Surface Engineering Strategies of Layered LiCoO₂ Cathode Material to Realize High-Energy and High-Voltage Li-Ion Cells

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Battery industries and research groups are further investigating LiCoO₂ to unravel the capacity at high-voltages (>4.3 vs Li). The research trends are towards the surface modification of the LiCoO₂ and stabilize it structurally and chemically. In this report, the recent progress in the surface-coating materials i.e., single-element, binary, and ternary hybrid-materials etc. and their coating methods are illustrated. Further, the importance of evaluating the surface-coated LiCoO₂ in the Li-ion full-cell is highlighted with our recent results. Mg,P-coated LiCoO₂ full-cells exhibit excellent thermal stability, high-temperature cycle and room-temperature rate capabilities with high energy-density of ≈1.4 W h cc⁻¹ at 10 C and 4.35 V. Besides, pouch-type full-cells with high-loading (18 mg cm⁻²) electrodes of layered-Li(Ni,Mn)O₂-coated LiCoO₂ not only deliver prolonged cycle-life at room and elevated-temperatures but also high energy-density of ≈2 W h cc⁻¹ after 100 cycles at 25 °C and 4.47 V (vs natural graphite). The post-mortem analyses and experimental results suggest enhanced electrochemical performances are attributed to the mechanistic behaviour of hybrid surface-coating layers that can mitigate undesirable side reactions and micro-crack formations on the surface of LiCoO₂ at the adverse conditions. Hence, the surface-engineering of electrode materials could be a viable path to achieve the high-energy Li-ion cells for future applications.

1. Introduction

Lithium-ion batteries (LIBs) are commercially prominent of their use in portable electronics since its development by Sony Corporation in 1991 and leads to their possible application in high-end applications such as electric vehicles (EVs) and electrical energy storage grids (EESGs). This has put their global market value of 17.5 billion US dollars in 2013 and supposed to increase fourfold by 2020.[1,2] Even then, LIB technology need to be upgraded with better capacity values with high energy and power densities, improved calendar life, and safety aspects of their future applications in EVs and EESGs. Such electrochemical improvements are achieved by individually tuning the constituents of LIB (such as anode, cathode, separator, and the electrolyte) and further efficient battery management system.[3,4] As cathode material weight contributes to >50% of the total battery weight, research focus towards cathode materials could lead to the improved energy density of LIB.[5,6]

Owing to simple and scalable production, high theoretical capacity (274 mA h g⁻¹), reasonable rate capability and good cycle life, LiCoO₂ is commercially viable cathode material in the present generation LIBs for mainly portable applications. Though, the theoretical capacity of LiCoO₂ is 274 mA h g⁻¹, the practical reversible capacity is only ≈140 mA h g⁻¹ (LiₓCoO₂, x > 0.5; > 4.2 V vs Li/Li⁺).[7,8] Such a large irreversible capacity is mainly attributed to not only cation disorder between Li and Co, but also phase transition from hexagonal to monoclinic phase at a charge cut-off voltage ≈4.2 V, resulting from dissolution of Co into the electrolyte, and thereby generating elastic strains (> 0.1%) and micro-cracks among and within the LiCoO₂ particles. This in turn responsible for internal resistance between the active material and the current collector and hence decrease in overall electrochemical performance of the cell.[9–13] The structural degradation and interfacial instability between the electrode and electrolyte confined implementation of LIBs in high-end applications. Numerous research attempts have been adopted to address above mentioned problems such as using additives in electrolytes,[14] doping of foreign elements in LiCoO₂, and surface coatings with inorganic materials (metal-oxides, phosphates, and fluorides) and electrochemically active materials by using wet-chemistry (sol-gel), radio frequency (RF) magnetron sputtering, chemical polymerization routes, and physical adsorption (atomic layer deposition) methods.[15–17]
With a special emphasis on improving thermal stability, electrochemical performances at a higher cut-off voltage (> 4.2 V) and elevated temperatures, various research groups have focused on doping and surface coating aspects. For example, Jang et al. [18] and Tukamoto et al. [19] reported partial doping of Al and Mg, respectively, into LiCoO₂. Along with mitigated cracks formation, Al doping could be able to improve capacity retention whereas Mg could not and resulting in lower capacity values in both cases when compared to bare LiCoO₂. Following metal oxide surface coatings on spinel LiMn₂O₄ by Bellcore to reduce Mn dissolution at elevated temperatures, [20] Cho et al. reported Al₂O₃ and ZrO₂ as an efficient surface coating materials at higher cut-off voltage (4.4 V) with excellent capacity retention in both cases and most importantly ZrO₂ contributed to excellent capacity retention even at 4.6 V cut-off. [10, 15] Similarly various other metal oxide coatings such as MgO, SnO₂, SiO₂, ZnO, and CuO etc., have been employed for LiCoO₂ but unfortunately couldn’t improve significant electrochemical performance at higher cut-off voltages. [21-24] Alongside, metal fluoride (CeF₃, AlF₃, MgF₂, and AlW₃F₁₂ etc.) coatings have been implemented and though improved cyclic stability but couldn’t enhance electrochemical performance at elevated conditions. [25-27] Among metal phosphates as surface coating materials, AlPO₄ coated LiCoO₂ showed an impressive overcharge stability and room temperature cycle performance at 4.8 V; [28] however, coating of pure phase AlPO₄ on LiCoO₂ is difficult (frequently results in the formation of Li residuals on the surface) and limits its deployment in commercial LiBs. Even though most of the coating materials are insulators, there is a reasonable improvement in electrochemical performance of coated LiCoO₂ when compared to bare ones. This is mainly attributed to various reasons such as facile Li-ion diffusion across the high surface area of the coated material and the origin of electrochemically active solid solution (Li-M-O) across the surface of LiCoO₂ and coating material during calcination process. [29, 30] On the other hand, surface coatings with Li-based electrochemically active materials such as LiCoPO₄, spinel LiMn₂O₄, and spinel LiₓCoO₄ etc., have been proposed, however, resulted in an unsatisfactory electrochemical performance at elevated temperatures. [21, 31, 32] For instance, though spinel LiₓCoO₄ coated LiCoO₂ revealed improved capacity retention and charge transfer when compared to that of bare at room temperature, but failed to show the elevated temperature cycle performance and improved rate capability at higher cut-off voltages. The aforementioned surface coating materials improved the room temperature electrochemical performance of LiCoO₂, however, upon charged states, and further no evidence of improved electrochemical performance in full-cell has been reported both at elevated temperatures and high cut-off voltages. These results are due to uneven coating layer and even at higher cut-off voltages, structural instability from the Co dissolution that is initiated from the surface. These phenomena can be directly observed in the cycling or storage tests at 60 °C over weeks.

