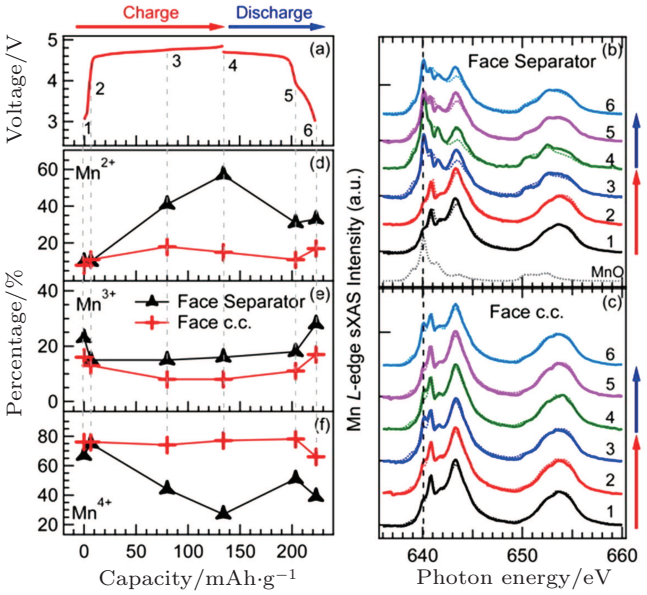


Fig. 5. Evolution of the chemical valence of Mn in electrodes based on $LiNi_{0.5}Mn_{1.5}O_4$. (a) The electrodes with different SOC used for sXAS measurements are marked on the voltage profiles. (b) and (c) Mn L-edge sXAS spectra (TEY) collected on the sides of electrodes facing separator (b) and current collector (c). Dotted lines on top of the spectra are simulated results for obtaining the quantitative values of Mn^{2+}, Mn^{3+}, and Mn^{4+} concentration. (d)–(f) Evolution of the Mn valence deduced from spectral simulations, with respect to the charge/discharge states.[69]

4.3. Surface evolution of $LiFePO_4$ materials

$LiFePO_4$ is considered to have superior thermal stability, which is due to the strong P–O covalent bonds in the olivine structure. The stable structure can restrain oxygen release. $LiFePO_4$ in electrochemical cycling usually shows excellent stability. However at elevated temperatures, a performance fade can still be observed.[70–73] Electrochemical inactive $LiFePO_4(OH)$ will form at the surface of $LiFePO_4$, when moisture (water) or hydroxyl groups contaminate the electrolytes.[43] This will lead the capacity fade and poor cycle performance.

These findings suggest that enhancing the stability of the surface structures of the electrode is the key to improve the long-term cycle performance of cathode materials. Efforts to stabilize the surface can significantly improve the capacity retention of cathodes. Representative approaches include different kinds of surface coating and electrolyte additives will be further discussed in the next two parts.

5. Solid electrolyte interphase on cathode

Forming stable SEI on cathode between the electrode and electrolyte is necessary to achieve satisfactory electrochemical performance of Li-ion batteries.[74] This interphase offers a channel for Li^+, but it is insulated for electrons. It plays an important role in the irreversible capacity, cycle performance and stability.[75] Compared with the relatively clear understanding of the SEI on anodes, the knowledge of SEI on cathodes is quite insufficient. It is suggested that past studies, analysis and understanding of the SEI strongly underline the significance of its many aspects.

Three formation mechanisms are proposed for the SEI on cathodes: i) the SEI on the cathode is formed during the charge discharge process.[76] ii) the SEI is produced by reduction of the anode, and it diffuses and deposits on the cathode, changing the structure of the cathode.[74] iii) The SEI is a product of the chemical reaction between the electrode and electrolyte.[77,78] Wang *et al.*[36,79,80] found that $LiCoO_2$ spontaneously reacts with commercial electrolyte $LiPF_6$/EC-DMC. FTIR and Raman spectrum show that the reduction products are $(ROCO_2Li)_2$ and Li_2CO_3 etc. Meanwhile, the surface of $LiCoO_2$ was reduced to Co_3O_4 and Co_2O_3. Liu *et al.*[81] found that SEI can also form on the surface of nanosize $LiCoO_2$ particles after storage in dimethyl carbonate (DMC) solvent, and the SEI film becomes more uniform upon cycling. Figure 6 shows TEM images of SEI layers at nanosize $LiCoO_2$ particle at different situations. Similar behaviors are also found in $LiNi_{0.5}Mn_{1.5}O_4$,[82] $LiMn_2O_4$, and $LiFePO_4$ cathodes.[83,84]

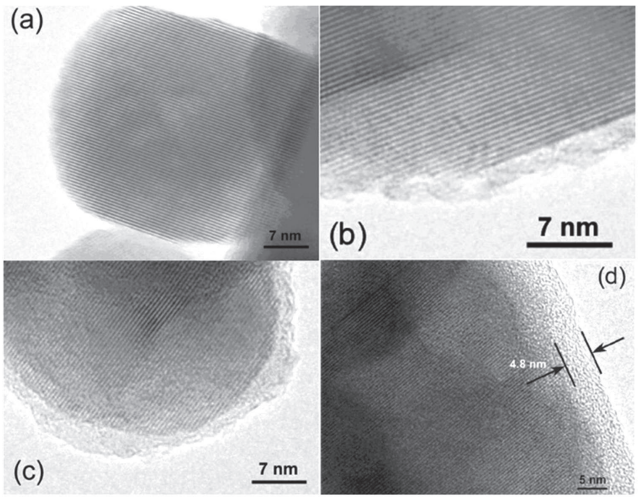


Fig. 6. TEM images of nanosize $LiCoO_2$ particle in different situations: (a) pristine, (b) soaked by 1 M $LiPF_6$ dissolved in EC/DMC (1:1 in volume) electrolyte for 7 days, (c) soaked by anhydrous DMC (< 10 ppm) for 7 days, and (d) after 10 cycles in a $LiCoO_2$/Li cell at a voltage range of 2.5–4.3 V.[81]

Some candidate additives have been reported to provide a stable SEI film for cathodes. Tris(pentafluorophenyl)borane ($(C_6F_5)_3B$, TPFPB) is an effective anion receptor. The released oxygen species in the form of oxygen anions (O_2^{2-}/O_2^-) or radicals ($O_2\cdot^-$–/$O\cdot^-$) may be trapped in the vicinity of TPFPB instead of attacking the electrolyte. Zheng *et al.*[85] demonstrated that TPFPB enhances the stability of electrode/electrolyte interface and thus improves the

cycling stability of lithium-rich manganese layered oxides $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$. In the presence of 0.2 M TPFPB, $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ shows an improved capacity retention of 76.8% after 500 cycles. TPFPB was even reported to improve the performances of batteries containing graphite,[86] $LiMn_2O_4$[87,88] and $Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O_2$[89] by partially dissolving byproducts such as LiF and Li_2O. Yang *et al*. reported that TPFPB can reduce the capacity fade of $LiMn_2O_4$.[90]

6. Surface coating layer

Surface coating is the main method to improve the electrochemical performance and protect the cathode surface. The two most successful cases are carbon[91] and metal oxide[92] coating. The key mechanisms that have been proposed to explain the positive effect of surface coating on the performance of cathode materials include the following:[93] (i) electron-conducting media that facilitates the charge transfer at the surface of particles; (ii) modification of cathode surface chemistry that improves the cathode performance; (iii) HF scavenger that reduces the acidity of non-aqueous electrolyte and suppresses transition metal dissolution from the cathode materials; and (iv) a physical protection barrier that impedes the side reactions between cathode materials and non-aqueous electrolytes.

The major problem of olivine $LiFePO_4$ cathode material is its low electric conductivity and sluggish lithium diffusion.[94] This leads to the poor rate performance of uncoated $LiFePO_4$. One of the main breakthroughs lies in the formation of a thin conductive carbon coating at the surface of $LiFePO_4$ nanoparticles.[91] Carbon coating can improve the electron transfer through the interface of the cathode material particles and provide extra electron-conducting pathways among the cathode material particles and between the cathode material particles and the current collector. The significant positive effect of carbon coating on the cathode performance has been widely reported.[95,96] Wang *et al.*[97] have reviewed the development of carbon coating on $LiFePO_4$ cathodes. However, the role of carbon is still not completely understood in spite of its importance in the rate capability and cycle stability of $LiFePO_4$ electrodes.[98]

No-carbon second phase (e.g. metal oxides, metal phosphate, and polymers) coating were also reported to modify the $LiFePO_4$ surface.[100–102] Cho *et al.*[103] reported an electrical network composed of a thin carbon layer coated on spinel $LiMn_2O_4$ nanoclusters for ultrahigh-rate lithium-ion batteries. Carbon coating is also used in other cathode materials.

Cho *et al.*[92,104] first introduced the surface coating of ZrO_2 and Al_2O_3 to $LiCoO_2$ layered materials. They pointed out that coating $LiCoO_2$ with oxides can improve the capacity retention of $LiCoO_2$ cycled to 4.4 V. A number of other groups have confirmed this finding.[48,49] *In situ* XRD studies by Wang *et al.*[16,105,106] provide that the contribution of the surface coating to the capacity retention is not due to suppression of the variation of lattice parameters but just the opposite: the variation of the lattice parameter is a structural change in response to the lithium intercalation/deintercalation. They also suggest that it is the surface of $LiCoO_2$, not bulk structural changes, a phenomenon that holds the key to solving the problem of the capacity fade of $LiCoO_2$ during high-voltage cycling. Besides the metal oxide, AlF_3,[107–109] $AlPO_4$,[110] $LiAlO_2$,[111] Li_3PO_4,[112] $FePO_4$,[113] and MgO[114] etc. are also effective coating candidates. Using one active material to coat another active is also effective.[115,116]

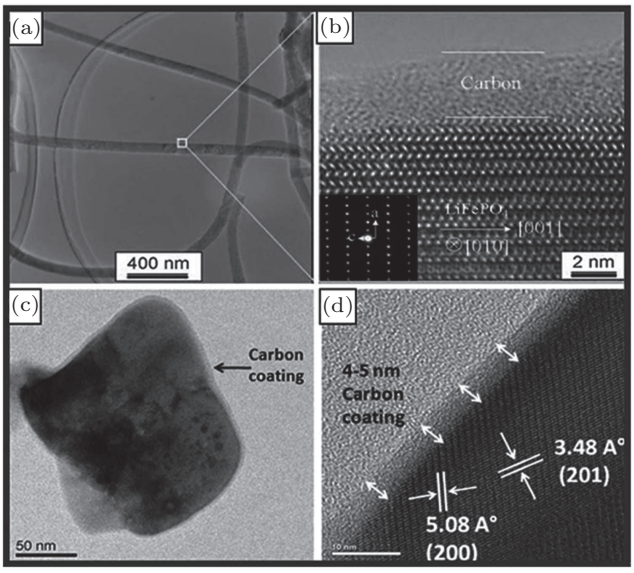


Fig. 7. (a) TEM image and (b) high-resolution TEM image of single-crystalline $LiFePO_4$/C nanowires,[95] (c) TEM image and (d) high-resolution TEM image of $LiFePO_4$/C nanoplate.[99]

Recent years, ALD (atomic layer deposition)[113,117–120] is believed to be an important technique for the research of high performance cathode materials, for its advantage in excellent uniformity and conformity. Core–shell[121–124] and gradient materials[125,126] have been reported to combine the high electrochemical performance of the core material and the low reactivity of the shell material.

7. Tools for investigating surface

In the research of Li-ion batteries, it is important to know the bulk and surface structure evolution of the equilibrium and nonequilibrium states to understand the performance fade mechanism and improve it. Figure 8 shows the space-resolution scheme of experimental techniques in Li-ion batteries.[127] It covers the scale range from 0.05 nm to 10 mm. X-ray and neutron diffraction can offer the average structure evolution. They can find a new phase with high crystallinity and certain volume fraction ($> 1\%$–5%). NMR and hard x-ray absorption spectroscopy offer the local structure information

of the bulk. Selected area electron diffraction (SAED) can be used for the structure information in a nano or micron area. Spherical aberration corrected scanning transmission electron microscopy (Cs-corrected STEM) can bring the information of the atomic structure of the surface and near-surface. Secondary ion mass spectroscopy (SIMS) and electron-probe x-ray micro-analysis (EPMA) can get the element concentration in the bulk and the surface. X-ray photoelectron spectroscopy (XPS) and soft x-ray absorption spectroscopy are sensitive to the chemical state and charge transfer of the surface. They are effective in checking the surface structure and chemical evolution.

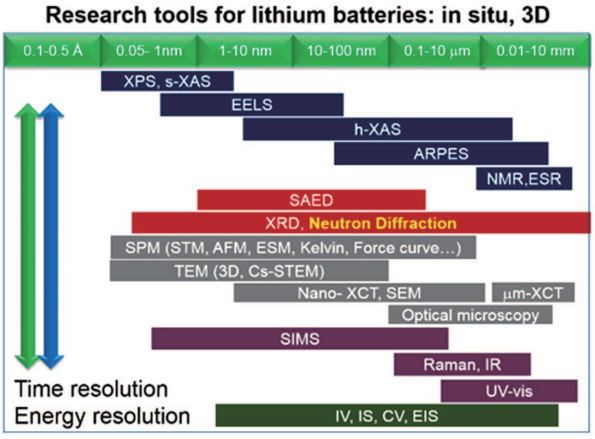


Fig. 8. Space-resolution scheme of experimental techniques in Li-ion batteries.[127]

In practical studies, it is usually necessary to combine two or more techniques to understand a scientific issue. For example, in the study on multi-electron transfer and structure evolution of $Li_{1.2}Cr_{0.4}Mn_{0.4}O_2$, h-XAS can give the average chemical state change that Cr^{3+} are oxidized to Cr^{6+} during charge, and migrated to tetrahedral sites in lithium layers; Mn^{4+} is reduced to Mn^{3+} during the discharge at low voltage. Cs-STEM can give the information that some transition metal at the surface has transferred to the lithium layer octahedral sites, forming ordered rock-salt structure.[31] S-XAS confirms that Mn^{2+} may be contained at surface of the materials. Combining the tools for bulk and surface, the processes can be fully understood.

8. Summary

The behavior of cathodes for lithium ion batteries depends strongly on their surface chemistry. The surface chemistry stability is a big challenge during the cycle. In the past two decades, the energy density of Li-ion batteries ($LiCoO_2$/C cell) has nearly reach the theoretical limits. The cycle performance has improved to over 800 cycles. In order to develop Li-ion batteries of adequate energy density and cycle performance, and excellent safety performance for EV and HEV, it is important to improve the surface stability of the cathode materials. Prevention of surface structural degradation can provide the means to produce and retain high capacity, as well as stabilize the cycle life of cathode materials for lithium ion batteries. Improving the reversibility of the oxygen redox reaction and restraining the dissolution and migration of transition metal ions at the electrode surface will result in the development of high-capacity cathode materials.

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