



The Formation, Detriment and Solution of Residual Lithium Compounds on Ni-Rich Layered Oxides in Lithium-Ion Batteries

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Ni-rich layered transition-metal oxides with high specific capacity and energy density are regarded as one of the most promising cathode materials for next generation lithium-ion batteries. However, the notorious surface impurities and high air sensitivity of Ni-rich layered oxides remain great challenges for its large-scale application. In this respect, surface impurities are mainly derived from excessive Li addition to reduce the Li/Ni mixing degree and to compensate for the Li volatilization during sintering. Owing to the high sensitivity to moisture and CO₂ in ambient air, the Ni-rich layered oxides are prone to form residual lithium compounds (e.g. LiOH and Li₂CO₃) on the surface, subsequently engendering the detrimental subsurface phase transformation. Consequently, Ni-rich layered oxides often have inferior storage and processing performance. More seriously, the residual lithium compounds increase the cell polarization, as well as aggravate battery swelling during long-term cycling. This review focuses on the origin and evolution of residual lithium compounds. Moreover, the negative effects of residual lithium compounds on storage performance, processing performance and electrochemical performance are discussed in detail. Finally, the feasible solutions and future prospects on how to reduce or even eliminate residual lithium compounds are proposed.

Keywords: ni-rich cathode, air storage performance, residual lithium compounds, surface degradation, modification

INTRODUCTION

Although LiCoO₂ is one of the earliest successfully commercialized cathode materials, with a low energy density, high cost and toxicity, it is not suitable to be applied as a power battery material (Lu et al., 2019; Xian et al., 2020; Cheng et al. 2020). By substituting cobalt (Co) with nickel (Ni), LiNiO₂ has a similar layered crystal structure to LiCoO₂. However, it possesses a larger energy density and costs less (Ohzuku et al., 1993; Deng et al., 2019; Mu et al., 2020). Unfortunately, due to the large cation mixing degree during synthesis (preparing stoichiometry LiNiO₂ is actually difficult) and extreme air sensitivity, the practical application of LiNiO₂ is very challenging (Liu et al., 2007; Manthiram et al., 2016; Das et al., 2017). In this respect, substituting the fractional Ni atoms in

LiNiO₂ with other metallic elements, Ni-rich layered oxide materials (LiNi_xM_yO₂, M = Co, Mn, Al, $x + y = 1$ and $x \geq 0.6$) will be more stable than pristine LiNiO₂ (ChongYoon et al., 2015; Manthiram et al., 2017; Li et al., 2018; Ryu et al., 2018; Zhang et al., 2019c). Taking NCM (LiNi_xCo_yMn_zO₂) materials as an example, through replacing some Ni atoms at the 3b site with Co and Mn, with a favorable synergistic effect, they exhibit equalizing performance, where Ni is the main capacity provider with two redox couples including Ni²⁺/Ni³⁺ and Ni³⁺/Ni⁴⁺, Co³⁺ is beneficial in suppressing Li/Ni mixing and enhances systematic ionic conductivity, furthermore, Mn⁴⁺ can also stabilize the lattice structure and improve thermal stability (Deng and Manthiram, 2011; Liang et al., 2016; Masoumi et al., 2017). However, with the increase of Ni content, some intrinsic defects originating from LiNiO₂ are prone to be more obvious, such as: Li/Ni cation mixing, air sensitivity, serious slurry gelation, and unwanted gas evolution, which should be solved urgently before their large-scale application (Park et al., 2016; Zhao et al., 2017; Kim et al., 2019a; Duan et al., 2019; Zhang, 2020).

Li/Ni mixing is one of the characteristic defects of Ni-rich layered oxides since Ni²⁺ (0.69 Å) and Li⁺ (0.76 Å) have a similar ionic radius, and Ni²⁺ is difficult to fully oxidized into Ni³⁺ during the sintering synthesis process. In order to minimize the Li/Ni mixing degree, the synthesis process needs to be carried out under an oxygen atmosphere by adding an excessive Li source (Wu et al., 2015; Park and Choi, 2018; Li et al., 2019a; Zhang et al., 2019b). However, after sintering, the residual lithium remains on the surface of the final product, which is prone to absorbing and reacting with moisture and carbon dioxide (CO₂) in air. Therefore, residual lithium compounds spontaneously generate (Cho et al., 2014). In addition, the external Ni³⁺ ions with high chemical activity have a tendency to be reduced into Ni²⁺, together with the lattice oxygen release, the growth of residual lithium compounds, and the surface phase transition during air exposure (Jo et al., 2014b; Tian et al., 2018; Yang et al., 2019a). Those are the main reasons why residual lithium compounds increase on the surface of Ni-rich cathode materials with an air exposure time extension.

Furthermore, the formation of residual lithium compounds not only influences the electrode preparation, but also results in capacity fading and is a safety hazard. During the electrode slurry preparation, the high alkaline Ni-rich cathode materials (pH ≈ 11) will give rise to polyvinylidene fluoride (PVDF) degradation and slurry gelation, thus worsening the processability of the electrode slurry (Ross et al., 2000). Another issue is that due to the intrinsic insulation of surface impurities, the Li⁺ diffusion is seriously restricted, leading to the increased cell polarization and inferior cycling performance (Chen et al., 2019; Wang et al., 2019). Moreover, the electrochemical decomposition of residual lithium compounds will cause cell swelling and localized heating, which are potential safety risks in its practical application (Min et al., 2017; Mao et al., 2019; Renfrew et al., 2019). As a consequence, how to effectively reduce surface residual lithium compounds of Ni-rich cathode materials, has become a current research hotspot.

Up to now, various strategies have been put forward to overcome the aforementioned issues, such as a washing process,

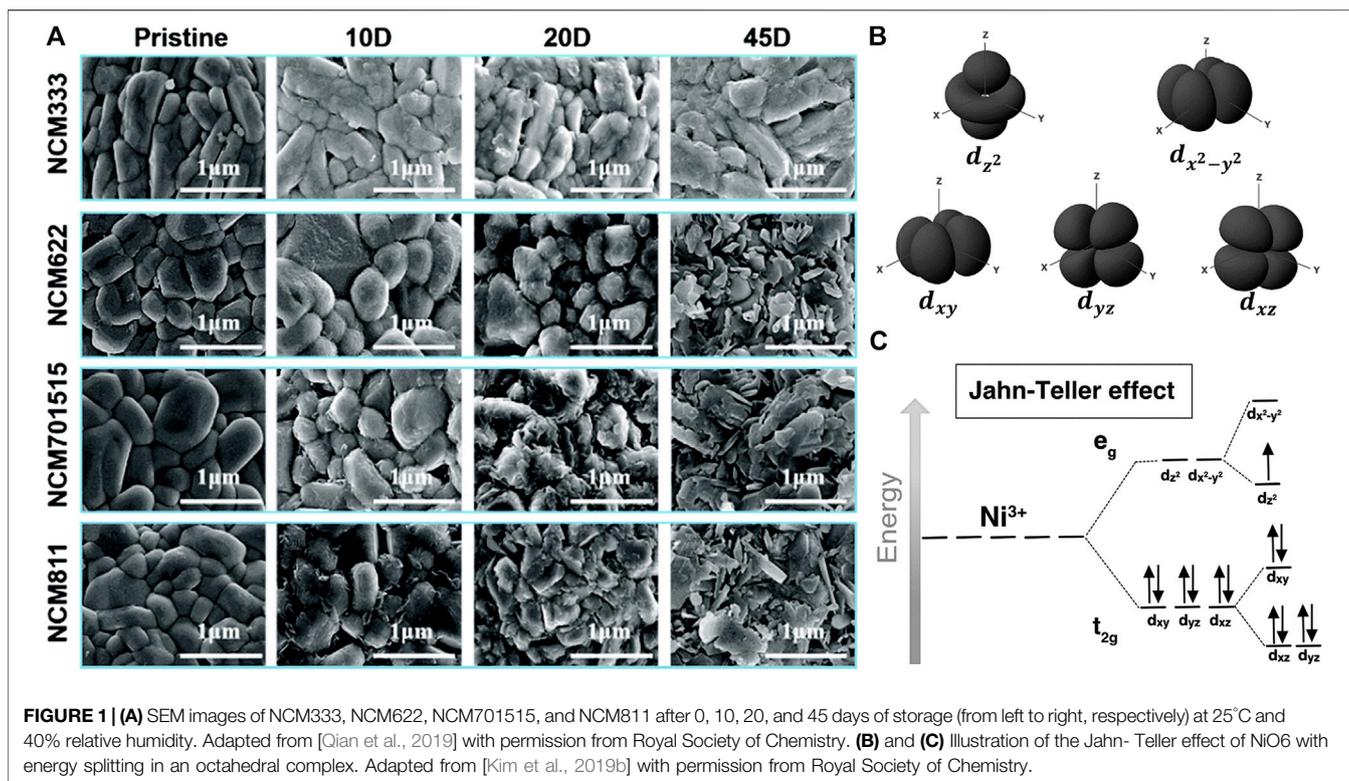
secondary sintering, surface coating, heterogeneous doping and slurry additives, which will be introduced later. In addition, recently, Renfrew et al. found that, up to 4.8 V vs Li/Li⁺ on the first charge, the decomposition of residual lithium compounds was the main source of CO and CO₂ evolution, not the electrolyte decomposition (Renfrew and McCloskey, 2017). They also suggested that oxygen evolution from the lattice of Ni-rich layered oxides decreased after removing partial residual Li₂CO₃, implying that the residual lithium impurities may facilitate the generation of oxygen, which is different from what we knew before, that lattice oxygen release originates from an irreversible H2 to H3 phase transition (Flores et al., 2020). Therefore, understanding the origin of residual lithium compounds and the possible solutions of how to remove them appear to be particularly necessary.

SOURCES OF RESIDUAL LITHIUM COMPOUNDS

Excessive Addition of Lithium in Synthesis

For the purpose of gaining Ni-rich layered oxides, the transition metal hydroxide precursor, usually prepared by a co-precipitation method, is uniformly mixed with a lithium source (e.g. lithium hydroxide and lithium carbonate) and sintered in high temperature at oxygen atmosphere for a period of time. The sintering temperature must be higher than the melting point of the lithium sources. For example, LiOH, the most commonly used lithium source, with a melting point lower than 500°C, is basically sintered above 750°C with a Ni-rich hydroxide precursor. Therefore, the volatilization of lithium during sintering should be taken into consideration. Moreover, due to the similar radius of Li⁺ (0.76 Å) and Ni²⁺ (0.69 Å), if the ratio of lithium and the precursor is 1, the Li⁺/Ni²⁺ cation mixing will be severe. To reduce the impact of this defect, Arai et al. demonstrated that excessive lithium addition was beneficial to suppress cation mixing so that the resultant Ni-rich materials remained a well-ordered layered structure with ameliorative cycling performance (Arai et al., 1995). For those reasons, in order to compensate for the lithium volatilization at high temperature and to reduce the cation mixing degree, it is necessary to introduce excessive lithium, which normally ranges from 1% to 5%. However, the mass of excess lithium addition is highly related to the sintering temperature and sintering time (Wang et al., 2017; Kong et al., 2019). As a result, after sintering, a part of unreacted lithium remains on the surface mainly in the form of lithium oxide (Li₂O). It is worth noting that the lithium oxide on the surface is chemically unstable, and tends to absorb and react with moisture and CO₂ in air to further form residual lithium compounds, including LiOH, LiHCO₃, and Li₂CO₃. Cho et al. also reported that, if too much residual lithium (Li₂O) remained on the surface of the final product after calcination, LiOH would be the major constituent part (Cho et al., 2014). The total reactions of residual lithium and air can be described as **Equation 1-3**:



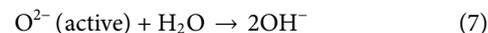
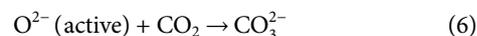
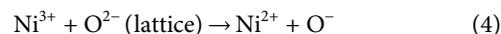


Air Sensitivity

Apart from the formation of Li₂O after sintering, with a strong alkaline surface, Ni-rich cathode materials are also intrinsically sensitive to moisture and CO₂, forming residual lithium compounds on the surface during the unavoidable air contact. However, the surface degradation mechanisms of Ni-rich cathode materials exposed to ambient air still remains controversial, which can be mainly divided into two kinds: a redox reaction mechanism and a proton-lithium exchange mechanism.

By comparing the amounts of surface impurities on LiNi_xCo_yMn_zO₂ with different Ni contents, Noh et al. found more carbonates and hydroxides grew on the higher Ni content cathode surface (Noh et al., 2013), revealing that the formation of surface residual lithium compounds was related to surface Nickel ions. Similarly, on the basis of density functional theory (DFT) calculation, Qian et al. promoted that with the increase of Ni content, the charge transfer ability and moisture adsorption energy of Ni-rich layered oxides were prone to being more robust (Qian et al., 2019), suggesting that the growth of Li₂CO₃ in high Ni content cathodes was faster than it is in a low Ni content one (Figure 1A). As a matter of fact, in view of the crystal field theory, Ni³⁺ at the octahedral site with an electron configuration of t_{2g}⁶e_g¹ is not stable and is prone to giving rise to the Jahn-Teller (J-T) effect, inducing lattice distortion, while Ni²⁺ with an electron configuration of t_{2g}⁶e_g² is an inactive J-T ion (Figure 1B) (Kong et al., 2018; Kim et al., 2019b). The chemical active Ni³⁺ ions

therefore tend to be converted to Ni²⁺, which could alleviate local lattice distortion of Ni-O octahedral and can release partial residual stress and reduce system energy at the same time. Furthermore, the reduction reaction of Ni³⁺ will accelerate the production of highly active oxygen species (Xiao and Sun, 2018). Consequently, when Ni-rich layered oxides are exposed to ambient air, the active oxygen species will react with the absorbed moisture and CO₂ to form hydroxyl and carbonate species, along with the release of lattice oxygen to form oxygen gas. The formed hydroxyl and carbonate species react with lithium ions from host material and finally generate residual lithium compounds (mainly LiOH and Li₂CO₃), together with the phase transition from a layered structure to a NiO-like rock-salt structure (Huang et al., 2019a; Martinez et al., 2020). The total reaction can be expressed as the following equations:



Except for the formation of Li₂CO₃ and LiOH, LiHCO₃ is also considered to be a residual lithium compound which may be produced by the reaction between LiOH and CO₂ under ambient atmosphere.

In addition, the composition and content of residual lithium compounds are extremely concerned with the temperature, moisture, and CO₂ concentration around the storage environment. Thus, the

reaction between Ni-rich layered oxide cathodes and ambient atmosphere are more complicated in different conditions. Faenza et al. indicated that moisture was essential for the formation of residual lithium compounds at room temperature, suggesting that Ni-rich layered oxide materials should be stored in a cool and moisture-free space to suppress the spontaneous formation of residual impurities (Faenza et al., 2017). Whereas Shizuka et al. reported that $\text{Li}_{1.04}\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) could react with pure CO_2 to form Li_2CO_3 at 400°C , without the participation of moisture (Shizuka et al., 2007). Furthermore, Cho et al. demonstrated that if too much residual lithium (Li_2O) remains on the surface of the final product after calcination, LiOH will be the major constituent part (Cho et al., 2014). Apart from the residual compounds and various absorbed species, Chen et al. found a delithiation layer existing on the subsurface of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622) stored at 55°C with 80% relative humidity, which implied that the extraction of lithium from host material to surface region really occurred (Chen et al., 2017b). In conclusion, the surface degradation of Ni-rich layered oxides during air exposure are driven by the reduction of chemical active Ni^{3+} to more stable Ni^{2+} , causing the release of lattice oxygen and the formation of residual lithium compounds on the surface. Owing to the consumption of surface lattice lithium, a NiO-like rock-salt phase layer and a delithiation layer are also generated. Surface coating combined with surface doping, an effective method to stabilize the layered structure and reduce surface reactivity of the active material, has been widely reported to enhance the air stability of Ni-rich layered oxides, which will be subsequently discussed.

Except for the above-mentioned redox mechanism, the additional proton–lithium exchange mechanism has also been proposed, which is supposed to take place in the near surface regions in concert with redox reactions (Shkrob et al., 2017; Toma et al., 2020). The released H^+ from surface absorbed water molecular exchanges with the out-migration Li^+ and occupy Li^+ site, form residual lithium compounds. The H^+/Li^+ exchange mechanism can be described with the following equations:



Exposing $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) to humid air, Shkrob et al. provided some evidence for a proton–lithium exchange mechanism (Shkrob et al., 2017). First, the contraction of *c* lattice was observed by XRD, which was mainly attributed to the stronger interaction force between H^+ and lattice oxygen. Subsequently, the partial capacity recovery has been detected during several initial charging/discharging cycles since the H^+ intercalation was reversible and could be replaced by Li^+ again in electrochemical (de)lithiation.

Although the proton–lithium exchange mechanism indicates that moisture is necessary to start the degradation of Ni-rich layered oxides, it cannot explain the acceleration effect of high Ni content on the growth rate of residual lithium compounds. Therefore, the H^+/Li^+ exchange mechanism is considered to play a minor role in surface degradation of Ni-rich cathode during air exposure, which usually emerges at the primary stage of air exposure.

NEGATIVE EFFECTS OF RESIDUAL LITHIUM COMPOUNDS

The formation of residual lithium compounds not only puts forward a strict requirement of storage atmosphere for Ni-rich cathode materials, but also sets great challenges for the subsequent slurry processing, cycling performance, and safety issues. In this section, the negative effects of residual compounds are analyzed.

Increase Storage Costs

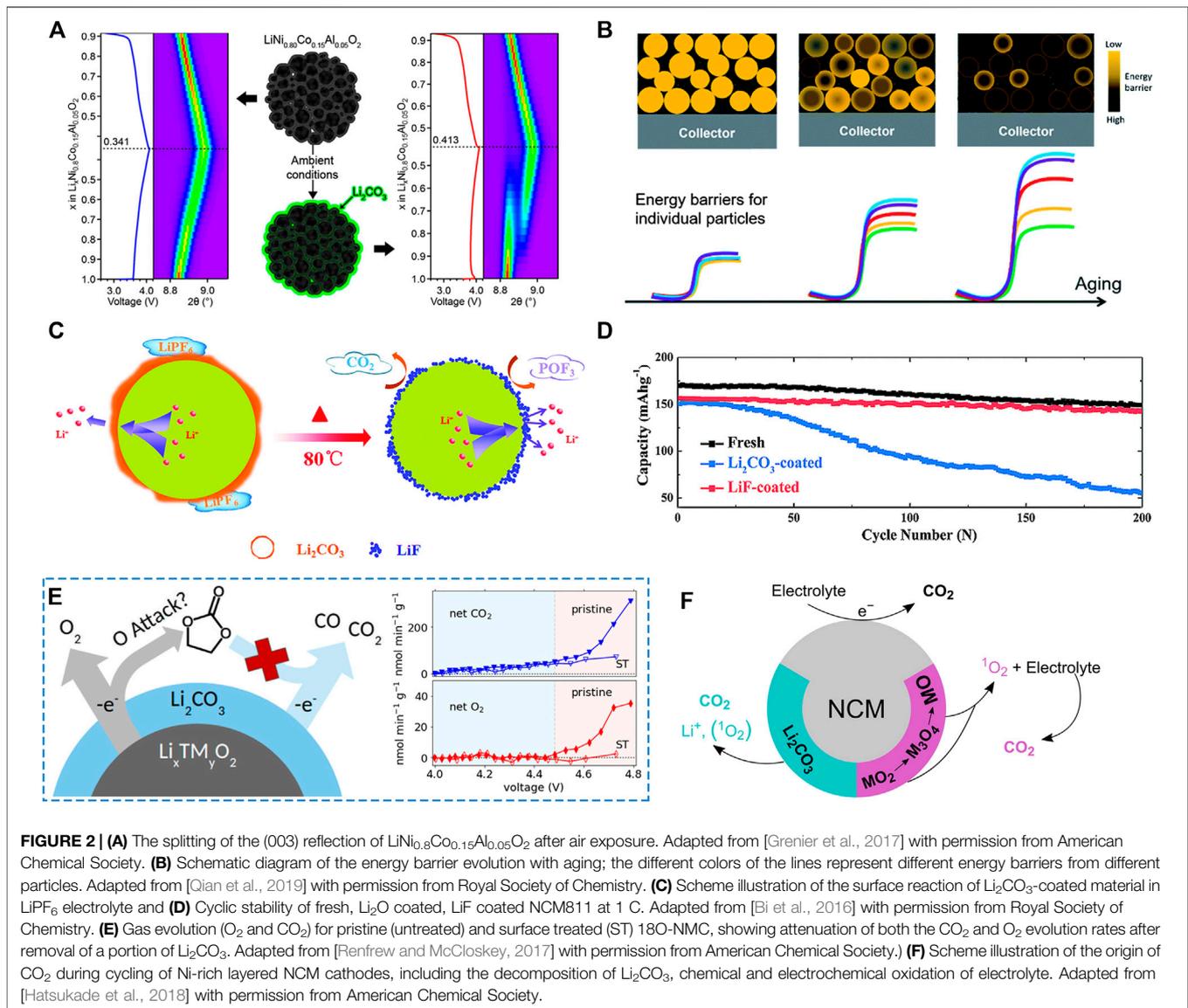
As shown by the spontaneous growth of detrimental residual lithium compounds on the surface of Ni-rich cathode materials during air exposure, it is inappropriate to store Ni-rich cathode materials in ambient air. Generally, for practical application, Ni-rich cathode materials are stored under vacuum or inert atmosphere conditions, which significantly enhance the storage cost to some extent, leading to inconveniences in production and application. Recently, Faenza et al. compared the growth of residual lithium compounds on $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ stored at different conditions for 2 weeks, including ambient air, dry CO_2 with less 10 ppm H_2O , pure argon (Ar) and a dry room (with dew point about -35°C) (Faenza et al., 2017). The results clearly demonstrate that the formation of residual lithium compounds can be effectively suppressed when the sample is stored in a dry room with a low moisture content. It is therefore suggested that Ni-rich layered oxides are stored at a very low relative humidity condition. Additionally, in order to reduce storage requirements and cost, some surface modifications need to be conducted, such as surface coating and doping, which will be discussed later.

Slurry Processing Performance Deterioration

Poly(vinylidene fluoride) (PVDF) is the most used binder for the preparation of a cathode slurry. Generally, PVDF can be fully dissolved in N-methyl-2-pyrrolidone (NMP) solution, but it is insoluble in an aqueous solution. It is worth noting that PVDF is prone to a defluorination reaction under an alkaline condition (Ross et al., 2001). As a result, when it encounters a Ni-rich cathode, strong alkaline residual lithium compounds, such as LiOH , can react with PVDF, thereby causing PVDF degradation, reducing the cohesiveness of slurry, and generating H_2O simultaneously. Additionally, PVDF will be rapidly condensed and gelatinized in water, severely deteriorating the slurry processing performance. In fact, slurry is unavoidably exposed to air, making alkaline slurry prone to absorbing the moisture from air, which will make the slurry fabrication difficult. Hence, the air humidity should be strictly controlled in the manufacturing plant to reduce the harmful effects of moisture absorption.

Electrochemical Degradation

As mentioned above, Ni-rich cathode materials exposed to ambient air may cause severe surface degradation, consuming Li^+ from host materials, further leading to the formation of the delithiation layer, the rock-salt cubic phase layer, and the residual lithium compounds layer. As a result, the loss of Li from host

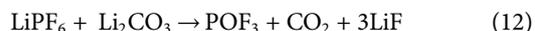


material directly triggers the initial capacity fading. Even worse, being covered by poor ionic/electron conductivity impurities and subsurface rock-salt cubic phase layer, the Li^+ diffusion in the interface of the cathode and electrolyte will be significantly suppressed. As a consequence, the charge transfer resistance increases so drastically that battery polarization obviously intensifies, further cutting down discharge capacity and worsening rate performance. By coating $\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$ with a Li_2O layer, Cho et al. simulated the effect of residual lithium compounds growing on the surface of Ni-rich cathode materials (Cho et al., 2014). They indicated that a larger irreversible capacity with limited discharge capacity emerged in $\text{LiNi}_{0.7}\text{Mn}_{0.3}\text{O}_2$, which was attributed to the suppressed Li^+ diffusion by insulating the Li_2O layer. In addition, the electrochemical reaction heterogeneity caused by surface insulating the Li_2CO_3 film was reported, which was demonstrated by the splitting of the (003) reflection using the

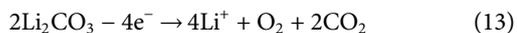
in-situ XRD analysis as presented in **Figure 2A** (Grenier et al., 2017). In a further step, Qian et al. proposed that the reaction heterogeneity that originated from different energy barriers and activation energies for (de)lithiation of individual particles was due to the uneven growth of residual lithium compounds (**Figure 2B**) (Qian et al., 2019). More seriously, the augment of impedance may lead to the accelerated localized heating, which increases the risk of catastrophically destroying the batteries or igniting the liquid organic electrolyte. For this reason, safety issues derived from the formation of insulating residual lithium compounds should be taken seriously.