Hence, it is essential to design alternative hybrid surface treatment (simultaneous metal oxide coating and surface doping, see Figure 1) approaches for LiCoO₂ which can withstand under adverse conditions (elevated temperatures and high cut-off voltages) for their use in future applications such as redox flow batteries for energy storage.
as smartphones and mobile devices. Not only the electrochemical performance of surface coating material, but also its chemical association with the host cathode material is critical without forming any impurity phases on the surface, thereby results in sustainable long-term use under adverse conditions.

In this progress report, firstly we have focused on the research strategies in the surface engineering of LiCoO₂ for achieving high energy density LIBs. Further, the recent developments in the hybrid surface treatments of LiCoO₂ for better electrochemical performance at high charge cut-off voltage and elevated temperature conditions have been emphasized. Especially and most importantly, we have also focused on our own experimental outcomes in the new insights of surface engineering of LiCoO₂ for realizing high energy LIBs in the full-cell configuration. Lastly, the future prospects and critical opinions have been discussed in terms of further optimization of surface treatment of LiCoO₂ and its electrodes for realizing LIBs for next-generation practical applications.

2. Surface Coating Methods

The outline of various surface coating methods employed for LiCoO₂ has been illustrated in Figure 2, and the brief description is as follows. Further, the advantages and disadvantages of these coating methods and their influence on LCO electrochemical performance has been tabulated in Table 1.

2.1. Wet Chemical Routes

Amongst various wet chemical synthesis methods, the sol-gel method is one of the...
Table 1. Outline of various surface coating methods for LiCoO₂ with their advantages/disadvantages and examples.

<table>
<thead>
<tr>
<th>Surface coating method</th>
<th>Advantages/Disadvantages</th>
<th>Examples of electrochemical performance</th>
<th>Ref.</th>
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<td>Wet chemical routes</td>
<td></td>
<td>Mg and P-based coated LCO full-cell: 120 mA h g⁻¹ and energy density of 1.5 W h cc⁻¹ at 10 C; 100 mA h g⁻¹ after 100 cycles at 1 C, 4.35 V, 60 °C</td>
<td>This work</td>
</tr>
<tr>
<td>(Sol-gel, hydro/solvothermal etc.)</td>
<td>Advantages:</td>
<td>LiNi₀.₅Mn₀.₅O₂ coated LCO pouch-type full-cell: 148 mA h g⁻¹ and energy density of 2 W h cc⁻¹ after 100 cycles at 1 C, 4.47 V</td>
<td>This work</td>
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<td>Chemical polymerization routes</td>
<td>Advantages:</td>
<td>PAN coated LCO half-cell:</td>
<td>[113]</td>
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<tr>
<td>Deposition techniques</td>
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<tr>
<td>(Sputtering, PLD, ALD etc.)</td>
<td>Advantages:</td>
<td>Sputtering based Li₃PO₄ coated LCO half-cell: 140 mA h g⁻¹ at 100°C cycle at 4.5V, 50 °C</td>
<td>[112]</td>
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Future perspective

Advantages:

ALD based AlₓWᵧₓFᵧ coated LCO half-cell:

162 mA h g⁻¹ after 50 cycles at 20 mA g⁻¹, 4.4 V

[27]

Wet Chemical + Deposition

Advantages:

ALD based AlₓOᵧ coated LCO powders: =140 mA h g⁻¹ (vs 70 mA h g⁻¹ for bare LCO) after 100 cycles

[81]

Disadvantages:

ALD based AlₓOᵧ coated LCO electrodes: =125 mA h g⁻¹ (vs 55 mA h g⁻¹ for bare LCO) after 120 cycles

[81]

Electrochemical performance examples of respective surface coating methods are represented across them in the table. Besides surface coating material and coating method, the electrochemical performance of battery depends on the morphology and size of the LCO particle, coating thickness, electrode composition, density and loading mass, customized electrolyte, and electrochemical testing conditions; uniform coating layer can be obtained especially using PLD and ALD; in case of PLD, uniform layer-by-layer deposition is hindered by micrometer size particles.

