Roles of Surface Chemistry on Safety and Electrochemistry in Lithium Ion Batteries

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CONSPECTUS

Motivated by new applications including electric vehicles and the smart grid, interest in advanced lithium ion batteries has increased significantly over the past decade. Therefore, research in this field has intensified to produce safer devices with better electrochemical performance. Most research has focused on the development of new electrode materials through the optimization of bulk properties such as crystal structure, ionic diffusivity, and electric conductivity. More recently, researchers have also considered the surface properties of electrodes as critical factors for optimizing performance. In particular, the electrolyte decomposition at the electrode surface relates to both a

lithium ion battery's electrochemical performance and safety. In this Account, we give an overview of the major developments in the area of surface chemistry for lithium ion batteries. These ideas will provide the basis for the design of advanced electrode materials.

Initially, we present a brief background to lithium ion batteries such as major chemical components and reactions that occur in lithium ion batteries. Then, we highlight the role of surface chemistry in the safety of lithium ion batteries. We examine the thermal stability of cathode materials: For example, we discuss the oxygen generation from cathode materials and describe how cells can swell and heat up in response to specific conditions. We also demonstrate how coating the surfaces of electrodes can improve safety. The surface chemistry can also affect the electrochemistry of lithium ion batteries. The surface coating strategy improved the energy density and cycle performance for layered $LiCoO_2$, $xLi_2MnO_3 \cdot (1 - x)LiMO_2$ (M = Mn, Ni, Co, and their combinations), and $LiMn_2O_4$ spinel materials, and we describe a working mechanism for these enhancements.

Although coating the surfaces of cathodes with inorganic materials such as metal oxides and phosphates improves the electrochemical performance and safety properties of batteries, the microstructure of the coating layers and the mechanism of action are not fully understood. Therefore, researchers will need to further investigate the surface coating strategy during the development of new lithium ion batteries.
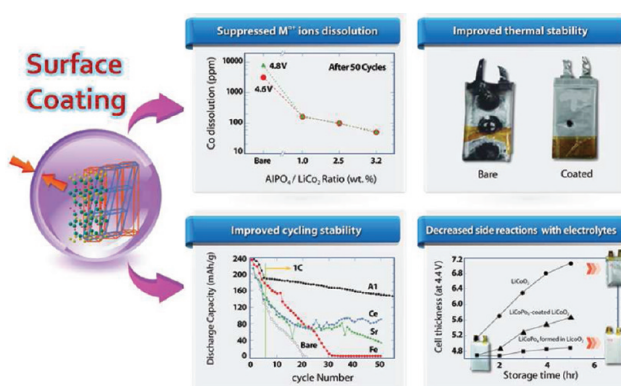
1. Introduction

Environmental pollution and the effects of global warming have forced us to look for alternative energy storage and conversion systems, such as electric vehicles and smart grids. These new energy systems require various functional performances depending on the application. For example, the performance properties of energy density and cost are relatively more emphasized in stationary energy storage systems such as smart grids. Also, the power and energy densities,

safety, and cycleability are key factors to meet the demands of energy systems in electric vehicles. On the basis of this view, many the recent efforts to improve power sources have been focused on lithium ion batteries due to their various advantages including higher energy density compared to previous power sources such as Ni-MH batteries or supercapacitors.[1] Lithium ion batteries have also been successfully used in various applications such as hybrid electric vehicles, mobile electric applications, and renewable energy storage devices.

Li ion batteries are composed of three major components: a cathode, an anode, and an electrolyte. Li ions move from the cathode to the anode through the electrolyte, or vice versa, during electrochemical reactions. There are three steps for the electrochemical reaction of the batteries: Li ion diffusion within solid-state electrode materials, a charge transfer reaction at the interface between the electrode and electrolyte, and Li ion movement in the electrolyte. These reactions are highly reversible, and therefore, lithium ion batteries are rechargeable. However, the reactions in lithium ion batteries include not only reversible reactions but also irreversible reactions. For example, one of the irreversible reactions is the decomposition of electrolytes on the surface of the electrode materials, which results in the forming of a solid electrolyte interphase (SEI).[2] This SEI can affect the kinetics of batteries in terms of rate performance, because SEI layers impede the charge transfer reaction, although the solid state diffusion of Li ions is considered to be the rate-determining step of Li ion batteries.[3] A thinner and more ionic conductive SEI shows better kinetics. However, SEI can improve the safety and cycleability of electrode materials by the formation of more stable SEI layers.[4] Without a stable SEI, irreversible reactions on the surface of the electrodes will not be stopped, because the unstable surface of the electrodes continues to be exposed to the electrolyte, resulting in the degradation of battery properties.

These irreversible reactions are dependent on the species of the surface, and, thus, different surfaces of materials induce different irreversible reactions, resulting in different levels of battery performance. Therefore, from this point of view, it is necessary to attain a comprehensive understanding of the roles of surface chemistry, which is a very important factor in improving the performance of lithium ion batteries. This Account thus presents the various roles and fundamentals of surface chemistry in cathode materials for lithium ion batteries.

2. Role of Surface Chemistry on Safety

One of the key issues in current battery science is how to improve the safety properties of lithium rechargeable batteries including both Li and Li ion batteries, because it is still ambiguous whether or not Li rechargeable batteries are safe enough to be used in hybrid electric vehicles or in purely electric vehicles. Li batteries use highly explosive Li metal, and even Li ion batteries are composed of highly oxidizing and reducing electrode materials and flammable electrolytes based on organic solvents, which might induce poor thermal stability due to thermal runaway. The temperature
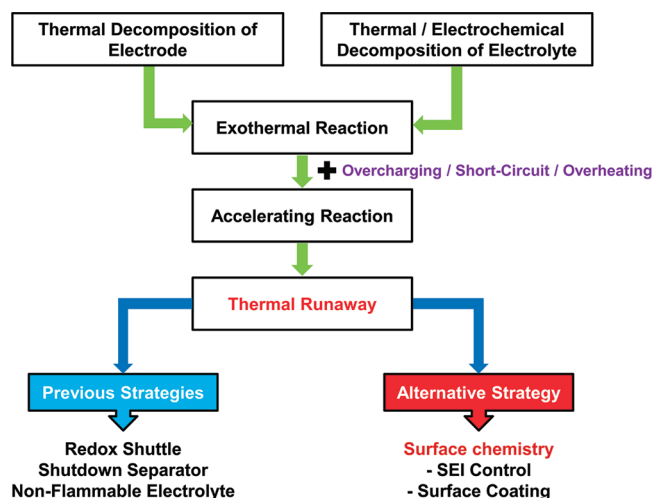

FIGURE 1. Schematic diagram of the thermal runaway mechanism and the safety improvement by various strategies.

of battery cells abruptly increases when the heat generation rate of the cell is higher than the heat dissipation rate via exothermal reactions; further, thermal runaway causes an internal short circuit through the melting of separators.

Several irreversible exothermal reactions causing thermal runaway are known such as (i) thermal and electrochemical decomposition of the electrolyte and (ii) thermal decomposition of the anode and the cathode (Figure 1).[5] These reactions are usually accelerated by abusive conditions such as overcharging, external and internal short circuits, overheating, and so on. The safety of lithium rechargeable batteries has been improved by using several strategies:[6] (i) Redox shuttles as additives in electrolytes. These have slightly higher oxidation potential than the charging potential of the cathode materials. During overcharging, the oxidized redox shuttles diffuse to the anode, are reduced on the anode, and then return to the cathode. Thus, redox shuttles shelter the battery from the overcharging as a result of repetitive reversible oxidation and reduction of shuttling additives. (ii) Use of a shutdown separator. This prevents ionic transport between electrodes by closing the micropores of the separators due to the separator polymers, which are soften when the cell temperature increases abnormally in abusive conditions such as overcharging. (iii) Nonflammable electrolytes such as ionic liquids.

It is still hard to satisfy the safety measures being demanded for electric vehicles, although the discussed strategies advance the safety properties of lithium ion batteries. Thus, many efforts have been made to develop safer electrode materials, and some promising safety improvements
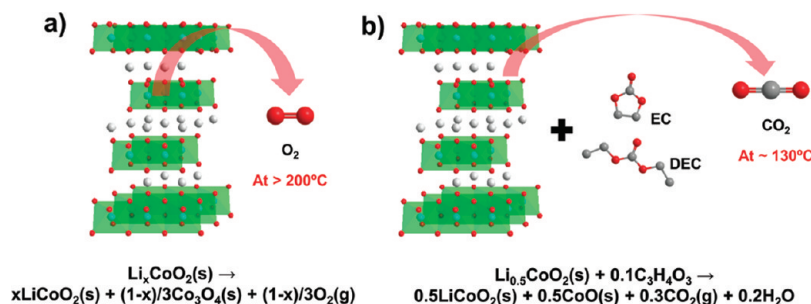
FIGURE 2. Comparison of thermal stability of Li_xCoO_2 ($x < 1$) in between (a) an inert gas and (b) an electrolyte. When Li_xCoO_2 is in contact with the electrolyte, the reaction temperature that the oxygen loss from Li_xCoO_2 happens is lower due to the different mechanism of oxygen evolution.

have been reported through the adopting of surface chemistry techniques. This part of the Account, therefore, will cover how the surface chemistry acts to enhance the safety of cathode materials; especially, it will focus on $LiCoO_2$[7] because this material has been most extensively studied in the area of safety.

Although $LiCoO_2$ is stable at high temperature, delithiated Li_xCoO_2 ($x < 1$) is known to be metastable and can be decomposed with the release of oxygen by heating it in air or in an inert gas; its instability increases as the value of x in Li_xCoO_2 decreases. This released oxygen combusts the solvent and, therefore, is closely related to thermal runaway. The phase transition of Li_xCoO_2 from a monoclinic ($R3^-m$) to a spinel structure ($Fd3m$) occurs below 200 °C, and then oxygen loss from Li_xCoO_2 itself occurs above ca. 200 °C according to the reaction in Figure 2a.[8] However, the battery chemistry is not that simple, because the cathode material is in contact with an electrolyte solution composed of salt and organic solvent. The decomposition of $Li_{0.5}CoO_2$ in the presence of electrolytes begins much earlier than in their absence due to the reaction between $Li_{0.5}CoO_2$ and significant amounts of solvent. Based on a study that used thermal analysis and X-ray diffraction, it has been reported that the reaction of $Li_{0.5}CoO_2$ with the mixed solvents of ethylene carbonate and diethyl carbonate initiates at a temperature as low as 130 °C by reducing the power of the solvent for Co_3O_4 to CoO, according to the following reaction[9] in Figure 2b, assuming the full combustion of the solvent of ethylene carbonate. Also, this reaction of Li_xCoO_2 with electrolytes shows an autocatalytic mechanism. In other words, the exothermic reaction initially proceeds slowly, but accelerates rapidly due to self-heating, as the reaction products promoting the reaction itself are formed. This results in an abrupt increase of heat generation. The self-heating rates were greater for both the smaller particle size of Li_xCoO_2 and the lower value of x in Li_xCoO_2 as charged to higher voltage.[10] The decomposition of $Li_{0.5}CoO_2$ is also

affected by salts in the electrolyte such as $LiPF_6$.[11] It is well-known that $LiPF_6$ itself is not thermally stable and, therefore, $LiPF_6$ is reversibly decomposed into LiF (s) and PF_5 (g) by heating at around 300 °C and is irreversibly decomposed in the electrolyte with the formation of LiF (s) and PF_5 (g) at near 230 °C. It is suggested that the decomposed PF_5 reacts with water present as an impurity in the electrolyte, resulting in the formation of HF according to

$$PF_5 + H_2O \rightarrow 2HF + PF_3O$$

Then, HF or PF_5 initializes the polymerization of ethylene carbonate into polyethylene-oxide-like polymers by ring-opening polymerization of cyclic carbonate. Therefore, the decomposition of $LiPF_6$ leads to the deposit of a polymer film on the surface of the $Li_{0.5}CoO_2$ particles and slows the reaction between $Li_{0.5}CoO_2$ and the solvent, resulting in the impedance of the self-heating reaction with the release of oxygen. Actually, the electrolyte of $LiPF_6$ in ethylene carbonate, itself, is less thermally stable than the electrolytes based on imide-type salts such as $Li-N(CF_3SO_2)_2$ and $Li-N(C_2F_5SO_2)_2$. However, when these electrolytes are combined with $Li_{0.5}CoO_2$, the $LiPF_6$ electrolyte is more thermally stable than the electrolytes based on imide-type salts, because these salts do not produce a protective polymer film, allowing the $Li_{0.5}CoO_2$ to react with the solvents more strongly. Therefore, the polymer film created by the decomposition of the electrolyte can act as a protective layer for the oxygen release reaction of $Li_{0.5}CoO_2$. It is notable that a surface film on active materials can induce more thermally stable and safer electrodes by a controlled decomposition of electrolytes. Also, it is well-known that water molecules are detrimental to battery performance because water induces the decomposition of electrolytes, resulting in increasing polarization. However, ironically,
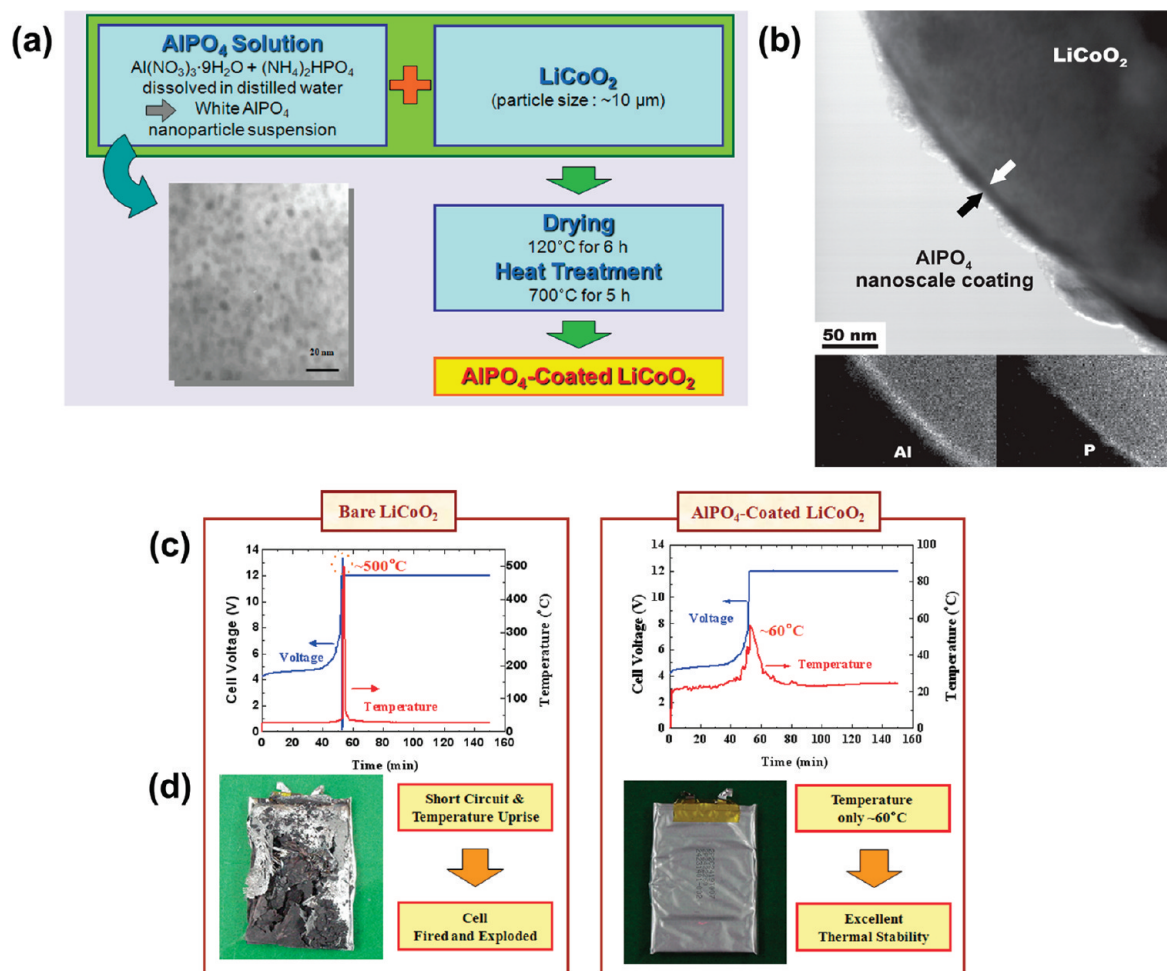
FIGURE 3. Comparison of safety between bare $LiCoO_2$ and $AlPO_4$-coated $LiCoO_2$ cathode materials. (a) Schematic diagram of $AlPO_4$ nanoparticle coating method. The inset shows a TEM image of $AlPO_4$ nanoparticles. (b) TEM bright-field image of the $AlPO_4$ nanoparticle-coated $LiCoO_2$; EDS confirms the Al and P components in the coating layer. (c) Voltage and temperature profiles of cells with bare $LiCoO_2$ and $AlPO_4$-coated $LiCoO_2$ cathodes, as a function of time. (d) Pictures of cells containing a bare $LiCoO_2$ and $AlPO_4$-coated $LiCoO_2$ cathode after the 12 V overcharge test; the cell of a bare $LiCoO_2$ burned and exploded at that voltage, but no explosion was observed for the cell of $AlPO_4$-coated $LiCoO_2$. Reproduced from ref 12. Copyright 2003 Wiley-VCH.

a little water helps to make a safer battery by the formation of a more stable solid electrolyte interphase. This means that the surface treatment on $LiCoO_2$ can cause an improvement in the thermal stability of delithiated Li_xCoO_2.

Cho's group extensively studied the effect of coating layers on the $LiCoO_2$ thermal stability. Recently, they homogeneously coated $AlPO_4$ layers (ca. 3 wt.% and ca. 15 nm thickness) on $LiCoO_2$ powders (ca. 10 μm size) using $AlPO_4$ nanoparticle suspension and additional heat treatment (Figure 3).[12] Then, the thermal stability of $AlPO_4$-coated $LiCoO_2$ was examined through overcharge safety tests. Both cells composed of bare $LiCoO_2$ and $AlPO_4$-coated $LiCoO_2$ were charged to 12 V, and maintained at that voltage for 2 h. In the case of bare $LiCoO_2$, during overcharge, the electrolyte

decomposition occurs at approximately 5 V vs Li/Li$^+$, followed by a rapid increase in the cell voltage to 12 V. As shown in Figure 3, immediately after the cell voltage reaches 12 V, the surface temperature of the cell increases to almost 500 °C and an internal short circuit occurs because a separator melts down at ca. 120 °C, resulting in fires and the explosion of the cell. In contrast to bare $LiCoO_2$, $AlPO_4$-coated $LiCoO_2$ showed better thermal stability. The cells with $AlPO_4$-coated $LiCoO_2$ did not exhibit the internal short circuit problem because the surface temperature increased to only ca. 60 °C although the cells were swollen due to electrolyte decomposition. This enhanced thermal stability seems to be attributable to the strong P=O bond and the strong covalency between the PO_4 polyanion and the Al^{3+} ion in $AlPO_4$. Also, it was additionally reported that

$AlPO_4$-coated $LiCoO_2$ exhibits thermal stability that is better than that of $Li_{1.05}Mn_{1.95}O_2$ spinel. $Li_{1.05}Mn_{1.95}O_2$ spinel is known to be one of most thermally stable cathode materials.[13] In addition, for the enhancement of thermal stability, $AlPO_4$ coating has been successfully adopted in other cathode materials such as $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$.[14]

However, although Cho's group reported $AlPO_4$ nanoparticles are coated on the cathode materials, there was a debate about the microstructure of the $AlPO_4$ coating layer. Considering the detailed transmission electron microscopy (TEM) with energy dispersive X-ray mapping and X-ray photoelectron spectroscopy (XPS) studies, it is suggested that the $AlPO_4$ reacts with $LiCoO_2$ to form a Li_3PO_4 coating layer and Al-substituted $LiAl_yCo_{1-y}O_2$.[15] Therefore, further studies of the microstructure of the $AlPO_4$ coating layer are needed in order to fully understand the role of such a coating layer on the thermal stability.

Many other coating layers have also been suggested to improve the thermal stability of $LiCoO_2$. For example, $LiCoPO_4$ was coated on $LiCoO_2$ by heating the precipitated $Co_3(PO_4)_2$ on $LiCoO_2$.[16] $Co_3(PO_4)_2$ reacts with the Li in $LiCoO_2$ to form $LiCoPO_4$, resulting in the formation of lithium deficient $Li_{1-x}CoO_2$. $LiCoPO_4$ is one of the electrochemically active materials, and its redox potential is about 5 V vs Li/Li^+. $LiCoPO_4$ is known to be a very stable compound due to strong P=O bonding. The swelling property of $LiCoPO_4$-coated $LiCoO_2$ cells was compared with those of bare $LiCoO_2$ and $AlPO_4$-coated $LiCoO_2$ cells. The cells were charged to 4.4 V and stored at 90 °C for 5 h. By electrolyte decomposition and gas evolution, the cell thickness increases when the charged cells are stored at high temperature. In the case of bare $LiCoO_2$, the cell thickness increased from 4.6 to 7 mm, but these values in $AlPO_4$-coated and $LiCoPO_4$-coated $LiCoO_2$ cells increased from 4.6 mm to 6 and 4.9 mm, respectively. Even $AlPO_4$-coated $LiCoO_2$ cells swelled by ca. 30%, and this swelling seems to have been caused by the residual LiOH and Li_2CO_3 in the $AlPO_4$-coated $LiCoO_2$. During the $AlPO_4$-coating process, Li dissolution from $LiCoO_2$ can happen because water is used as a solvent. Dissolved Li sources are precipitated in the forms of LiOH or Li_2CO_3 and reside on the surface of the particles. Unlike $AlPO_4$, $Co_3(PO_4)_2$ can be reacted with Li salts to form $LiCoPO_4$ at high temperature, and thus no Li salt impurities remained in the $LiCoPO_4$-coated $LiCoO_2$ cells, resulting in very little electrolyte decomposition and ignorable swelling. The better thermal stability of $LiCoPO_4$-coated $LiCoO_2$ cells is confirmed by one other experiment, conducted under harsh conditions. After the nail penetration test, the cell surface temperature of bare $LiCoO_2$ increased to about 500 °C and fires broke out; however, the temperature of the $LiCoPO_4$-coated $LiCoO_2$ increased to only 80 °C.

3. Role of Surface Chemistry in Electrochemistry

As mentioned in the Introduction, aspects of electrochemical performance such as the energy density and cycleability of lithium ion batteries need to be improved in order to use these materials as power sources in new applications such as smart grids and electric vehicles. Energy density (working voltage ($V = J/C$) × specific capacity (C/g)) can be increased in two ways: one is to develop new cathode materials with higher redox potentials; the other is to increase the specific capacity. The former method should be accompanied by the development of new stable electrolytes at higher redox potential, which is another big obstacle. The latter strategy is also available through the development of new electrode materials with higher specific capacity, but this method is limited to increasing Li storage sites by using topotatic chemistry.

An alternative to these methods is to try to utilize as much capacity as possible within the theoretical values. In the case of $LiCoO_2$, when all of the Li is extracted from $LiCoO_2$, its theoretical capacity is 274 mAh/g. However, only a little over half of the theoretical capacity is practically utilized, because Li ion insertion/deinsertion in the range of ≥ 4.3 V vs Li/Li^+ degrades the $LiCoO_2$ cell, resulting in rapid capacity fading. Thus, many studies have been performed to utilize more of the reversible capacity of $LiCoO_2$ by using the enhanced structural stability of the doped variants $LiM_xCo_{1-x}O_2$ (M = Al, Cr, Mg). Also, notable improvements have been obtained by adopting surface chemistry. The details of doped variants have already been addressed in detail in other reviews.[17] Therefore, this part of the Account will look at how the surface chemistry acts to improve the electrochemical performance of cathode materials in such areas as energy density and cycleability, based on various materials such as layered $LiCoO_2$, $xLi_2MnO_3 \cdot (1-x)LiMO_2$ (M = Mn, Ni, Co, and their combinations), and $LiMn_2O_4$ spinel.

$LiCoO_2$ adopts a layered α-$NaFeO_2$ structure with consecutive alternating of the CoO_2 and Li layers. Both Co and Li are octahedrally coordinated, and Co^{3+} and Li^+ reside in the 3a site and 3b site, respectively, in the $R\bar{3}m$ ccp packed O^{2-} lattice. As shown in Figure 4,[18] the electrochemical Li removal reaction from $LiCoO_2$ happens according to (i) an expansion of the interlayer c axis as a result of electrostatic repulsion of the oxygen layers $x \leq 0.5$,[19] (ii) a hexagonal-monoclinic transformation at $x =$ ca. 0.5 (order−disorder transition),[19a,20]

(a)

(b)
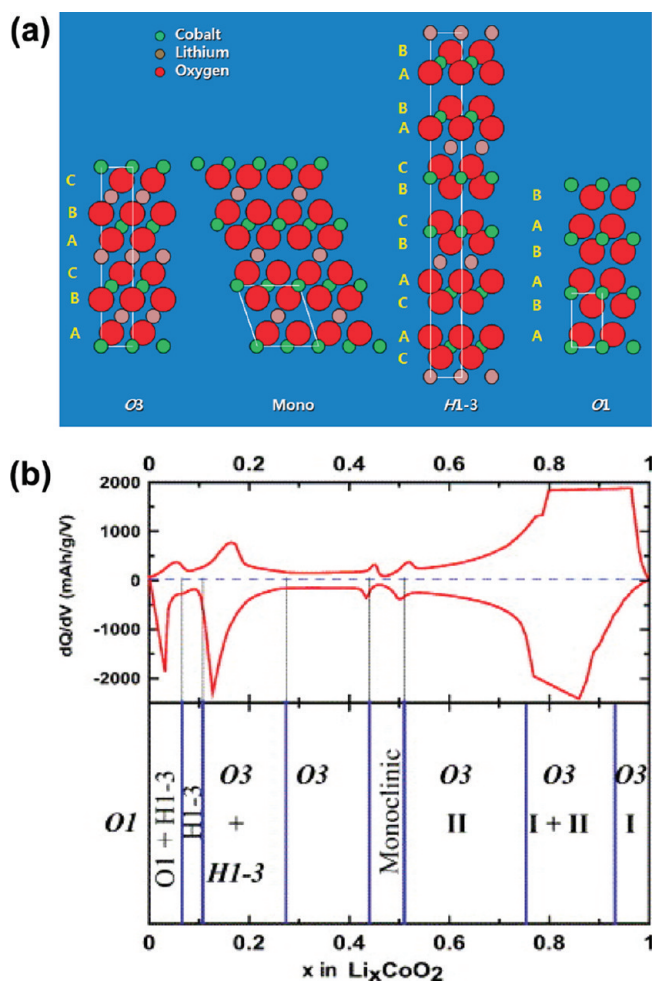
FIGURE 4. Phase transitions in Li_xCoO_2. (a) A view of the O3, mono-clinic, H1−3 and O1 structures. (b) Differential capacity vs Li concentration in Li_xCoO_2 and the corresponding phase diagram of Li_xCoO_2. Reproduced from ref 18. Copyright 2004 Elsevier.

(iii) a transformation of the O3 $LiCoO_2$ phase (close-packed oxygen layers with an ABCABC stacking sequence) into the O1 Li_xCoO_2 phase (ABAB stacking sequence) at x = ca. 0.05,[19b,21] and (iv) the transformation via an intermediate phase, $Li_{0.12}CoO_2$, (H1−3) a hybrid host structure that encompasses both the O3 and O1 stacking sequences.[22] When the cutoff voltage of $LiCoO_2$ increases from 4.3 to 4.5 V, the x in $Li_{1-x}CoO_2$ increases from 0.55 to 0.7, accompanied by a large anisotropic volume change of over 3% due to the phase transition through the hexagonal, monoclinic, and H1−3 phases. This large internal strain induces the mechanical and structural degradation of Li_xCoO_2. In addition, Co and Li ions dissolution at 4.5 V and elevated temperature at the surface of $LiCoO_2$ induce an accelerated structural instability. Thus, it is difficult to extract more than 0.5 Li in the $LiCoO_2$ structure, and these degradations cause growth of impedance for charge and mass transfer kinetics

in lithium ion batteries, resulting in poor cycleability. The chemical instability of the Li-poor phase of $Li_{1-x}CoO_2$ ($1 − x < 0.5$) is more emphasized when it is in contact with electrolytes. Due to the overlap of the redox active $Co^{3+/4+}$: t_{2g} band with the top of the O^{2-}:2p band, $Li_{1-x}CoO_2$ ($1 − x < 0.5$) shows oxygen loss and hydrogen incorporation, forming $[Li_{1-x}H_y]$-$CoO_{2-\delta}$.[23] Hydrogen is generated from the organic solvent of the electrolytes. Also, it is noticeable that electrolytes decomposition easily occurs on the surface of Li_xCoO_2 due to the highly oxidized Co^{4+} ions, resulting in substantial amounts of gas and heat generation with high polarization.[24] Because of these entire factors, we should focus on the role of the surface in improving the electrochemical performance of $LiCoO_2$.

Cho et al. first introduced MO_x-coated $LiCoO_2$ (M = Zr, Al, Ti, B) samples that exhibit little capacity fading, although the cutoff voltage of $LiCoO_2$ increased to 4.4 V vs Li/Li^+.[25] They suggested that the coated oxide layer reacts with $LiCoO_2$ during the heating process and forms a $LiM_xCo_{1-x}O_2$ solid solution thin layer. The improvement of cycleability was considered to be attributable to the suppressing of the c-axis expansion of Li_xCoO_2 and the cobalt dissolution in the electrolyte during cycling between 2.75 and 4.4 V. However, other factors have also been considered to explain the role of metal oxide coating layers in the enhanced cycleability of $LiCoO_2$.[18,26] Based on careful XRD studies, it has been suggested that Al_2O_3 and ZrO_2-coated $LiCoO_2$ samples do not form solid solution phases on the surface of $LiCoO_2$. Thus, it was considered that the metal oxide coating layers do not suppress the strain during phase transitions, but, due to moisture elimination during the additional heating process, these layers reduce the side reactions caused by (i) the decomposed residuals such as LiOH or Li_2CO_3 present on the $LiCoO_2$ due to moisture or (ii) HF that is formed by side reactions of $LiPF_6$ with water. Also, it has been reported that the precipitation of the electrolyte decomposition products on the surface of $LiCoO_2$ at high voltage increases the polarization, resulting in poor cycle performance. However, a ZrO_2 coating layer helps to reduce the polarization, and this reduction is attributed to the fact that the coating layer provides a decrease of the amount of electrolyte decomposition or leads to a better species of SEI on the $LiCoO_2$ surface.[27] The same behavior was observed in the case of surface-modified $LiMn_{1.42}Ni_{0.42}Co_{0.16}O_4$ cathode with nanostructured oxide coating such as Al_2O_3.[28] The surface modifications slow down the kinetics of the electrolyte decomposition reaction at the interface between the electrolyte and the electrode materials. Also, the different surface
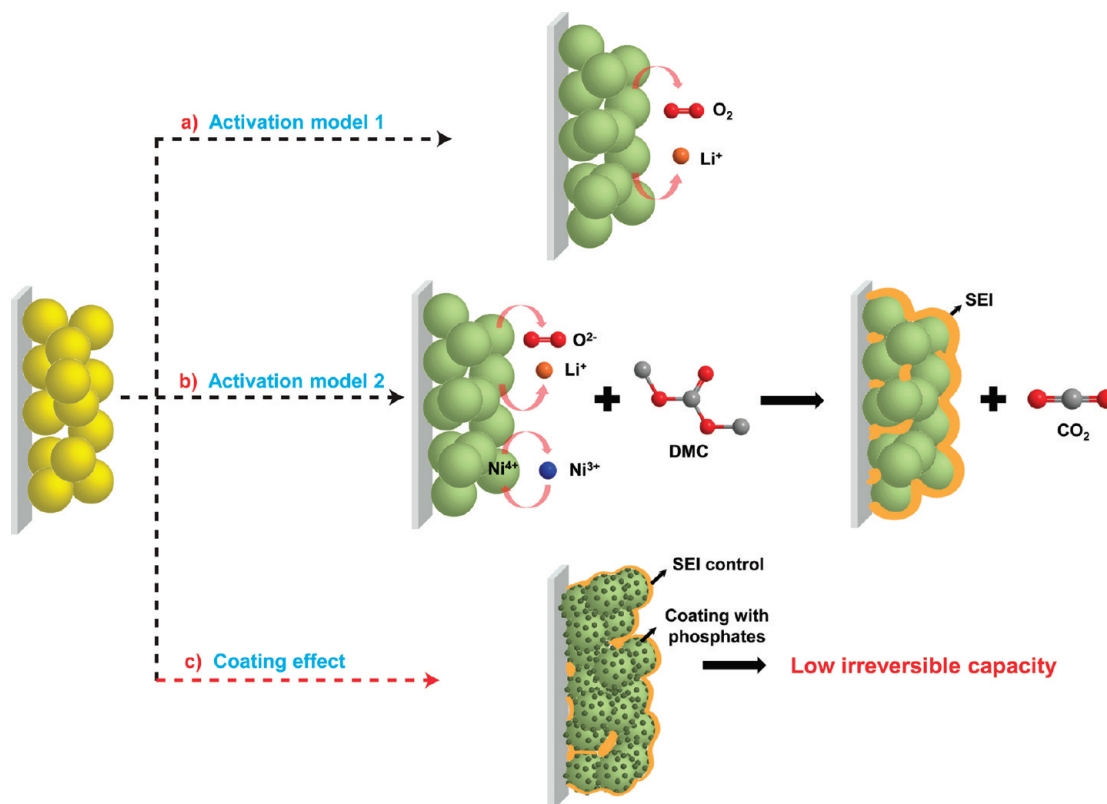
FIGURE 5. Electrochemical activation mechanisms of $x\text{Li}_2\text{MnO}_3 - (1-x)\text{LiMO}_2$ (M = Mn, Ni, Co, and their combinations): (a) direct oxygen gas evolution model and (b) electrolyte decomposition model. (c) AlPO_4 coating effect on the irreversible capacity of $\text{Li}[\text{Li}_{(1-x)/3}\text{Mn}_{(2-x)/3}\text{Ni}_{x/3}\text{Co}_{x/3}]\text{O}_2$.

of LiCoO_2 due to the different species of coating layers (Al_2O_3, Bi_2O_3, ZnO, AlPO_4) induces different behavior of electrolyte decomposition, and this indicates that the battery performance can be improved by surface control.

The beneficial effect of surface chemistry is also observed in a different cathode material, $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ (M = Mn, Ni, Co, and their combinations) as a composite structure.[29] It was also first described as a solid solution, $\text{Li}[\text{Ni}_y\text{Li}_{(1/3-2y/3)}\text{Mn}_{(1/3-2y/3)}]\text{O}_2$ for the composition of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$.[30] The advantage of this material is that it has a high reversible capacity (200–300 mAh/g), following an activation process. The activation is associated with leaching of Li_2O from Li_2MnO_3, resulting in high irreversible capacity. The electrochemical activation achieved by charging at >4.5 V is proved by the direct detection of oxygen gas evolution (Figure 5a).[31] However, it has also been proposed that some of the Li_2O extraction is associated with the direct oxidation of solvents in the electrolyte by the highly oxidized electrode material, accompanied by a change in Ni oxidation state ($\text{Ni}^{4+} \leftrightarrow \text{Ni}^{3+}$) (Figure 5b).[32] It is notable that the surface chemistry is related with the electrochemical activation, because the surface coating with AlPO_4 on $\text{Li}[\text{Li}_{(1-x)/3}\text{Mn}_{(2-x)/3}\text{Ni}_{x/3}\text{Co}_{x/3}]\text{O}_2$ reduces the irreversible capacity

induced by the electrochemical activation (Figure 5c).[33] Of course, the change of bulk structure in $\text{Li}[\text{Li}_{(1-x)/3}\text{Mn}_{(2-x)/3}\text{Ni}_{x/3}\text{Co}_{x/3}]\text{O}_2$ after coating of AlPO_4 with heat treatment is also considered as a factor that reduces the irreversible capacity. It has been suggested that the bonding of the coating layer to the surface of the layered oxide lattice suppresses the diffusion of the oxygen vacancies and their elimination, resulting in the increase of reversible capacity and the decrease of irreversible capacity.

Another impressive role of surface modification with metal oxide coating is noticeable in the spinel LiMn_2O_4 material. LiMn_2O_4 offers excellent safety and high power capability, but shows severe capacity fading at elevated temperature (>50 °C). The poor cycleability is attributed to several problems such as (i) Jahn–Teller distortion of Mn^{3+},[34] (ii) formation of oxygen deficient LiMn_2O_4 upon cycling,[35] (iii) microstrain caused by lattice mismatch between the two distinct cubic phases formed on cycling,[36] and (iv) the dissolution of LiMn_2O_4 in HF-containing acidic electrolytes formed by the hydrolysis of LiPF_6 in electrolytes.[37] Mn dissolution happens in two ways:[38] (i) the formation of soluble Mn^{2+} through the disproportionation reaction of LiMn_2O_4 ($\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$) and (ii) acid dissolution by
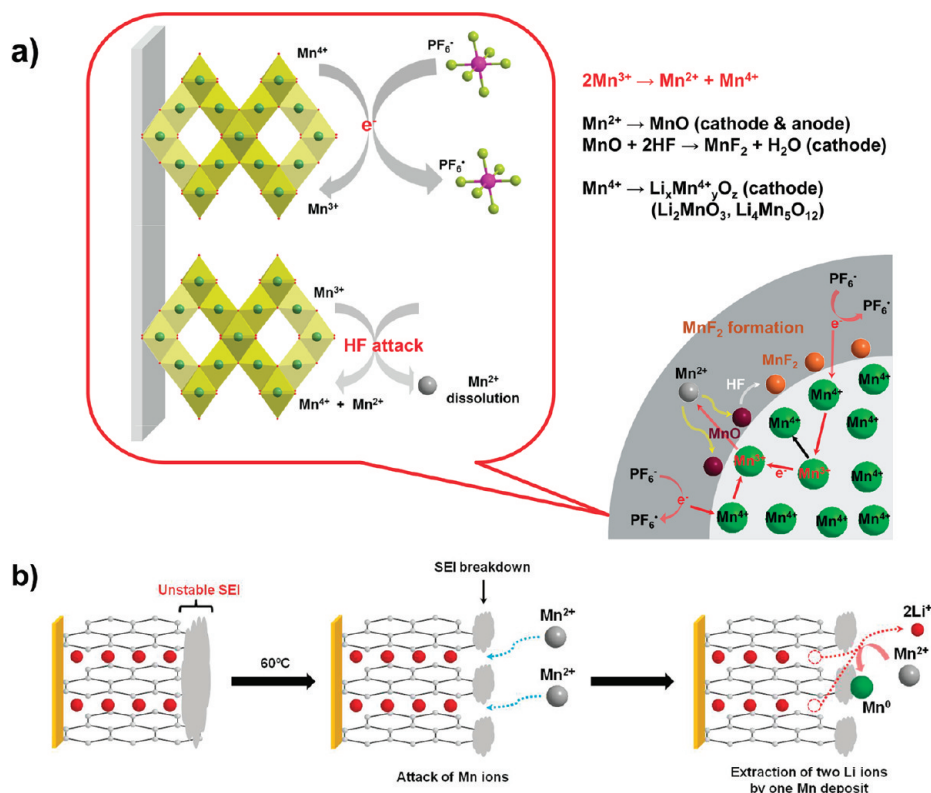
FIGURE 6. Role of Mn dissolution in $LiMn_2O_4$ spinel on the capacity fading. (a) Schematic mechanisms of the Mn^{3+} dissolution and electrolyte decomposition. (b) Schematic presentation the irreversible Li ion loss by Mn reduction at anode surface. Mn^{2+} ions are diffused from $LiMn_2O_4$ cathode due to Mn dissolution.

HF ($Li_{1-x}Mn_2O_4 + HF \rightarrow \lambda\text{-}Mn_2O_4 + LiF + Mn^{2+} + H_2O$). Between these, it is considered that capacity fading is mostly affected by Mn dissolution, because the dissolved Mn ions are reprecipitated on the surface of $LiMn_2O_4$ or diffuse into the anode surface, accompanied by a reduction of Mn ions and irreversible deintercalation of Li^+ ions (Figure 6).[39] Therefore, this method would be the most efficient way to prevent the formation of HF in electrolytes for the enhancement of cycleability, but it is not possible to perfectly control moisture content in this industry. An alternative is to coat MO_x on $LiMn_2O_4$, which plays a role of HF scavenger.[40] MO_x can be reacted with HF to form MF_y and H_2O. Recently, various MO_x (M = Mg, Zr, V, Zn, Al, Co) were examined as a coating layer, and MO_x-coated $LiMn_2O_4$ samples showed much improved cycle performance at elevated temperature.[41]

4. Concluding Remarks

In the past decade, there has been exciting progress in the area of Li ion batteries as energy storage systems, resulting in the application of lithium ion batteries in areas ranging from small portable electric devices such as laptops to large power systems such as hybrid electric vehicles. Promising electrochemical performance, low cost, and high energy density are factors that have driven research interest in these batteries. However, the safety and electrochemical performance of current cathode materials in lithium ion batteries are not still sufficient to meet the demands of new markets in such areas as electric vehicles. Therefore, solutions to obtain cathode materials with safer and better electrochemical performance are being sought. We believe that the modification of surface chemistry will be one of the solutions. Surface treatment based on coating technology has shown improvements in those properties in the area of commercialized $LiCoO_2$, and the coating technology is practical because of its strong advantages such as facile scalable synthesis and low cost. Therefore, it is expected that surface chemistry will play an important role in other promising cathode and anode materials for next generation batteries including lithium-sulfur and lithium-air batteries. For example, recently, the importance of Si anode surfaces has attracted attention, because the binding chemistry between Si and the binder is a key factor in the improvement of electrochemical performance.

In the area of lithium ion batteries, the role of surface chemistry has been under-evaluated because many aspects

of the mechanism in surface chemistry had not been clearly understood and it was difficult to find a proper instrumental analysis that could study the surface chemistry of electrode materials. However, recently, various in situ instrumental analysis tools for surface chemistry have been introduced, and thus, these tools enable us to perform solid investigations of surfaces in order to improve our overall understanding. Therefore, we believe it is possible that we will find a breakthrough technology in the area of surface chemistry for lithium ion batteries.

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FOOTNOTES

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The authors declare no competing financial interest.

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