Furthermore, the presence of residual lithium compounds at the interface of electrode and electrolyte could also cause adverse reactions with the LiPF_6 -based electrolyte, generating CO_2 gas and LiF (**Figure 2C**). In order to confirm the influence of surface LiF and Li_2CO_3 on the performance of Ni-rich cathode materials, Bi et al. compared the electrochemical performance of both Li_2CO_3 -

coated and LiF-coated $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM811) (Bi et al., 2016). As shown in **Figure 2D**, the surface Li_2CO_3 coating layer had a severely negative impact on the cycling stability while it was negligible for the surface LiF coating, which could be attributed to the decomposition of Li_2CO_3 reacting with the electrolyte. This reaction can be described as follows:

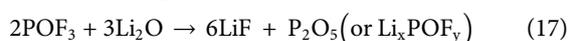


In fact, Li_2CO_3 is mainly in the form of the amorphous state, and its electrochemical stability is very poor, which is easily decomposed at a high potential (Wang et al., 2018). Hatsukade et al. employed an isotope labeling method to investigate the origins of CO_2 during the cycling of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622) (Hatsukade et al., 2018). The CO_2 formation at the first charge process was attributed to the surface Li_2CO_3 decomposition at high potential. However, with prolonged cycling and the decrease of surface Li_2CO_3 , CO_2 stemming from the chemical oxidation (with lattice oxygen) and electrochemical oxidation at high potential of electrolyte solvent became dominant (**Figure 2F**). In addition, there is an ambiguous understanding on whether the decomposition of Li_2CO_3 will produce oxygen simultaneously, because oxygen may also originate from lattice. In this respect, the oxidation of Li_2CO_3 has already been studied in Li-air cells (Mahne et al., 2018), producing O_2 and CO_2 , which can be described as follows:



Subversively, Renfrew et al. observed the CO_2/CO emission caused by the decomposition of residual Li_2CO_3 during the first charge, and the oxygen evolution from the lattice of Ni-rich cathode materials also decreased after removing a portion of surface Li_2CO_3 (Renfrew and McCloskey, 2017), suggesting that the oxidation of Li_2CO_3 is related to the lattice oxygen release (**Figure 2E**). Inspired by this research, quantitative studies of the influence of surface impurities on the structure evolution of Ni-rich cathode materials during the cycling tests are needed. Although the decomposition mechanism of Li_2CO_3 is not fully understood, the decomposition of Li_2CO_3 reduces the Coulombic efficiency of the initial several cycles. It also highlights the seriousness of safety issues, such as increasing batteries' internal pressure and heat generation.

Moreover, the CO_2 stemming from the decomposition of Li_2CO_3 and electrolyte solvents can react with LiOH to reformate trace H_2O and Li_2CO_3 (Robert et al., 2015). Even worse, the trace H_2O is harmful to electrolyte salt, resulting in the decomposition of LiPF_6 and the formation of HF and other by-products. This process can be expressed as follows:



The resultant HF is detrimental to the electrochemical performance of Lithium-ion batteries. On the one hand, HF accelerates the decomposition of surface impurities including Li_2CO_3 and LiOH. On the other hand, HF corrodes the surface of Ni-rich cathode materials to promote the dissolution of transition metal ions, especially Ni ion, leading to rapid capacity loss and surface degradation. Moreover, after the removal of surface impurities, a greater electrochemically active surface will be exposed to the electrolyte, which will further boost the dissolution of transition metal ions and the decomposition of electrolyte solvent at high potential (Kleiner et al., 2015; Kim et al., 2016; Liang et al., 2019).

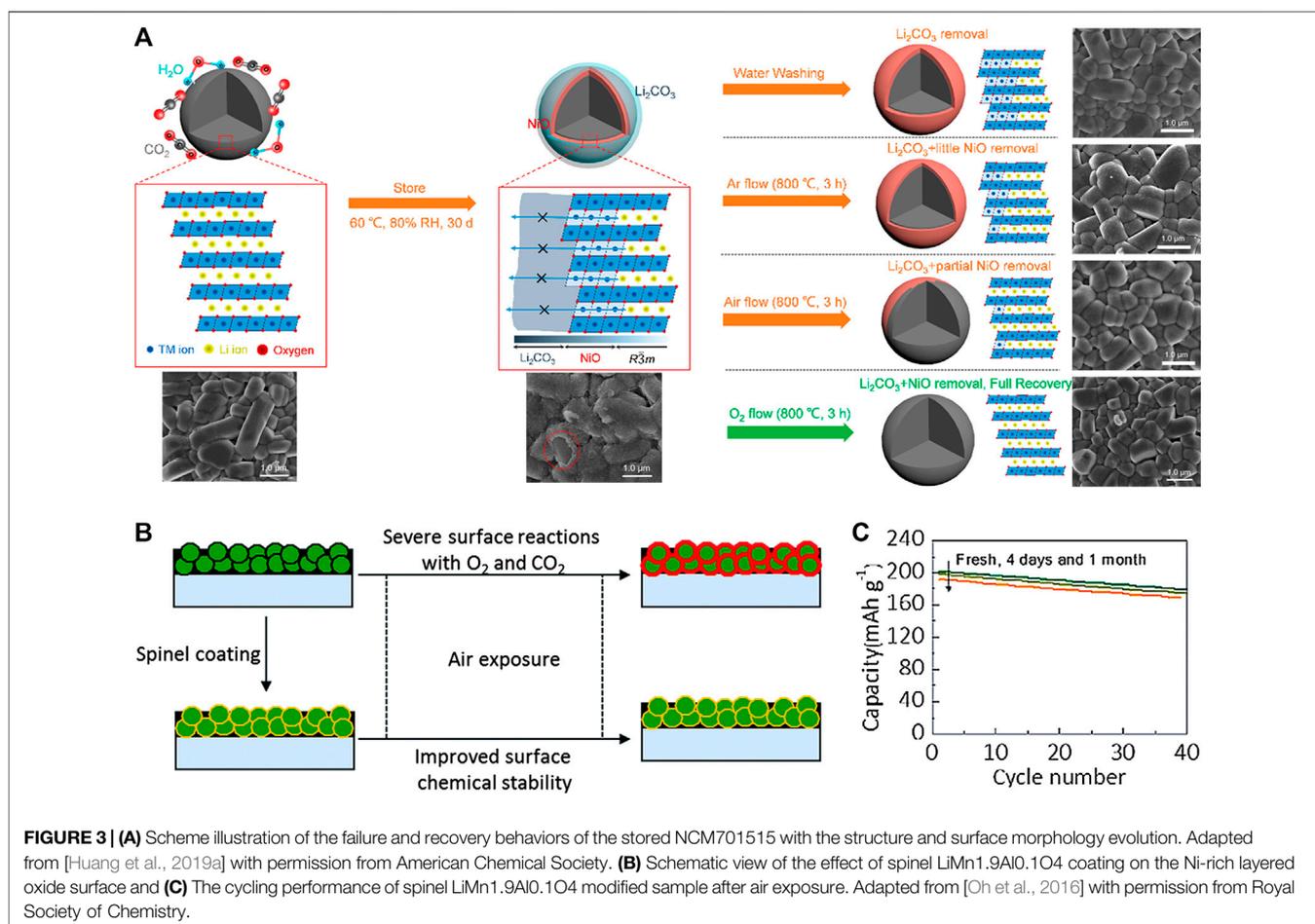
CHALLENGES AND SOLUTIONS TO RESIDUAL LITHIUM COMPOUNDS

To avoid the adverse effects of residual lithium compounds on powder storage, slurry processing and electrochemical performance of Ni-rich cathode materials, numerous methods are conducted to remove the surface impurities and to enhance the air-storage stability.

Washing & Annealing Process

Washing with water is widely applied in practical industrial manufacturing to eliminate the detrimental residual lithium compounds. To be specific, the alkaline Ni-rich cathode materials are stirred in deionized water to remove surface residual lithium compounds and dried at a high temperature in an air-free atmosphere after filtration, which is called the washing & annealing process (Kim et al., 2018). The concentration of residual lithium compounds and powder pH value can be effectively reduced after washing. As a consequence, gas evolution of the washed cathode materials is significantly suppressed during the charging process. Furthermore, after the washing and annealing process, the cycling performance and capacity retention are dramatically improved with a slight initial discharge capacity decline.

However, it should be mentioned that the capacity degradation of Ni-rich cathode materials may be accelerated after the washing process owing to an improper annealing temperature. As Xiong et al. reported, NCM811 annealed at 300°C after washing exhibited the worst specific capacity and cycling stability compared to the washed or non-washed sample annealed at 700°C (Xiong et al., 2013). Except for water washing, a faintly acidic solution is also a substitution (Park et al., 2017; Xu et al., 2017; Wu et al., 2018). Park et al. compared two kinds of solvents, de-ionized water and diluted nitric acid with a solvent evaporation process. They suggest that the diluted nitric acid eliminates surface residual compounds more efficiently than de-ionized water. The sample treated with diluted nitric acid exhibited the superior cycling performance (Park et al., 2017). Analogously, compared to water washing, mild polyaniline (PANI) could also be utilized as a solvent to remove residual impurities, and to synchronously form a protective layer on the surface, which greatly enhances the surface stability of Ni-rich



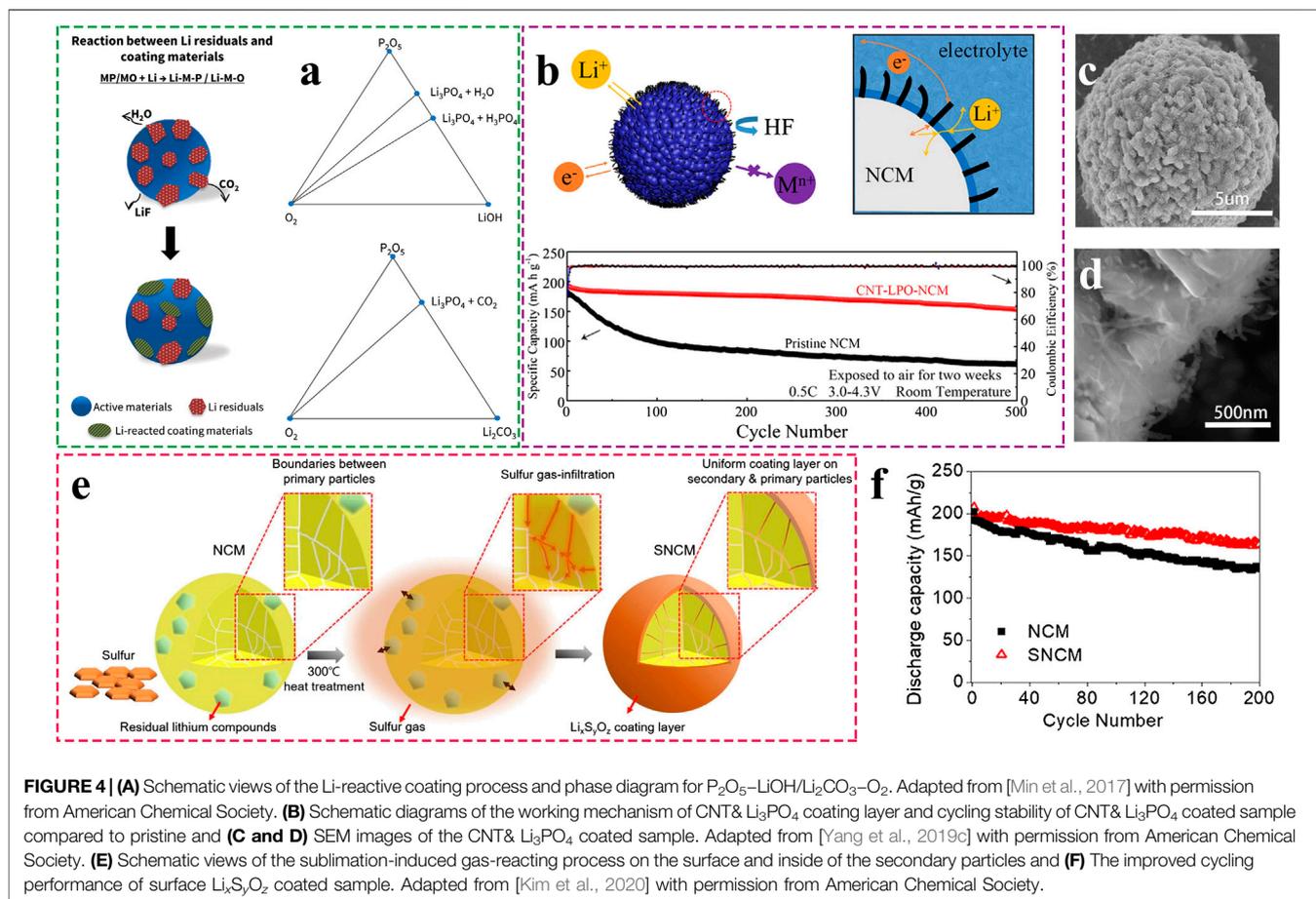
cathode materials (Xu et al., 2017). In addition to the above washing solvents, alcohol washing is a “compromise” process, which can reduce the lithium residue and does not destroy the surface structure (Cao et al., 2019). However, the solubility of LiOH and Li_2CO_3 in ethanol is low, which should be further improved. Apart from annealing temperature and washing solvent, the electrochemical performance of washed materials is closely related to the powder-to-solvent ratio and washing time, which is a complex technical method.

Although the residual lithium compounds and powder pH can be effectively reduced by the washing process, the washed Ni-rich cathode materials are more air sensitive than non-washed materials because of more chemically active surfaces (Xiong et al., 2013; Kim et al., 2018). After being exposed to the air for the same time, a thicker amorphous residual lithium layer is formed on the surface of washed Ni-rich cathode materials (Jo et al., 2016). During the formation of an amorphous residual lithium layer, a part of lithium on the subsurface of Ni-rich cathode materials will be extracted from the host structure along with the increased cationic disorder. As a result, a rock-salt NiO -like surface is generated, which significantly deteriorates the electrochemical performance of Ni-rich cathode materials. Therefore, taking air sensitivity of washed Ni-rich cathode materials into consideration, it is very important to store them in an air free- or humidity and CO_2 controlled conditions.

Moreover, in practical application, washing treatment is generally combined with other treatments such as surface coating, aiming to prevent a chemically unstable surface from ambient air. In addition, due to the generation of waste water, the increased processing time and capital cost of waste water treatment should also be considered, and still remains a huge challenge for its practical implementation.

Secondary Sintering

Secondary sintering is similar to the annealing process after washing. However, compared to the washing process, secondary sintering does not involve the generation of waste water, which is a solid phase reaction process mainly including the decomposition of residual lithium compounds and surface reconstruction. In order to decompose the residual lithium compounds sufficiently, the sintering temperature is usually increased to the initial sintering temperature, sometimes even higher. It is important to note that the evaporation of Li_2O should be taken into account to reduce capacity loss, so that the secondary sintering time is not long. Furthermore, calcination atmosphere is another factor effecting secondary sintering as well. According to previous literature reported by Jo and co-workers [Ross et al., 2001], for freshly sintered or few surface residual impurities materials, when being reheated in air atmosphere, a sintering temperature between 200°C and



400°C is optimal, otherwise the structural integrity will be destroyed at a higher temperature.

Recently, Huang et al. conducted secondary sintering on the degraded $LiNi_{0.70}Co_{0.15}Mn_{0.15}O_2$ under various atmospheres at a high temperature (800°C) (Figure 4A) (Huang et al., 2019a). To get the degraded sample, the aging process was carried out at 60°C and 80% relative humidity for 30 days, in which a residual lithium compound layer, mainly composed of Li_2CO_3 with ~90 nm thickness, was detected on the surface with a NiO-like layer formed at the near surface region. Successfully, the degraded $LiNi_{0.70}Co_{0.15}Mn_{0.15}O_2$ re-sintered at 800°C under flowing oxygen atmosphere for 3 h, exhibited a comparable electrochemical performance to the pristine one. Interestingly, after high temperature calcination under oxygen atmosphere, the surface impurities layer and NiO-like layer disappeared, and the surface was reconstructed to the layered structure. However, under other atmospheres such as air and argon, the surface structure can barely recover to the original layered structure and a NiO-like layer still remains, indicating that the oxidizing atmosphere is necessary for the reversion of degraded materials during the secondary sintering treatment.

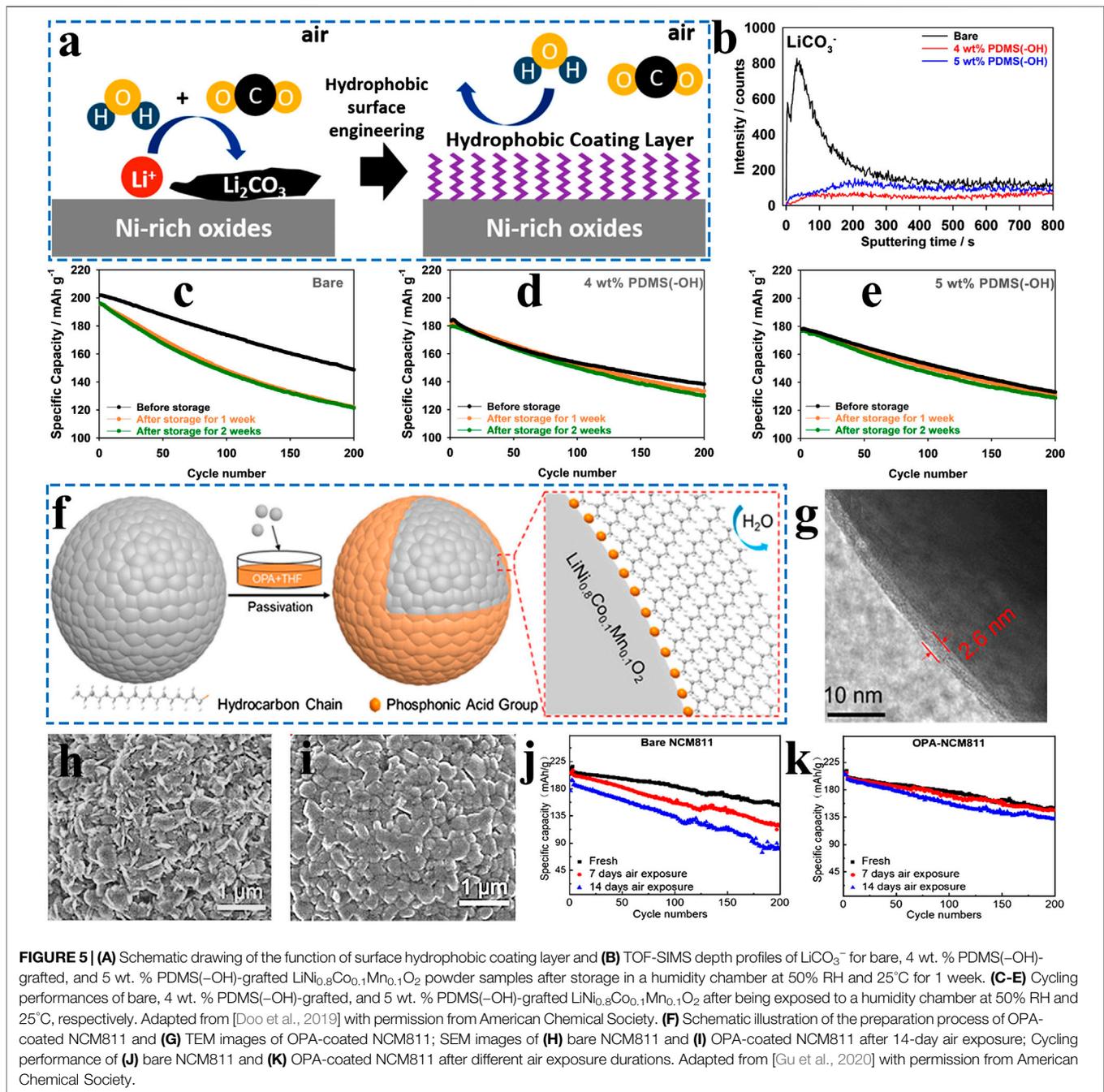
Slurry Additives

Some additives are often added into slurry to reduce residual lithium compounds and slurry pH, thereby meliorating slurry

processability. In detail, the additives should be moderate so that they only react with surface impurities without other undesirable side effects. This strategy is considered to be one of the most convenient methods for practical manufacturing. For instance, $LiPF_6$ is adopted as a slurry additive to wipe off alkaline residual lithium compounds in NCM811 slurry, finally forming into LiF and Li_3PO_4 (Zhang et al., 2019d). With 0.5–1.0 wt. % $LiPF_6$ addition (versus the mass of NCM811), the cycling stability and rate capacity of NCM811-Li cells are improved, which can be attributed to the formation of stable LiF and Li_3PO_4 and the decrease of insulating residual impurities.

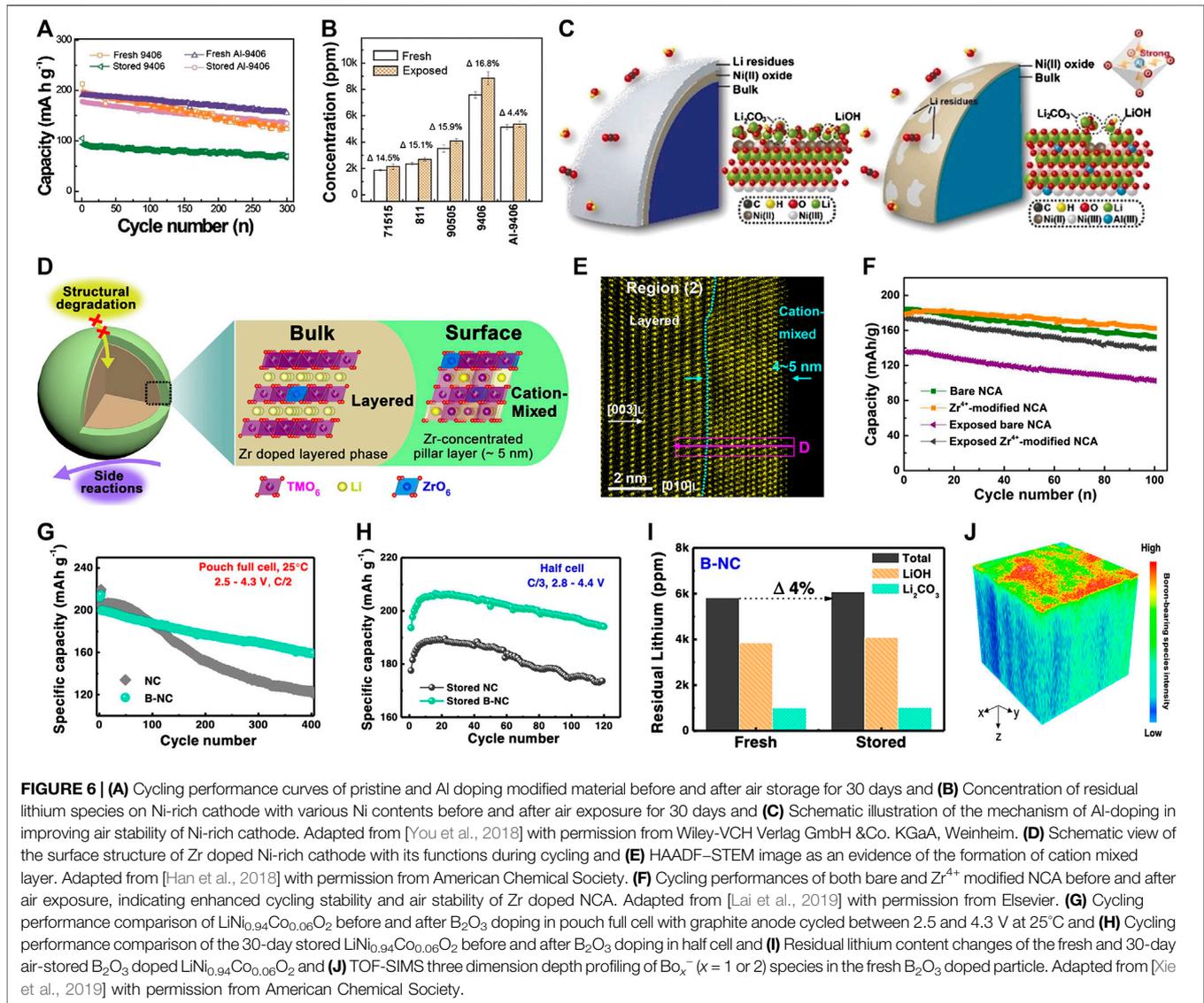
Surface Coating

Although the surface residual impurities and lithium compounds can be removed after washing or secondary sintering treatment, the air sensitivity of Ni-rich cathode materials still cannot be fully solved. Therefore, Ni-rich cathode materials should be strictly stored in an atmosphere-controlled condition to avoid contact with H_2O and CO_2 . In order to overcome this problem, various surface modification methods are developed. In this respect, surface coating is one of the most widely used methods in laboratory investigation. Generally, surface coating layers can not only enhance the air-storage stability of Ni-rich cathode materials, but also protect Ni-rich cathode materials from HF corrosion and detrimental side



reactions with electrolyte at high potential. Up to now, various surface coating agents have been adopted to reduce the residual lithium impurities and to enhance the air storage stability of Ni-rich cathode materials, including phosphates (Jo et al., 2014a; Chen et al., 2017a; Min et al., 2018; Fan et al., 2019; Zou et al., 2020), fluoride (Dai et al., 2019; Huang et al., 2019b), conducting polymers (Sun et al., 2018; Gan et al., 2019; Yang et al., 2019b), and metallic oxides (Min et al., 2018; Zhao et al., 2018; Becker et al., 2019; Ho et al., 2020; Mo et al., 2020; Zhao et al., 2020). However, the formation mechanisms and functions of these coating layers are quite different, and need to be further investigated.

First, a coating layer can be physically formed on the Ni-rich cathode surface without reacting with residual lithium compounds. This kind of coating layer is electrochemically stable and nonreactive with electrolytes. As shown in **Figure 3B, C**, the air-storage stability of $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ coated with chemically stable spinel $\text{LiMn}_{1.9}\text{Al}_{0.1}\text{O}_4$ is significantly improved. After being exposed to ambient air for 1 month, the capacity retention of the $\text{LiMn}_{1.9}\text{Al}_{0.1}\text{O}_4$ coated $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ sample is compared to the fresh one (Oh et al., 2016). In addition, MnO_2 coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ can effectively prevent $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ from absorbing the



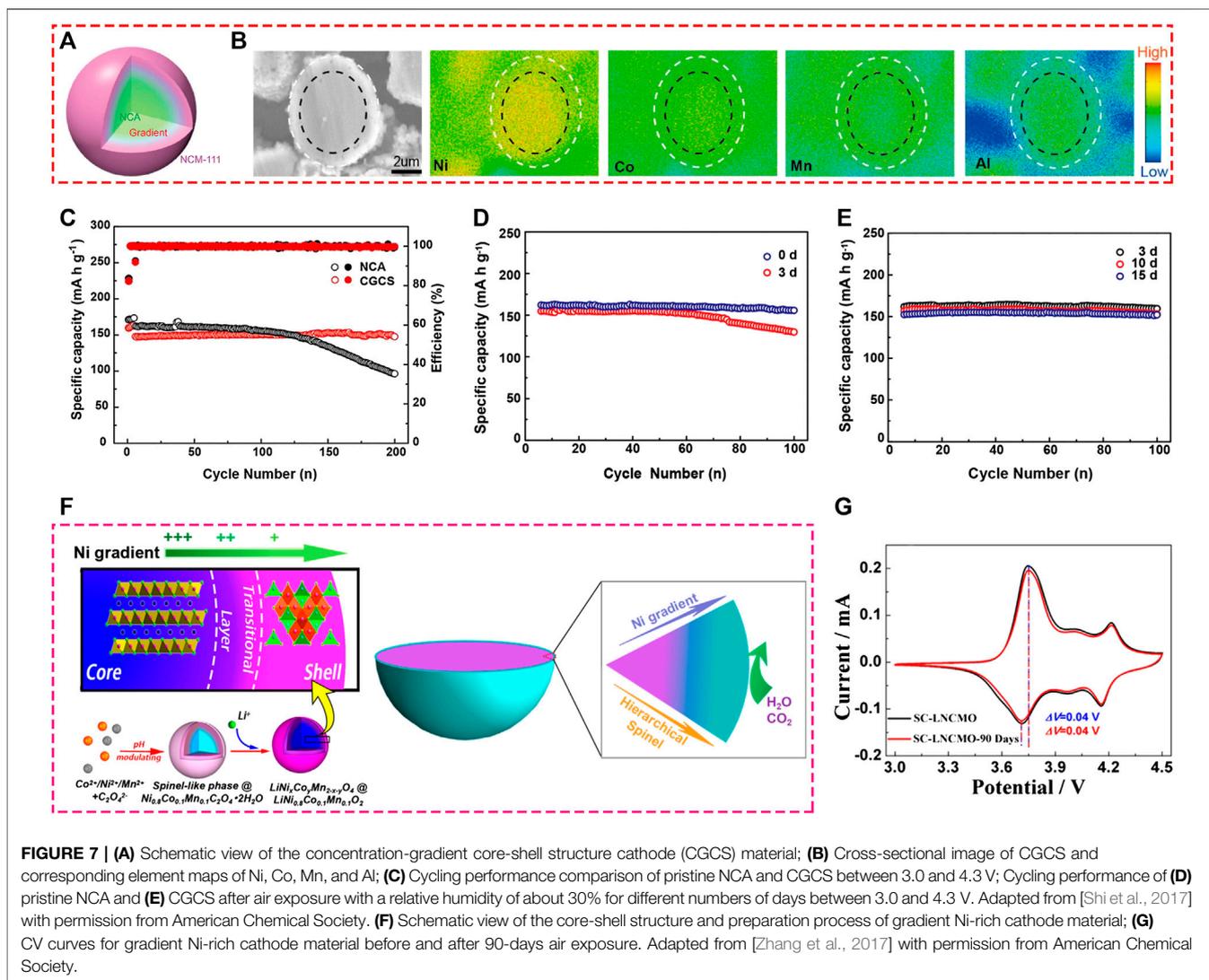
moisture and CO₂ in air atmosphere and the HF erosion during long-term cycling (Zhao et al., 2018). Furthermore, TiO₂ (Mo et al., 2020), ZrO₂ and other oxides are also employed to construct protective layers on the surface of the Ni-rich cathode to decrease air sensitivity.

Moreover, the coating layers can be formed *in-situ* on the surface of Ni-rich cathode materials *via* chemical reactions between coating media and residual lithium compounds, which could eliminate surface impurities as well as form a functional film on the surface. For example, H₃PO₄ (Jo et al., 2014a; Min et al., 2017; Yang et al., 2019c), an acidic coating media, can react with the residual lithium compounds, such as LiOH and Li₂CO₃ to form a Li₃PO₄ coating layer, which has been verified to effectively enhance the surface stability of Ni-rich cathode materials. Due to the reduced surface insulating impurities and high ionic conductivity of newly generated Li₃PO₄, the capacity retention and rate capability of Li₃PO₄-

coated NCM622 are greatly improved (Jo et al., 2014a). Additionally, Li₃PO₄ reacts with trace water in electrolytes to suppress the formation of HF, thereby preventing electrode erosion, which can be described as follows:



Furthermore, Min et al. investigated metal phosphates and metal oxides reacted with residual lithium compounds using a hybrid functional theory calculation (Min et al., 2017). As shown in **Figure 4A**, metal phosphates could effectively reduce both LiOH and Li₂CO₃, whereas metal oxides tend to react with LiOH more, in which P₂O₅ may be an optimal choice. In a further step, Yang et al. constructed a four-phase cathode electrolyte interface on NCM811, as described in **Figure 4B** (Yang et al., 2019c). The phosphoric acid reacted with surface



residual lithium compounds to form an ionic conductive Li_3PO_4 layer, and carbon nanotubes were coated on the surface to penetrate through the Li_3PO_4 layer (Figure 4C, D). Thus, the ionic conductivity and electronic conductivity of NCM811 were both enhanced, leading to the greatly improved rate performance and capacity retention after surface modification. More importantly, even after being exposed to high moist air for 2 weeks, the modified sample could still deliver $154.2 \text{ mA h g}^{-1}$ at 0.5 C after 500 cycles (Figure 4B).

Apart from the liquid-solid reaction, the gas-solid reaction is also employed to eliminate surface impurities, which could essentially avoid the generation of waste water. As illustrated in Figure 4E, the pioneering work (Kim et al., 2020) reported by Kim and co-workers presented a novel sublimation-induced gas-reacting (SIGR) process on NCM811. The gas-phase sulfur (S) reacted with residual lithium compounds at a low temperature of 300°C and *in-situ* constructed a $\text{Li}_x\text{S}_y\text{O}_z$ coating layer. Remarkably, the $\text{Li}_x\text{S}_y\text{O}_z$ phases uniformly generated on the surface of secondary particles, as well as in the boundaries

between internal primary particles. Consequently, the SIGR-treated NCM811 exhibited improved cycling stability, which were mainly attributed to the protected surface and suppressed anisotropic volume changes during (de)lithiation (Figure 4F).

Since moisture is one of the essential conditions for the formation of residual lithium compounds, thereby constructing a hydrophobic layer tightly coated on the cathode surface is highly expected to overcome this intractable issue (Doo et al., 2019; Gu et al., 2020). The modified hydrophobic surface effectively blocks the direct contact between moisture and the chemically unstable surface of Ni-rich cathode materials, further suppressing the formation of residual lithium compounds. Till now, various organic molecules are adopted as surface coating materials for modifying Ni-rich cathode materials. As shown in Figure 5A-E, hydrophobic polydimethylsiloxane (PDMS) coated NCM811, with a strong M–O–Si covalent bond, exhibited the enhanced air storage stability (Doo et al., 2019). Additionally, octadecyl phosphate (OPA) can be utilized to form a hydrophobic self-assembled monolayer on the surface of Ni-rich cathode

materials to improve air-storage stability (**Figures 5F-K**) (Gu et al., 2020).

Unfortunately, hydrophobic organic coating layers can only improve the storage property, but it has no obvious improvement in electrochemical performance. Meanwhile, the organic surface coating layer may dissolve into organic electrolyte during the long-term cycling. Even worse, the organic surface coating layers may be oxidized at high voltage, which will deteriorate the electrochemical performance of batteries, such as battery swelling, a thick solid electrolyte interface (SEI) layer and increased polarization.

Doping

Doping is another important strategy to enhance surface chemical and structural stability of Ni-rich cathode materials. By incorporating a small amount of cationic or anionic atoms into the crystal lattice of Ni-rich cathode materials, the air stability is significantly improved. The functions of cationic doping can be classified into two types. One type is the forming a strong covalent bond between doping cation and lattice oxygen to boost lattice structure and to suppress the loss lattice oxygen (You et al., 2018; Huang et al., 2019c). For example, You et al. successfully introduced a small amount of Al^{3+} into the surface lattice of $\text{LiNi}_{0.94}\text{Co}_{0.06}\text{O}_2$ by sintering a mixture of LiOH and precursor coated with $\text{Al}(\text{OH})_3$ at a high temperature (You et al., 2018). The Al-doped $\text{LiNi}_{0.94}\text{Co}_{0.06}\text{O}_2$ exhibited superior storage stability and capacity retention compared to the pristine one (**Figure 6A, B**). The enhanced surface lattice stability is mainly attributed to the robust Al-O bond (**Figure 6C**). Moreover, some high valent cations are doped to reduce the content of surface active Ni^{3+} (being reduced to stable Ni^{2+} to keep charge balance) (Han et al., 2018; Lai et al., 2019). As displayed in **Figure 6D, E** cation-mixed nanolayer with ~ 5 nm thickness forms on the surface of NCM811 after doping Zr^{4+} , in which Zr^{4+} ions occupy the transition metal site and increase the amount of Ni^{2+} to maintain the charge balance (Han et al., 2018). Owing to the highly reactive Ni^{3+} ions that are effectively reduced, the air-storage stability of NCM811 is improved. Similarly, Lai et al. demonstrated that the air-storage stability of $\text{LiNi}_{0.815}\text{Co}_{0.15}\text{Al}_{0.035}\text{O}_2$ can be significantly improved after 1% nano- ZrO_2 doping (**Figure 6F**) (Lai et al., 2019).

Anions doping, such as boron-based polyanion doping, has been verified as an effective strategy to improve the air-exposure stability of the Ni-rich cathode. It is worth noting that the discharge capacity, cycling retention, and air exposure stability are simultaneously strengthened. However, the working mechanism of the boron-based polyanion doped Ni-rich cathode is seldomly investigated (Park et al., 2018; Zhang et al., 2019a; Yang et al., 2020). Recently, Xie et al. promoted a boron spatial distribution of the B_2O_3 doped $\text{LiNi}_{0.94}\text{Co}_{0.06}\text{O}_2$ cathode material, in which $\text{BO}_x^-/\text{LiBO}_2^-$ species mainly existed on the surface and boron ions (B^{3+}) infiltrated into the host lattice in the tetrahedral interstitial sites of oxygen packing (**Figure 6J**) (Xie et al., 2019). The surface species were related to the formation of electrochemically stable cathode electrolyte interface (CEI), and the boron doping could effectively enhance the oxygen lattice stability, thus excellent performances were achieved after boron doping (**Figures 6G, H, I**).

Furthermore, the combination of doping strategy and surface coating technology is considered to be a promising method to improve overall performance of Ni-rich cathode materials. For instance, Li et al. reported the La/Al co-doping and La_2O_3 coating co-modified NCM811 Ni-rich cathode (Li et al., 2019b). The La and Al doped into the inner lattice play the role of a pillar, which could enhance the structural stability as well as suppress the phase transition. Furthermore, Ni concentrations decrease in the La-Al co-doped layer in the subsurface region. Additionally, the surface La_2O_3 coating protects the Ni-rich cathode from the detrimental reaction with air and electrolyte. Thus, the air storage stability and cycling performance are effectively improved. Moreover, the cycling performance and air storage stability of NCM811 could be successfully enhanced *via* the combination strategy of Li_2ZrO_3 coating and Zr^{4+} doping. The surface Li_2ZrO_3 protective layer as a good Li^+ conductor can suppress a surface side reaction as well as improve the Li-ion diffusion rate. More importantly, Zr^{4+} doping can stabilize the structural stability and reduce oxygen loss. In this way, the overall performance of NCM811 is improved. (Zhai et al., 2020).

Gradient Materials

It is widely accepted that the air-storage stability and thermal property of Ni-rich cathode materials are negatively related to the Ni concentration. In other words, the air storage stability can be improved by decreasing Ni concentration. However, this strategy will cause the capacity declination. So, can we reach an optimal equilibrium point where both relatively high discharge capacity and stable air-storage performance exist? Constructing gradient materials, with low a Ni concentration outer surface and high Ni content inner core, provides the answer. By changing the proportion of transition metal ions at different periods of coprecipitation, Shi et al. synthesized a surface concentration-gradient spherical Ni-rich cathode material with diverse elemental composition, in which the core inside was $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and the surface was composed of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (**Figures 7A, B**) (Shi et al., 2017). Compared to the pristine $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, the gradient material presented significantly enhanced air stability (**Figures 7D, E**) and excellent cycling performance (**Figures 7C**).

Moreover, depending on the different precipitation pH values for transition metal ions, a gradient precursor can be generated by regulating co-precipitation pH as well. **Figure 7F** illustrates the gradient Ni-rich cathode material consisting of a layer-structure $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ core, gradient Ni concentration interlayer, and spinel-like $\text{LiNi}_x\text{Co}_y\text{Mn}_{2-x-y}\text{O}_4$ shell (Zhang et al., 2017). Due to the reduced Ni concentration and the formation of an air-stable spinel layer in the surface region, the gradient Ni-rich cathode material presents greatly improved long-term air storage stability (**Figure 7G**).

SUMMARY AND PERSPECTIVES

In this review, the origins and negative effects of residual lithium compounds on air storage performance, processing performance,

and electrochemical performance of Ni-rich cathode materials were analyzed. Owing to the residue lithium and chemical active Ni^{3+} on the surface, Ni-rich cathode materials are chemically sensitive to moisture and CO_2 . Residual lithium compounds generate on the surface during air exposure, which have adverse effects on the processing and electrochemical performance of Ni-rich cathode materials. Residual lithium compounds with a strong alkaline feature will cause the decomposition of PVDF and lead to the gelation of the cathode slurry. In addition, due to the insulating impurities on the surface, the Li^+ diffusion in the interface of the cathode and electrolyte will be suppressed and battery polarization will increase. Even worse, at the cost of consuming Li^+ from host materials, the structure near the surface region of Ni-rich cathode materials is deteriorated, as well as the electrochemical performance. It is worth noting that the existence of Li_2CO_3 has negative effects on the cycling stability of Ni-rich cathode materials. Quantitative studies related to the mechanism of the effect of Li_2CO_3 on the electrochemical performance of Ni-rich cathode materials are therefore still required. In addition, under high temperature and high voltage ($\geq 55^\circ\text{C}$, $> 4.3\text{ V}$), the mechanism of CO_2 production and its influence on electrochemical performance should be further studied.

Since Ni-rich cathode materials will deteriorate during the long-term air exposure, one option is to store them in a vacuum or in an inert atmosphere. However, this strategy will increase the cost of storage, and it is not convenient for production and application. Instead, storing them in a low relative humidity condition seems more practical. To remove surface residual lithium compounds, new types of cleaning agents that can effectively remove lithium residue, but not destroy the surface structure, should be further screened. Furthermore, washing combined with an annealing process and secondary sintering are widely implemented in large-scale application. The washing time and powder-to-solvent ratio should be systematically studied to obtain an optimal design. Moreover, the washing process always takes place in conjunction with surface coating to overcome the disadvantages as Ni-rich cathode materials are more sensitive to air after washing. Secondary sintering is

preponderant in the reversion of the severely degraded Ni-rich materials, in which sintering temperature and time should be carefully controlled.

Although the surface residual impurities and lithium compounds can be removed after washing or secondary sintering treatment, the intrinsic air sensitivity of Ni-rich cathode materials still cannot be fully solved. Combining a doping strategy and surface coating technology is one useful solution to reinforce the air storage stability of Ni-rich cathode materials. In future studies, it is important to enhance the lattice matching of the doping and coating interface and to develop a facile method for large-scale production. Another solution is constructing gradient materials with low Ni concentration at the outer surface. We believe that this review provides an in-depth understanding of the residual lithium compounds in Ni-rich cathode materials.

AUTHOR CONTRIBUTIONS

AC: Writing—original draft preparation. KW: Writing—original draft preparation. JL: Writing—original draft preparation. QM: Writing—Reviewing and Editing. ZX: Visualization. DZ: Writing—Reviewing and Editing. GW: Visualization. PL: Writing—original draft preparation. JH: Writing—Reviewing and Editing. YY: Writing—Reviewing and Editing. YX: Conceptualization, Supervision.

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Conflict of Interest: Author QM was employed by the company Zhejiang Meidu Hitrans Lithium Battery Technology Co., Ltd. Author DZ was employed by the company SolaXPower Network Technology (Zhejiang) Co., Ltd. Author GW was employed by the company Hengdian Group DMEGC Magnetics Co. Ltd. Author PL was employed by the company Farasis Energy Inc.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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