Traditional methods for surface coating technology of the cathode materials for rechargeable secondary batteries. It is most viable and economical due to various advantages such as homogeneous mixing at the atomic or molecular level, lower synthesis controlling temperature, shorter calcination time, good stoichiometric control, better crystallinity, uniform particle size distribution and smaller particle size at nano (or micro) meter level and most importantly the viable method for possible scale-up production.[33] There are various steps involved in this method as follows: mixing (of precursor salts), casting, gelation, ageing, drying, dehydration or chemical stabilization, and densification.[34] To understand the feasibility of sol-gel method, consider LIB technology, in which various electrode materials are prepared using this sol-gel method, such as lithium cobalt oxides, lithium nickel oxides, spinel and layered lithium manganese oxides, vanadium oxides and ferrous phosphates (cathode materials) and transition metal oxides (anode materials).[35,36] For example, commercially well know LiCoO₂ (LCO) material in mobile phone batteries, is generally prepared by solid-state reaction method (physical mixing of precursor salts in a powder state and further heat-treatment).[37] Such type of reaction needs a long heating time and a high temperature to get uniform and good products. In order to overcome these problems, sol-gel methods are preferred, and they can be used to prepare not only LCO but also various classes of materials with dopants and surface coatings.[38] On the other hand, there have been various reports on the surface coating of electrode materials using hydro/solvothermal synthesis method.[40–42] For example, Li₂ZrO₃ was coated on LCO via solvothermal method followed by lithiation process and improved electrochemical performance and capacity retention of the LCO due to the synergistic effect of Li-ion conductive Li₂ZrO₃ and Zrₓ⁺⁺ doping at local sites to improve crystallinity of layered structure.[40] These hydro/solvothermal synthesis routes are similar in their operation with high vapour pressures, however, varied in their solvents used i.e., aqueous and non-aqueous, respectively.
Although these wet chemical routes are simple, there are problems/challenges associated with scale-up (low yield and high precursor cost), consistency, and uniformity (and optimization) of the coating layer on the host material, the evolution of acidic gases during heat treatment, the low shelf life of sols.

2.2. Chemical Polymerization Routes

As mentioned earlier, various inorganic materials are coated on the cathode materials using wet chemical routes, however, resulted in the uneven/discontinuous deposition of the surface coating material on the host and some cases coating layer tends to be inert for ionic conductivity. Soft conductive polymers such as Polypyrrole (PPy), Polyaniline (PANI), Poly(3,4-ethylendioxythiophene) (PEDOT) etc., are considered to be one of the potential surface coating candidates owing to efficient ionic host in the acceptable voltage range of cathode materials (2.0 – 4.5 V vs Li/Li$^+$), act as a stress buffers with excellent mechanical and chemical stability over electrochemical cycling. The main role of polymers as a coating material also includes minimizing the polarization between the cathode material and the electrolyte, and thus results in the facile ionic intercalation and de-intercalation during electrochemical process. For instance, PPy coated LCO showed enhanced electrochemical performance. However, it is important to note that the conducting polymers alone as cathode materials in practical applications are not possible due to their poor inherent capacity values.

Chemical polymerization route is considered to be one of the well-established techniques for the polymeric coating on the host materials. This chemical polymerization method is broadly classified into two approaches such as in situ and ex situ. In the in situ method, the host materials are prepared within a polymer matrix by chemical reduction of precursors dissolved in the polymeric solution or decomposition via thermalysis, photolysis, radiolysis, etc., on the other hand, in the ex situ method, the host material is prepared via wet chemical routes prior to dispersion into the polymeric matrices. This ex situ approach is most convenient and commonly used practices in surface coating techniques for cathode materials. For example, PEDOT polymer was introduced onto Li$_{10.9}$Mn$_{1.97}$O$_4$ particles by simple oxidation and subsequent polymerization of EDOT, and thus enhanced the cycling stability of those lithium-ion cells, and similar enhanced electrochemical performance due to PEDOT coating was revealed in the case of LiFePO$_4$. In the similar lines, further research advancement lead to the preparation of semi-interpenetrating polymer network (semi-IPN) on LCO particles. This semi-IPN layer consists of thermally stable polyimide (PI) and polyvinyl pyrrolidone (PVP) with Lewis basic site. Such a strategic surface polymeric coating together with chemical functionality significantly improved electrochemical performance due to various factors associated with developing stable polymeric film on the particles and enhancing interfacial stabilities between the LCO and the electrolyte, presence of pyrrolidone rings with Lewis basic sites reduce the Hydrofluoric acid (HF) attack (as illustrated in Figure 2), and excellent thermal stability due to presence of PI without any chemical functional groups. