Research on Advanced Materials for Li-ion Batteries

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In order to address power and energy demands of mobile electronics and electric cars, Li-ion technology is urgently being optimized by using alternative materials. This article presents a review of our recent progress dedicated to the anode and cathode materials that have the potential to fulfill the crucial factors of cost, safety, lifetime, durability, power density, and energy density. Nanostructured inorganic compounds have been extensively investigated. Size effects revealed in the storage of lithium through micropores (hard carbon spheres), alloys (Si, SnSb), and conversion reactions (Cr₂O₃, MnO) are studied. The formation of nano/micro core–shell, dispersed composite, and surface pinning structures can improve their cycling performance. Surface coating on LiCoO₂ and LiMn₂O₄ was found to be an effective way to enhance their thermal and chemical stability and the mechanisms are discussed. Theoretical simulations and experiments on LiFePO₄ reveal that alkali metal ions and nitrogen doping into the LiFePO₄ lattice are possible approaches to increase its electronic conductivity and does not block transport of lithium ion along the 1D channel.

1. Introduction

New energy technologies are critical for the realization of an energy future that is compatible with the goal of sustainable development. Lithium ion batteries are becoming a key-enabling technology for electric vehicles and hybrid electric vehicles.[1] Since researchers at Sony Energytech developed the first commercial Li-ion batteries in the late 1980s,[2–4] a variety of efforts have been undertaken to improve the battery materials. Using nanosized and nanostructured materials presents new opportunities in rechargeable Li-ion batteries for energy density, exceptionally high rate of charge and discharge, and better cyclability.[5] Comprehensive studies of the unusual features of the transport and storage behaviors of ions at the nanometer scale may lead to advanced energy storage devices.[6] In particular, spinel lithium manganese oxide and olivine LiFePO₄ are the most promising candidates up to now for use as cathode materials of hybrid electric (HEV) and electric vehicle (EV) batteries.[7,8] This article presents a review of our recent progress dedicated to nanosized or nanostructured anode materials and the modifications of cathode materials for the next generation of Li-ion batteries.

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2. Anode Materials

2.1. Hard Carbon Spheres (HCS)

Rechargeable lithium batteries based on the intercalation concept were first suggested by Armand in 1972.[9] Because of safety considerations, metal lithium has been replaced by alloys, oxides, chalcogenides, and carbonaceous materials as anode materials.[4] In 1990, coke was used by SONY as an anode to solve the propylene carbonate co-intercalation problem.[4] After introducing ethylene carbonate into the non-aqueous electrolyte,[10] graphite can be used properly in Li-ion batteries. Later, graphitized mesosphere microbeads (MCMBs) became more popular.[11,12] Graphite has a theoretical capacity of 372 mA h g⁻¹ to form LiC₆. Since 1990, many efforts have been made to develop high capacity anode materials to replace graphite. Non-graphitized carbon materials, including soft carbon and hard carbon, have been studied widely.[13–15] Soft carbon materials show a very high reversible Li-storage capacity but a serious voltage hysteresis during delithiation.[13–15] Hard carbon shows a high capacity of 200–600 mA h g⁻¹ over a voltage range of 1.5–0 V vs Li/Li⁺. The voltage profile is mainly composed of two regimes, a sloped regime in a voltage range of 1.0–0.1 V with a capacity around 150–250 mA h g⁻¹, and a plateau region with a capacity around 100–400 mA h g⁻¹.[13–15] Hard carbon materials have disadvantages such as low initial columbic efficiency and low tap density. Spherical hard carbon materials are desirable, however, they are difficult to prepare through direct pyrolyzing of organic or polymer precursors.

In 2000, a hydrothermal method to prepare spherical hard carbon materials from a sugar solution was developed for the first time by us.[16] The sugar molecules are first dewatered to form LiC₆. Since 1990, many efforts have been made to develop high capacity anode materials to replace graphite. Non-graphitized carbon materials, including soft carbon and hard carbon, have been studied widely.[13–15] Soft carbon materials show a very high reversible Li-storage capacity but a serious voltage hysteresis during delithiation.[13–15] Hard carbon shows a high capacity of 200–600 mA h g⁻¹ over a voltage range of 1.5–0 V vs Li/Li⁺. The voltage profile is mainly composed of two regimes, a sloped regime in a voltage range of 1.0–0.1 V with a capacity around 150–250 mA h g⁻¹, and a plateau region with a capacity around 100–400 mA h g⁻¹.[13–15] Hard carbon materials have disadvantages such as low initial columbic efficiency and low tap density. Spherical hard carbon materials are desirable, however, they are difficult to prepare through direct pyrolyzing of organic or polymer precursors.

In 2000, a hydrothermal method to prepare spherical hard carbon materials from a sugar solution was developed for the first time by us.[16] The sugar molecules are first dewatered to form micelles in solution, and further dewatering leads to the appearance of nuclei-oligomers within the micelles in the form of tiny particles. These nuclei grow gradually into nanometer-sized nucleation points. Through polymerization of the grown nuclei with dewatered sugar dissolved in an aqueous phase, spherical hard carbon materials of micrometer-scale (size of micelles) spherules by consumption of the micelles. Through polymerization of the grown nuclei with dewatered sugar dissolved in an aqueous phase, spherical micrometer-scale spherules are finally formed until all the sugar has been depleted. The above scheme for the formation of HCS is shown in Figure 1. The following carbonization process has little effect on the morphology of spherules, consequently mono-dispersed HCS are obtained, as shown in Figure 2.

The obtained HCS materials show a perfect spherical morphology with a smooth surface. High-resolution transmis-
Transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) investigations indicate that the interior part of the particle has a disordered structure. It cannot be graphitized at 2500°C.[17] HCS is rich in 0.4–0.8 nm micropores. The specific surface area is about 400 m² g⁻¹. This value can be increased by activation and decreased after chemical vapor deposition (CVD) treatment. The micropore size is influenced by the preparation method and condition. For example, the average pore size is 0.45 nm for HCS1 obtained by a normal hydrothermal method, while HCS2 with smaller micropores (0.39 nm) was obtained by a microemulsion-mediated hydrothermal method.[18]

The particle size of the HCS can be controlled by adjusting the concentration. The maximum particle obtained is about 5 μm when the sugar solution is 5 M. The size was reduced to 250 nm when the concentration of the sugar solution was decreased to 0.15 M.[17] HCS with diameters of 100–200 nm (nano-HCS) could be also prepared through a modified hydrothermal method with polyacrylamide (PAM) as additive,[19] as shown in Figure 2b.

HCS have also been prepared by other authors from glucose and starch.[20,21] They have been used as templates for synthesis,[22] catalyst supports,[23–25] counter electrodes for dye-sensitized solar cells (DSSCs),[26] and as anodes for Li-ion batteries.[16–19] as shown below.

Li storage in HCS shows a typical feature of hard carbon as shown in Figure 2c and 2d. The voltage profile is composed of two parts: one is the slope region at a higher voltage (>0.09 V), and the other is the flat region at lower voltage (<0.09 V). The first part is very similar to the voltage profile of coke,[14,15] and is related to lithium in the buckled graphene sheets and edges. The second part is ascribed to the filling of lithium in the micropores, which occurs at a lower voltage. Stevens and Dahn confirmed this mechanism in pyrolyzed glucose near 0 V (vs Li/Li⁺) by means of in-situ small-angle X-ray scattering techniques.[27] It is not possible to see the few lithium atoms in the micropores by imaging techniques, however, it might be possible to see lithium grains or clusters in the large pores. We performed HRTEM experiments to observe lithium storage in pores directly for the first time. For this purpose, a special carbon nanotube material with a bamboo-like large cavity, polymerized carbon nitride nanobells (CNNBs), was selected as a model material.[28,29]

CNNBs were fully lithiated by discharging to 0.0 V vs Li/Li⁺. As shown in Figure 3 b and 3c, it is noticed that some tiny nanocrystallites with a stripe spacing in the range of 0.25–0.29 nm are found inside the tube. Correspondingly, there are some scattered diffraction dots in the inset selected area electron diffraction (SAED) pattern compared with the initial material. The nanocrystallites are distributed in the cavities inside the tube and are rarely found in the surface regions and the tube walls. These tiny grains disappear after delithiation (Fig. 3d). The fringe spacings of lithium–graphite intercalation compounds (Li-GICs) cannot drop in the above ranges according to the lattice parameters and the distribution of the nanosized crystallites. At ambient conditions, the stable lattice structure of lithium is body centered cubic (bcc), and the corresponding spacing is 0.248 nm for the (110) plane. Hence the stripes in the samples were ascribed to metallic lithium nanocrystallites.[30,31]

It should be mentioned that outside the tube wall, there is a uniform amorphous film with a thickness of about 5–7 nm. That is the so called solid electrolyte interphase (SEI) layer formed by the reduction of the electrolyte.[32,33] It is also noticed that the thickness

Figure 1. Scheme of the preparation of HCS from a sugar solution by the hydrothermal method. Reproduced with permission from [17]. Copyright 2002, Elsevier.

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of the SEI film at a delithiated state (Fig. 3d) was thinner than that at the full lithiated state (Fig. 3b). The thickest part is only 3 nm and some places were almost naked. This means that the SEI was decomposed at high voltage during the charging process. This finding is against the normal impression that the SEI on a carbon anode is stable.

Li storage in nano-HCS has also been investigated by HRTEM. It was found that inserted lithium did not appear, but about 4–6 layers of parallel graphene sheets appear after full lithiation. It seems that disordered nano-HCS become slightly ordered. In order to clarify this, Raman spectra of HCS materials with different hydrogen content were recorded after different cycle numbers. It was found that the La value of the nano-HCS1 with more hydrogen (H/C = 0.14 at./at.) is increased for the first five cycles while the La value of the nano-HCS2 with less hydrogen (H/C = 0.07 at./at.) does not vary significantly. A Li-replace-H mechanism was proposed to explain this disorder-to-order phenomenon. This result indicates that the host atoms, i.e., carbon, may be mobile and rearrange to be ordered to a certain level upon lithiation and delithiation.

Li storage in micropores occurs at a very low voltage around 0 V vs Li/Li⁺. Different materials and electrodes have different polarization situations. Therefore, the Li-storage capacity in HCS was significantly influenced by the cut-off voltage. As shown in Figure 2d, there is a large irreversible capacity loss for nano-HCS, caused mainly by the formation of a thick SEI film. The existence of an insulating SEI film may lead to an increase of the internal resistance of the electrode. Consequently, the voltage plateau for Li storage in micropores does not appear for nano-HCS. When the cut-off voltage was extended to −20 mV, or by coating a conductive carbon layer on it, larger Li-storage capacities at low voltage are achieved, as shown in Figure 4e and 4f.

The kinetic performances of HCS materials were also investigated. It was found that the capacities at a higher voltage (0.09–2 V) almost do not vary with the current density. But the capacities at a lower voltage (0–0.09 V) are influenced strongly by the current density. This indicates that Li storage in micropores near 0 V shows poor kinetic performance.
2.2. Tin-based Oxides

In 1995, Idota et al. of the Fuji Film Co. claimed a class of amorphous tin-based composite oxides (TCOs) as anode active materials. These materials showed 500–600 mA h g\(^{-1}\) reversible capacities. At that time, it was announced that Sn\(^{11}\)–O is the active center for lithium insertion and other glass-forming elements, which make up an oxide network. \(^7\)Li NMR measurements evidenced the high ionic state of lithium retained in the lithiation state. Idota et al. believed that there was a new Li-storage mechanism. This finding attracted great attention.

According to in-situ XRD results reported by Dahn’s group and Raman spectroscopy studies performed in this group, it is clear that lithium storage in tin-based oxides occurs by a two-step mechanism. Taking SnO as an example, the reaction equations can be written as:

\[
2\text{Li} + \text{SnO} \rightarrow \text{Li}_2\text{O} + \text{Sn}
\] (1)

\[
4.4\text{Li} + \text{Sn} \leftrightarrow \text{Li}_{22}\text{Sn}_5
\] (2)

This mechanism was also supported by the fact that five reversible redox peaks can be observed in the cyclic voltamogram of the SnO anode, which is hard to be explained by other mechanisms.\(^{38}\)

It was well known that Li–Sn alloy reactions in a stand-alone Sn electrode showed a very poor cyclic performance since the formation of Li\(_2\)Sn leads to a significant volume expansion and the electrode tends to pulverize during cycling. Therefore, Courtney and Dahn proposed that the Li\(_2\)O matrix acts as a glue to retard the aggregation of tin atoms into large coherent regions in the case of tin oxides.\(^{36}\) A direct image of a fully lithiated nano-SnO anode was given in 1998 by us for the first time.\(^{39}\) As shown in Figure 5, nanometer-SnO maintains its particle shape after full lithiation (1551 mA h g\(^{-1}\)) but the interior part was converted into a nanocomposite where Li–Sn crystallites (2–20 nm) are dispersed within an amorphous Li\(_2\)O matrix. This result shows a clear picture that the enhanced cyclic performance of the alloy reaction in the case of tin-based oxides could be benefited from two structural factors: alloy grains are on the nanometer scale and are dispersed in another inactive phase. The formation of nanocomposites becomes an important strategy for the design of high-capacity anode materials as discussed later.

As shown in Figure 5, a layer of thin film (1.6 nm) can be seen clearly on the surface of the reacted nanoparticles. As analyzed by the results of FTIR spectroscopy,\(^{39}\) it is the SEI film, similar to the SEI film on a carbon anode.

After Fuji’s finding, great efforts have been paid to explore oxide anodes that contain active elements able to form an alloy with lithium. Since Reaction (1) is normally irreversible, the initial efficiency is less than 70% in most of cases, researchers’ attentions were shifted to alloy materials, such as Si, Sn, and Sb, or alloy-based composites.

Before further discussion on the alloy anode, it is worth mentioning that Reaction (1) is partially reversible, as confirmed recently by Xue and Fu.\(^{40}\)

![Figure 5. HRTEM images of fully lithiated nano-SnO (7.8 Li). a) Low magnification and b,c) different regions inside the particle. Reproduced with permission from [39]. Copyright 1998, ECS.](image-url)
into Si leads to a distorted angular bond distribution. With an increase in doping dose, the bond distortion becomes more obvious and at last destroys the silicon structure. At room temperature, sluggish diffusion of Si inhibits the formation of an ordered Li/Si alloy phase. It was observed that a more ordered structure of lithiated SiNWs appeared after annealing at 400°C for 5 h under vacuum conditions.[49]

It was also found that serious agglomeration occurs after one cycle, as shown in Figure 7e and 7f.[49] Nanosized materials have a high surface energy. They tend to form large agglomerates, however, in most of cases, nanoparticles do not merge together at room temperature because of slow transport kinetics of the host atoms and poor contact. During electrochemical lithiation, the particles are expanded, which increases their contact probability. After delithiation, most Si atoms are in a dangling bond state with high energy. They tend to bond together if no other atom can bond with them or prevent their transport, as shown in the case of SnO. Consequently, very dense agglomerates are formed after electrochemical cycling (see Fig. 7f). We called this phenomenon ‘electrochemical agglomeration’. It has been observed in most of the alloy anodes mentioned later.

Because of the difficulty of synthesizing nanosized silicon at that time, a SnSb alloy attracted our attention. Besenhard et al. prepared a Sn0.78Sb0.22 alloy (0.56Sn + 0.22SnSb) with a particle size of about 200 nm by electroplate and reductive precipitation.[44,52,53] As proposed by Besenhard et al., reacted SnSb may be embedded in the unreacted soft and ductile Sn matrix.[44] The SnSb alloy can be regarded as an active/active composite at the atomic level.

It was interesting to find that several redox peaks appeared in the cyclic voltammogram of the nanosized SnSb alloy anode. It seems that Li/SnSb alloy reactions occur first during lithiation, and then followed the Li/Sn alloy reactions. This was confirmed clearly by ex-situ XRD results.[54]

Since the initial nano-SnSb alloy is a single-phase material. The successive phase transitions mean that inserted lithium first reacts with Sb locally. In this step, Sb atoms are enriched locally to form Li2Sb and Li3Sb domains. After Li3Sb is formed, the inserted lithium will react with Sn domains to form a series of Li/Sn alloys. Upon delithiation, the reverse steps occur. Separated Sn or Sb atoms or domains tend to rearrange to restore the original β-SnSb alloy structure. This result provides an example that reverse phase separation and restoration can occur at room temperature driven by electrochemical reactions. It means that the diffusion of Sn, Sb, and Li at room temperature should be very fast to follow the structure variation and the structure of the β-SnSb alloy phase is a thermodynamic favorable phase. The details of the local structure

Figure 6. a) Discharge/charging curves of a) SiNPs (weight ratio of SiNPs/carbon black = 1:1)[39] and b) SiNWs (no conductive additive) [46]. b) The cyclability of Si-based anodes at different conditions. The cell is: Si/1 M LiPF6, EC/DEC (1:1)/Li. The current density for curve 5 is 0.8 mA cm−2, others are 0.1 mA cm−2. Curve 1) μm-Si/CB (4:4), 0.0–0.8 V, 2) μm-Si/CB (4:4), 0.0–2.0 V, 3) SiNPs/CB (4:4), 0.0–2.0 V, 4) SiNPs/CB (9:1), 0.0–0.8 V, 5) SiNPs/CB (4:4), 0.0–0.8 V, and 6) SiNPs/CB (4:4), 0.0–0.8 V. Reproduced with permission from [45]. Copyright 1999, ECS.

Figure 7. a) SEM image of SiNPs. b) HRTEM image of SiNWs. A layer of SiOx covers the surface of the SiNWs. c) HRTEM image of lithiated SiNPs. d) HRTEM image of lithiated SiNWs. e) SEM image of lithiated SiNP electrode (with 1:1 carbon black). f) SEM image of lithiated SiNP electrode (no carbon black). White arrow: Cu substrate. Black arrow: agglomerated dense Si layers. Reproduced with permissions from [45] and [49]. Copyright 1999, ECS and 2000, Elsevier, respectively.
evolution, in addition to electron distribution, are still not understood clearly.

Similar to the Si anode, serious electrochemical agglomeration occurs for nano-SnSb alloys. In order to solve this problem, a nanosized SnSb alloy was deposited on the surface of MCMB and HCS respectively, as shown in Figure 8.

The cyclic performance of the nano-SnSb/HCS composite is improved significantly compared with nano-SnSb, as shown in Figure 9. However, it is found that the columbic efficiencies for these materials in each cycle are not very high (<99%), and this is not acceptable for real Li-ion batteries. The reason for the low efficiency is related to the direct exposure of the nanosized alloy particle to the electrolyte. Due to significant volume variation, the SEI film on the alloy particles may not be very stable during cycling, which leads to continuous formation of the SEI in freshly exposed areas that appear in each cycle. This problem could be solved by a strategy of embedding nanosized alloy particles in a carbon matrix or shell. The core-shell strategy has also been used successfully for Si anodes. Consequently, a high columbic efficiency (initial efficiency >85%, efficiency for each cycle >99%), high reversible capacity (>600 mA h g⁻¹), and excellent cyclic performance, as well as high tap density (>1 g cm⁻³) and low surface area (<5 m² g⁻¹) were achieved.

2.4. Transition Metal Oxides

In 2000, Poizot et al. reported for the first time that lithium can be stored reversibly in transition metal (TM) oxides through a heterogeneous conversion reaction:

\[ \text{Li} + \text{TMO} \rightarrow \text{Li}_2\text{O} + \text{TM} \]  \hspace{1cm} (3)

where TM is Co, Fe, Ni, and Cu. Later, reversible lithium storage was also observed in TM fluorides, sulfides, nitrides, and phosphides. It is very interesting in view of fundamental research that very inert LiF or Li₂O can react with a TM at room temperature. This was unexpected previously. Actually, in 1999, reversible lithium storage in CuO and Fe₂O₃ had been reported by us. However, we could not explain this behavior at that time. It is clear now that the enhanced electrochemical reactivity of LiF or Li₂O is mainly a benefit of the special microstructure where the converted LiX and TM components show an extremely small grain size (<5 nm) and intersperse with each other uniformly. The very short diffusion lengths and large contact areas in nanocomposites are kinetically favorable for unusual reversible electrochemical behaviors of LiX/TM nanocomposites.

In view of increasing the energy density of the batteries, besides a high capacity, a low average charging (delithiation) voltage of the anode material is another important factor. A typical value of the average charging voltage at a low rate is 0.3 V for graphite, 0.5 V for silicon, 0.7 V for Sn, and 1.6 V for Li₄Ti₅O₁₂. In addition, a small polarization (voltage difference between charging and discharging curve) of less than 0.2 V is necessary to achieve a high energy efficiency. This requirement is realized for anode and cathode materials by the intercalation or alloy mechanism. However, as for TM compounds that undergo a conversion reaction, most of the materials suffer from a high overpotential (voltage difference between the working voltage and thermodynamic equilibrium voltage) for both lithium insertion and extraction (about 1 V). Consequently, a theoretical

![Figure 8. SEM images of a,b) SnSb/MCMB and c,d) SnSb/HCS. Reproduced with permissions from [56] and [57]. Copyright 2001, RSC and 2002, ACS, respectively.](image)

![Figure 9. A) Voltage profile of nano-SnSb/HCS. B) Voltage profile of nano-SnSb/MCMB. C) Cyclic performance of a) nano-SnSb/MCMB, b) nano-SnSb/HCS, and c) nano-SnSb. D) Columbic efficiency of a) nano-SnSb/MCMB, b) nano-SnSb/HCS, and c) nano-SnSb. Reproduced with permission from [56] and [57]. Copyright 2001, RSC and 2002, ACS, respectively.](image)
lithiation capacity could be approached only when the thermo-
dynamic equilibrium voltage (also called electromotive force,
emf) of the material for the conversion reaction is higher
than 1 V.[79] Cr₂O₃ and MnO₂ are two transition metal oxides that have a
high lithiation capacity but relatively low emf values (1.085 and
1.032 V vs Li/Li⁺, respectively). [79] They are more suitable as
anode materials for Li-ion batteries.

Rhombohedral Cr₂O₃ (85-0869) has a theoretical density of
5.235 g cm⁻³ and shows a dark green color. Commercial Cr₂O₃
powder material shows a particle size of 200–500 nm and the
electronic conductivity is about 1.78 × 10⁻⁷ S cm⁻¹. [80] It has been
known that materials with a high electronic conductivity can
achieve a high columbic efficiency for conversion reactions, as
shown in the case of RuO₂. [78] Mg and Ni doping can improve the
conductivity of Cr₂O₃. [81–84] Therefore, Mg and Ni-doped Cr₂O₃
were also prepared. Their electronic conductivities were
improved to 3.11 × 10⁻⁴ and 9.57 × 10⁻⁵ S cm⁻¹, respectively,
after 2 mol % doping. [80]

The initial discharge capacities of Cr₂O₃ materials are
1200–1400 mA h g⁻¹ and are mainly contributed from a plateau
region at 0.15 V. [80,85] This capacity is larger than the theoretical
value of 1058 mA h g⁻¹ for Cr₂O₃ (6Li needed for a full reduction
of Cr₂O₃ into a 3Li₂O/2Cr composite). The initial charge
capacities are 700–800 mA h g⁻¹ in the voltage range from 0
to 3.0 V and the voltage profile shows mainly two sloped regions.
As discussed in recent papers for such behavior, [70,78,79,86] the
sloped region at a low voltage region could be assigned extra Li
storage at interfacial regions of the Liₓ/TM nanocomposite. In
the case of the Cr₂O₃ system, it contributes a Li-extraction capacity
of about 250 mA h g⁻¹. The sloped region above the emf value for
this reaction is related to the phase transformation from the Li₂O/
Cr to Cr₂O₃, as confirmed by the XPS results. [85] The charging
capacities are about 500 mA h g⁻¹, which are much lower than the
theoretical capacity for a complete Li-extraction reaction. It
indicates that almost half of the inserted lithium is trapped
irreversibly.

The average charging voltage for Cr₂O₃ is about 1.2 V, which is
much lower than most of the other TM compounds (TMX, in
brief) (>1.8 V). This is a significant advantage of Cr₂O₃ as an
anode material compared with other transition metal oxides and
fluorides, because of its low emf value of 1.058 V vs Li/Li⁺.

After full insertion, all particles are covered by amorphous species with a thickness of 20–90 nm (Fig. 10a). [80] This layer has been observed in many lithiated TMX anodes and
represents the so-called SEI. In a zoomed image in Figure 10b,
obvious disintegration of Cr₂O₃ grains is observed. Some tiny
gains of less than 5 nm are dispersed in amorphous regions.
Such a microstructure is similar to most other TM oxide anodes
observed. [77,78] After full lithiation, the interlayer part converts
back into a more ordered Cr₂O₃ phase (Fig. 10d) and the SEI
thickness is decreased to less than 5 nm, some particles are even
naked. Similar to previous observations, [69,77,78] the SEI on the
TM oxide anodes are electrochemically decomposable. Since
the thick SEI covers all particles, it is believed that the reversible
formation/decomposition of the SEI film is not favorable for
achieving good cyclic performance. It may lead to the peeling off
of active materials from the current collector. [85]

The SEI film is normally regarded as a passivating layer, which
does not decompose during charging and is around several

dimethyl carbonate (DMC) (1/1, w/w) as electrolyte. A layer of a
20–50 nm amorphous film was observed on a fully lithiated CBO
electrode. After analyzing the supernatant in a borosilicate
micro-fiber (Millipore) film separator recovered from Li/CBO
cells, the existence of MeOLi, CH₃OCO₂Li, and different
poly(ethylene oxide) (PEO) oligomer series were identified clearly
based on a high-resolution mass spectrometry (ESI-HRMS)
comparison analysis of a series of reference compounds. [88] In
order to determine the SEI components on the electrode, in
particular the electrochemically decomposable components, a
technique that combined thermogravimetry and mass spectrometry
(TG-MS) was applied [89] that was first used by Zhao et al. to
analyze the SEI film on a lithiated graphite electrode. [90] It was
found that the Cr₂O₃ electrode in the fully lithiated state shows a
continuous weight loss of up to 8.97% at 500 °C. While the electrodes charged at 1.1, 2.0, and 3.0 V show a 5.36%, 1.7%, and
1.51% weight loss at 500 °C, respectively. Since the main
inorganic species in the SEI film, i.e., Li₂CO₃, LiF, and lithiated
products of Cr, Li₂O, and unreacted Cr₂O₃, cannot be decomposed
below 500 °C, the thermally decomposable components in the
electrode are mainly organic or polymer species in the SEI
film. Accordingly, the electrode in the fully lithiated state should
have the largest quantity of organic and/or polymer-like species.
These results mean that the thermal decomposable species in the
fully lithiated Cr₂O₃ electrode are decomposed electrochemically
upon charging. The weight ratio of the SEI film in the Cr₂O₃
electrode is decreased by at least 7.5 wt. % after charging to 3.0 V.

Figure 10. HRTEM of nano-Cr₂O₃ particles in the: a,b) fully lithiated state and c,d) fully delithiated state.
This consists with the significant thinning of the SEI film on the Cr$_2$O$_3$ anode after charging as observed by TEM.

Based on mass spectrometry analysis, it was found that oligomers and polymers with ethylene oxide units are electrochemically decomposable species during charging, and ROCO$_2$Li is electrochemically relatively stable. The formation of a large amount of these species on lithiated Cr$_2$O$_3$ could be related to a strong catalytic effect from the nanosized TM nanograins, which needs further clarification. It was also found that the TG curves of MCMB and HCS are similar as the delithiated Cr$_2$O$_3$ samples. This means that much less thermal decomposable species are formed on the carbon electrode, which is consistent with Zhao et al.’s TG result that the SEI films on graphite is thin. In addition, it was found that ROCO$_2$Li could be the main thermal decomposable component in the SEI layers on MCMB and HCS electrodes.[85]

The cyclic performance of a pristine Cr$_2$O$_3$ electrode was very poor.[85] We supposed that the main reasons were a result of a loss of electronic contact of active particles and poor transport properties for electrons and ions within the active material. The first issue could be a result of a large volume variation of the electrode layer, which could be solved by decreasing the particle size, coating, and avoiding the formation of an unstable SEI film. The solution for solving the second issue could also be decreasing particle size, in addition to improving the intrinsic electronic conductivity by hetero-atom doping and keeping good contact with a conductive additive. Several material modifications that aim to solve the above problems have been performed,[80,85,89] including decreasing the particle size, hetero-atom doping, and preparation of a carbon/ Cr$_2$O$_3$ composite with different microstructures.

For samples (a) to (d) in Figure 11 the surface of the Cr$_2$O$_3$ particles is exposed to the electrolyte phase. Therefore, such a microstructure cannot avoid the formation of the unstable SEI film on the Cr$_2$O$_3$ particles. Carbon coating is very effective to improve the cyclic performance, as shown in the case of samples (e) and (h) in Figure 11. Carbon nanotubes (CNTs) grown on the Cr$_2$O$_3$ particle to form a composite where each Cr$_2$O$_3$ particle is fully covered by coiled CNTs, is also effective to improve the cyclic performance. However, such an urchin structure cannot avoid the formation of a SEI on the exposed area of Cr$_2$O$_3$. The sample (f) shows the best cyclic performance. Cr$_2$O$_3$ particles were first mixed with carbon black, and then the composite particles were coated with a layer of carbon. After that, the particles were treated by CVD to cover all the exposed area. Such a composite has the advantage of maintaining electronic contact and avoiding the formation of an unstable SEI film during cycling, as evidenced partially by TEM investigation.[80]

For anode materials based on the conversion reaction, there are three main disadvantages, which are low columbic efficiency, high average charging voltage, and high polarization.

The polarizations of different anodes have been compared by the $\Delta$V curves. The $\Delta$V curve is obtained by subtracting the discharging curve of the second cycle from the charging curve of the first cycle after normalization. It is the sum of the overpotentials of both charging and discharging at a galvanostatic mode. The $\Delta$V curve method was used to roughly compare the polarization of different materials.[91,92] As shown in Figure 12, the average polarization order is Li$_4$Ti$_5$O$_12$ < MCMB < Si < nano-SnSb < SnO < HCS < MnO < Cr$_2$O$_3$. Obviously, lithium storage in the conversion reaction shows the highest polarization. The main origin seems related to either X$^{n-}$ or M$^{n+}$ transport properties, and is not significantly dependent on the transport of electrons and lithium ions. Among TM oxides, MnO shows a low polarization, high capacity (450–550 mA h g$^{-1}$, 3500–4200 mA h cm$^{-2}$), and good rate performance.[92] Recently, MgH$_2$ was tested as an anode material, and underwent a similar conversion reaction mechanism. It was found that the average charging voltage was about 0.5 V and the $\Delta$V is about 0.5 V at 0.05 C.[91] This finding seems to support the viewpoint that transport of anions or cations from the host is a key factor to determine the polarization. How to decrease the high polarization of the conversion reaction is still a great challenge for most of the TMX materials.

![Figure 11. Cyclic performance of Cr$_2$O$_3$-based anodes. a) Pristine Cr$_2$O$_3$, b) Cr$_2$O$_3$ with 10 wt. % binder, c) nano-sized Cr$_2$O$_3$, d) 2 wt. % Mg-doped Cr$_2$O$_3$, e) carbon-coated Cr$_2$O$_3$, f) carbon-coated Cr$_2$O$_3$/carbon black mixture followed by a further CVD treatment, g) CNTs grown on a Cr$_2$O$_3$ nanocomposite, and h) carbon-coated Mg-doped Cr$_2$O$_3$.](image1)

![Figure 12. Polarization analysis ($\Delta$V curve) of anode materials at a low rate (0.05–0.2 C). a) Nano-HCS, b) SnO, c) Si, d) nano-SnSb, e) Cr$_2$O$_3$, f) MnO, g) MCMB, and h) Li$_4$Ti$_5$O$_12$.](image2)
3. Cathode Materials

3.1. Surface Coating on LiCoO₂ and LiMn₂O₄

With decades of study, the research on the cathode materials for lithium-ion batteries has been focused on layered, structured hexagonal LiCoO₂, spinel LiMn₂O₄, olivine LiFePO₄, and their derivatives. LiCoO₂ is the first cathode material that has been used in commercial Li-ion batteries.[4,94,95]

LiCoO₂ cathode materials are typically cycled between the fully lithiated discharge state LiCoO₂ (~3.0 V vs Li/Li⁺) and a roughly half-delithiated charge state Li₂CoO₂ (x = 0.5–0.6, 4.2 V vs Li/Li⁺) to yield a useable specific capacity below 150 mA h g⁻¹. When the Li/LiCoO₂ cell is cycled within a limited composition range of 0 < x < 0.5, it shows excellent cycling performance. However, its capacity fades rapidly when more Li is deintercalated from the lattice. Reimers and Dahn believed that overcharging leads to cathode degradation and electrolyte decomposition at high voltage.[96] As lithium is removed from Li₁ₓCoO₂, Co³⁺ is oxidized to unstable Co⁴⁺. A high concentration of Co⁴⁺ will damage the cathode crystallinity and result in a significant decrease of the c-axis dimension caused by a phase transition. The contraction along the c-axis results in mechanical failure in LiCoO₂ particles and rapid capacity fading.

Besides the interior lattice structural stability, it was evidenced that the performance degradation of LiCoO₂ is related to the dissolution of its Co³⁺ ions in the electrolyte solution.[97] Aurbach et al. reported that the electrochemical behaviors of LiₓMO₃ (M = Ni, Mn) cathode materials were strongly dependent on their surface chemistry.[98]

In order to improve structure stability, one early strategy was to coat the LiCoO₂ surface with inert oxides such as SnO₂, Al₂O₃, and MgO, by Kweon and Park and Cho et al. in 2000.[99–101] Among these, Al₂O₃-coated LiCoO₂ exhibits excellent capacity retention. It was suggested that the formation of a solid solution of Li₃CoO₂–Al₂O₃ improved the structural stability of LiCoO₂ during cycling.[102] However, many studies have been carried out to substitute Co with Al or Mg to form a solid solution and the capacity fading was still significant during cycling and the structural stability was not improved obviously.[102,103]

We developed a simple co-precipitation method to coat Al₂O₃ or MgO on commercial LiCoO₂ (Nippon Chemical Industry) and nano-LiCoO₂ in 2002.[104–106] As shown in Figure 13a, a 4 nm amorphous Al₂O₃ layer was coated on nano-LiCoO₂ uniformly. According to XRD patterns, the lattice of LiCoO₂ did not change. It means that the Al or Mg did not dipo into the LiCoO₂ lattice in the obtained sample.

We also demonstrated, as did Kweon and Park and Cho et al., that both Al₂O₃ and MgO surface coating improves the cycling stability of commercial LiCoO₂ significantly when the charge voltage extends to 4.5 V vs Li⁺/Li. Figure 13b shows the effect of an Al₂O₃ coating on improving the cyclic performance.[105]

The understanding of the coating mechanism was argued at that time. Cho et al. suggested that the effectiveness of the surface coating was attributed to the suppression of the variation of the c-value of LiCoO₂ in the case of the ZrO₂ coating, which leads to a zero-strain material.[107] Chen and Dahn argued that the ZrO₂ coating does not affect the variation of lattice parameters during cycling through their in-situ XRD studies.[108]

In order to clarify this, in-situ XRD data was collected on both Al₂O₃ coated and uncoated LiCoO₂ multiply cycled in the voltage range between 3 and 4.8 V. The 4.8 V high-voltage limit was chosen to accelerate the structural damage of the uncoated sample.

We performed in-situ XRD studies at the National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory, in collaboration with Yang et al.[109] For brevity, Figure 14 shows partial results of the in-situ XRD patterns during discharge. It was found that the XRD patterns of commercial LiCoO₂ remain unchanged during the whole discharge process (Fig. 9 in Ref. [109]), which indicated that the bulk structure of the commercial LiCoO₂ cathode material did not reversibly transform back from H2 (the phase at the end of a 5.2 V over-charge) to H1 (the phase of commercial LiCoO₂). When the Al₂O₃-coated LiCoO₂ cathode was charged to 5.2 V vs Li⁺/Li, the in-situ XRD patterns indicate that the material experiences a series of phase transitions, from H1 to H2, and then to O1a, and finally to O1 during the initial charge process. In the subsequent discharge process from 5.2 to 3 V, the phase transitions are fully reversible (Fig. 14b).

In addition to other results, the in-situ XRD analysis indicates clearly that the variation range of the lattice parameters is much larger in the Al₂O₃-coated LiCoO₂ than those in the pristine samples. Considering that the capacity fading of the Al₂O₃-coated sample is much smaller than that for the pristine cathode, we believe that surface coating does not suppress the phase transition during over-charging.

These results explain that the coating is effective in view of maintaining the structural stability. However, it was not understood why the coating could maintain the structural stability. Many authors believe that the surface coating improves the cycling stability of LiCoO₂ by physically separating the oxidized active material from the electrolyte.[110–113]

A comparison of the XPS results of the uncoated and MgO-coated LiCoO₂ at fully charged states seems to support the
above suggestions. Figure 15 shows O 1s spectra of the coated and uncoated LiCoO$_2$ charged at various voltages. The electronic structure of oxygen for uncoated LiCoO$_2$ varies steadily (at 529.4 eV in uncharged commercial LiCoO$_2$ electrode) with the increase of the charge voltage and a new component appears at 532.6 eV, which corresponds to oxygen atoms with a stronger oxidizing power. The content of such oxygen atoms increases with the charge voltage and becomes dominant in the electrode at high voltages. Oxygen atoms with a higher binding energy (at 531.6 eV) in the coated cathode, however, appear at a lower charge voltage but their content increases more slowly than in the uncoated commercial LiCoO$_2$ cathode (Fig. 15b). Moreover, as the binding energy of these oxygen atoms in the charged MgO-coated LiCoO$_2$ cathode is lower than in charged commercial LiCoO$_2$, their oxidizing power should also be weaker than those in the commercial LiCoO$_2$ cathode. These results indicate that modifying the surface of the LiCoO$_2$ particles may be helpful to suppress the release of oxygen, which may lead to instability of the interior structure and decomposition of the electrolyte.

It was noticed in 2003 by us that LiCoO$_2$ can react with the electrolyte spontaneously. Based on GC-MS analysis, the soaking of LiCoO$_2$ in EC/DMC solvents leads to the release of carbon dioxide (CO$_2$), carbon monoxide (CO), methane (CH$_4$), ethylene (C$_2$H$_4$), water (H$_2$O), ethane (C$_2$H$_6$), and oxygen (O$_2$), in the order of their maximum counts per second from high to low. FTIR spectroscopy detected the existence of ROLi and ROCO$_2$Li, and XRD detected the existence of Co$_2$O$_3$ and Co$_3$O$_4$. Later, we observed directly the existence of the surface film on nanosized LiCoO$_2$ as shown in Figure 16. As analyzed from corresponding SAED patterns, the Co$_3$O$_4$ phase appears after soaking in the solvent and in the electrolyte. ROCO$_2$Li was detected from the FTIR results. These results confirm that the surface of LiCoO$_2$ can react with the organic solvent spontaneously, especially for nanosized LiCoO$_2$. Actually, we did find that nanosized LiCoO$_2$ showed the worst cyclic performance at 10°C, as shown in Figure 17. When nanosized LiCoO$_2$ was sintered at 850°C and grown to a micrometer-sized particle, it showed a much improved cyclic performance at 10°C. As also shown in Figure 17, when the aged commercial LiCoO$_2$ was annealed at 850°C, it also showed good cyclic performance at 10°C. These results indicate that surface species exist on the uncoated samples (aged commercial product and nanosized LiCoO$_2$), which are not good for achieving good cyclic and rate performance. Coating or annealing can improve their properties by either forming a more stable surface or by decreasing the active surface area.

Another important issue is whether coated inert oxides are stable during storage and electrochemical cycling in Li-ion batteries. Kim et al. found that the ZrO$_2$ coating layer is converted into ZrF$_4$ in non-aqueous electrolyte. This is because of the existence of HF in the LiPF$_6$-based electrolyte. It was found by us that directly adding nanosized Al$_2$O$_3$ to the electrolyte was also very effective to improve the cyclic performance of aged LiCoO$_2$. Li$_3$AlF$_6$ and AlF$_3$ was found on LiCoO$_2$ after soaking in the nano-Al$_2$O$_3$-added electrolyte. These results indicate that the oxides for coating, such as Al$_2$O$_3$, MgO, and ZrO$_2$, may not be stable in a LiPF$_6$-based electrolyte that contains a trace amount of H$_2$O. They may convert into fluorides finally to stabilize the active surface of LiCoO$_2$. The formation of surface fluorides could be converted from coated oxides, or formed through complicated chemical reactions when Al$^{3+}$ or other cations exist in the...
LiCoO$_2$, b) nano-LiCoO$_2$, 850 °C, 24 h, c) commercial LiCoO$_2$, e) nano-LiCoO$_2$, 850 °C, 24 h, and f) commercial LiCoO$_2$, 850 °C, 24 h. Electrolyte: 1 M LiPF$_6$, EC/DMC (1:1, v/v).

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Figure 16. TEM images of nanosized LiCoO$_2$ particles at different situations. a) Pristine, b) soaked with 1 M LiPF$_6$ dissolved in EC/DMC (1: 1, v/v) electrolyte for 7 days, c) soaked with anhydrous DMC (<10 ppm) for 7 days, and d) after 10 cycles in a LiCoO$_2$/Li cell over a voltage range of 2.5–4.3 V. Reproduced with permission from [116]. Copyright 2006, ECS.

Figure 17. Cyclic performance of LiCoO$_2$ at 2.5–4.3 V at 10 C. a) Nano-LiCoO$_2$, b) nano-LiCoO$_2$, 850 °C, 6 h, c) nano-LiCoO$_2$, 650 °C, 24 h, d) commercial LiCoO$_2$, e) nano-LiCoO$_2$, 850 °C, 24 h, and f) commercial LiCoO$_2$, 850 °C, 24 h. Electrolyte: 1 M LiPF$_6$, EC/DMC (1: 1).

LiPF$_6$-based electrolyte. The possibility to form a surface layer driven by a chemical reaction may explain the facts that even a loose and incomplete oxide coating can still improve the performance of the cathode materials,[118–120] even when the coverage was as low as 13.7%.[120]

Recently, Sun et al. reported that a uniform 10 nm coating of AlF$_3$ on LiCoO$_2$ can improve the capacity retention at 3–4.5 V significantly.[121] They have extended this strategy to stabilize other layer-structured cathodes.[122,123] These achievements indicate that the coating effect could be more effective when the coating phase is stable in a non-aqueous electrolyte. This needs further investigation. One question still remains: when the coating layer is dense and uniformly covered on the surface of each particle of cathode material, how could electrons transport through a 10 nm insulating coating layer? Further careful studies should be performed to clarify this issue.

Enlightened by the achievement of the coating on improving the stability of LiCoO$_2$, we applied a similar strategy to LiMn$_2$O$_4$.[124,125] LiAlO$_2$ was coated on LiMn$_2$O$_4$ and formed a surface solid solution. The coated material showed an excellent cyclic performance, rate performance, and excellent capacity retention at 55 °C.[125]

3.2. Research on LiFePO$_4$

Iron-based compounds that contain compact tetrahedral ‘polyanion’ structural units (XO$_4$)$n$ (X = S, P, As, W, or Mo) have been investigated intensively as potential cathode materials for lithium ion batteries.[8,126–130] The elements in the compounds are abundant in the earth, inexpensive, and environmentally friendly. In particular, orthorhombic LiFePO$_4$ with an ordered olivine structure has attracted the most attention. However, this kind of compound is a wide-gap semiconductor (3.7 eV) and has an inherently extremely low electronic conductivity (~10$^{-9}$ S cm$^{-1}$) at room temperature. Various material processing approaches have been adopted to overcome this drawback, including methods to coat the phosphate particles with carbon.[131,132] Chung et al. found that controlled cation non-stoichiometry combined with solid solution doping by metals supervalent to Li, e.g., Mg, Zr, and Nb, increases the electronic conductivity of LiFePO$_4$ by a factor of 10$^8$.[133] However, the origin of the enhanced conductivity is under debate. Controversy is focused on whether the supervalent ions are actually doped into the lattice and the improved conductivity may be caused by a conductive nanonetwork.[134,135] Here, our efforts on doping are reviewed.

The first-principles calculation, which has already made an impact on the understanding of practical lithium-ion battery materials after Cedar et al.’s work,[136–141] was used by us for pure LiFePO$_4$ and its delithiated counterpart FePO$_4$. Experimentally, a doping system was studied by Goni et al.[142] who found that Fe$^{3+}$ can substitute some of the Li$^+$ ions in the LiMgPO$_4$ structure to form the solid solution Li$_{1-3x}$Fe$_x$MgPO$_4$(0, x, 0.1), to create cation vacancy channels along a certain crystallographic direction. Based on this experimental illumination, the electronic structure of Cr-doped LiFePO$_4$, namely, Li$_{1-3x}$Cr$_x$FePO$_4$ with $x = 1/32$, has been calculated from first-principles by a generalized gradient approximation (GGA) in order to elucidate the underlying conducting mechanism.[143] However, the obtained result did not give a proper bandgap.[143] In order to correct this, the calculation was performed again using the Vienna ab initio simulation program within the DFT+$U$ framework proposed by Zhou et al.[144] and core electrons were treated with the Projector Augmented Wave method. A $U$ value of 4.3 eV was used for Fe and the bandgap is well reproduced as shown in Figure 18.

As for doping, GGA+$U$ calculations show that although Cr doping introduces impurity states, the bandgap is still as large as 2 eV. Therefore, the possibility of p-type conduction by impurity states can be eliminated. Electron transport is probably in the form of small polaron hopping.[145] As the nearest Li–Fe distance in LiFePO$_4$ is 3.28 Å, while the nearest Fe–Fe distance is 3.87 Å, electron hopping between Fe and Cr in Li sites might be easier. It
is found that for Li$_{5/8}$Cr$_{1/8}$FePO$_4$, electronic states at the Fermi level mainly come from the Cr 3d, but contain hybridization with neighboring O 2p and Fe 3d bands of the O and Fe atoms near the dopant. This Cr-induced state may alter the conductivity with respect to the pure LiFePO$_4$, where no electronic state is located at the Fermi level.

Following the theoretical calculation, we also prepared the Cr-doped LiFePO$_4$ samples. It was found that its conductivity was enhanced after substituting a small amount of lithium ions. In Figure 19a, it can be seen that doped Li$_{0.97}$Cr$_{0.01}$FePO$_4$ and Li$_{0.91}$Cr$_{0.03}$FePO$_4$ show an electronic conductivity much higher than that of pure LiFePO$_4$ at room temperature. It should be noted that the activation energy $E_a = 0.186$ eV of pure LiFePO$_4$ obtained by us in a previous study is even smaller than the one (0.5 eV) given by Chung et al. for Mg, Zr, and Nb-doped samples. It was recognized later that the sample could be doped with Mg because one of the raw materials contained Mg impurities, the content of which was around 1% as determined later by inductively coupled plasma (ICP) analysis.

Pure phase LiFePO$_4$ was prepared again recently. High purity raw materials were used to eliminate the impurities, i.e., Mg, as determined by ICP. There was no carbon detected by Raman spectroscopic analysis. The dc-conductivity of pure phase LiFePO$_4$ was measured again using the same method as described in ref. [143]. It shows a conductivity of nearly $10^{-9}$ S cm$^{-1}$ at room temperature with an activation energy of 0.639 eV.

The diffusion mechanism of Li ions in the olivine LiFePO$_4$ was investigated by us from first-principles calculations. The energy barriers for possible spatial hopping pathways were calculated with the adiabatic trajectory method. The calculations show that the energy barrier along the c-axis was about 0.6 eV. However, the other migration pathways have much higher energy barriers that result in a very low probability of Li-ion migration. This means that the diffusion in LiFePO$_4$ is 1D. The 1D diffusion behavior has also been confirmed by a full ab initio molecular dynamics simulation, through which the diffusion behavior was directly observed.

Because of the feature of 1D ionic transport, it was necessary to know whether the Cr ions in the Li sites could block the diffusion of Li ions along the 1D diffusion pathway. We performed ab initio density functional theory (DFT)-based calculations using the Vienna ab initio simulation package VASP. This code solves the Kohn–Sham equations within the pseudopotential approximation whereby the electrons are described in the local-density approximation (LDA) by ultrasoft pseudopotentials. The valence electrons are expanded in a plane wave basis set and the effect of the core states on the valence electrons is treated with ultrasoft pseudopotentials. The structural energy minimization was performed for pure LiFePO$_4$ and Li$_{29/32}$Cr$_{1/32}$FePO$_4$ in a 2 x 2 x 2 super-cell. The Monkhorst–Pack scheme with 7 x 3 x 5 k point sets was used for the integration in the irreducible Brillouin zone. The energy cut-off for the plane waves was chosen to be 600 eV. In the structure optimization, partial occupancy at the Fermi level was treated according to Methfessel and Paxton. In the case of Li$_{29/32}$Cr$_{1/32}$FePO$_4$, there are two Li vacant sites in the super-cell; the optimized configuration was that the two vacancies lie nearby the Cr ions along the c-axis direction. The optimized configuration was obtained through the following: place the Cr ion in one Li site and change the locations of the two vacancies to construct new configurations. For each configuration the total energy was calculated after relaxation has occurred. The configuration with lowest total energy was considered to be the optimized one. In order to determine the migration energy barriers of the Li and Cr ions in the LiFePO$_4$ crystal, we employed the so-called ‘adiabatic trajectory method’ after structural optimization. The energy barrier was obtained conveniently through monitoring the changes of the total energy. The migration energy barrier was only considered as the migration of a Li ion from one occupied site to a nearby vacant site. When we considered the migration of one Li ion, we had already ‘created’ one vacant site in front of the moving Li ion. This was the same for the migration of the Cr ions with the vacancies pair (three vacancies in all). Figure 20a presents the migration energy barriers obtained by monitoring the total energy changes during the movement of the migration ions. It can be seen from the figure that the migration energy
induced by the Fe

the bandgap drops from 3.7 to 1.3 eV. The new states are

and electron-hole hopping along the Fe

occur.

property is expected in Na-doped LiFePO4 according to

narrower bandgap of 0.7 eV. An enhanced electron transport

impurity states appear when Na is doped, which leads to a much

smaller. Small polaron hopping mechanism is accepted in

conductivity and the activation energy

result of the substitution of a small amount of high valence metal

ions for lithium ions will not lead to improved electrochemical

performance. The reason lies in the blocking of the 1D pathways

by the heavy high-valence metal ions in the Li sites. The positive

contributions due to the enhanced electronic conductivity are

partially offset by the negative blocking effect of the Cr ions on

lithium ion motion.

Since doping at the Li site is not favorable for the diffusion of

Li, doping at the Fe or O site was considered. We proposed the

new strategies of Na-doping at Fe sites and N-doping at O sites.[158–160] First-principle calculations have been performed to

identify the doping effect on the electron structure. Calculations

were carried out within the DFT+U framework, and core

electrons were treated with the projector augmented wave

method. Two unit cells were used for calculation. The density of

states (DOS) of LiFe7/8N1/8PO4 is shown in Figure 18. The

impurity states appear when Na is doped, which leads to a much

narrower bandgap of 0.7 eV. An enhanced electron transport

property is expected in Na-doped LiFePO4 according to

calculations. As shown in Figure 19b, the Na-doped material

Li0.97Fe0.96Na0.05PO4 shows a much improved electronic

conductivity and the activation energy \( E_a = 0.035 \text{ eV} \) is also much

smaller. Small polaron hopping mechanism is accepted in

LiFePO4.[145, 161] Electron transport is dependent upon small

polaron hopping of Fe\(^{3+}\) holes within the lattice. Na-doping

introduces corresponding Fe\(^{3+}\), one of the occupied Fe\(^{3d}\) states

gets unoccupied after doping and this is the origin of the impurity

states.

Replacement of O by N could also introduce Fe\(^{5+}\). The DOS of

N-doped LiFePO4 is also shown in Figure 18.[162] New states

appear in the bandgap of pure LiFePO4 after N doping, and the

bandgap drops from 3.7 to 1.3 eV. The new states are

induced by the Fe–N bonding. Fe\(^{5+}\) formed as a result of electron redistribution. The hybridization of Fe 3d and N 2p leads to a narrower bandgap. When N is doped, it induces Fe\(^{5+}\) sites

and electron-hole hopping along the Fe–N–Fe chains may occur.

4. Summary and Outlook

Investigations on spherical hard carbon and polymerized carbon

nitride nanobells demonstrate that a large quantity of lithium can

be stored in carbon nanopores. When lithium was inserted, nanometer-SnO was converted into a nanocomposite where

Li–Sn crystallites (2–20 nm) are dispersed within an amorphous Li2O matrix. Nanometer-scale Si showed a very high capacity and

improved cycling performance. Surface coating improves the
cycling stability of LiCoO2 when its charge limit voltage is extended to 4.5 V vs Li\(^+/\)Li, which does not suppress the phase

transition during over-charging, rather, it suppresses the release

of oxygen. Na-doping into Fe sites and the partial replacement of

oxygen by nitrogen in LiFePO4 were proposed, which is different

from other approaches and was demonstrated theoretically as an
effective strategy to achieve high electronic conductivity but not

block the transport of lithium ion along the 1D channels.

Based on a decade's research, the performances of Li-ion

batteries are being improved by introducing new and enhanced

chemical combinations. Graphite anode could be replaced with

metals and oxides such as Si, Sn, Sb, SnO, Cr2O3, or MnO

because of their high capacity. Severe crystallographic volume

changes of high capacity materials during the lithiation and
delithiation process could be solved by using nanosized or

nanostructured materials. However, serious side reactions

observed in most stand-alone nanomaterials need to be controlled

for real battery applications. Combining the advantages of

nanometer and micrometer materials, surface modification,

the introduction of new additives for the electrolyte, and the

introduction of polymer-based electrolytes, are crucial to achieve a

stable electrode/electrolyte interface, which is very important for

the safety and service life of a battery. Therefore, the integration

strategy, considering the electrode materials, electrode structure,

and the electrode/electrolyte interface, is essential for future

research. In particular, for LiFePO4, transport of electrons and

ions in LiFePO4 has been well investigated by theoretical

calculations. However, experimental work based on single

crystals and thin films is needed to obtain precise data for

further confirmation and clarification. New synthetic methods ate

to be developed to introduce different dopants into LiFePO4. The
great interest in phosphates may not only lead to high

performance cathode materials for Li-ion batteries but also

may shed some light on new applications as electronic

materials.
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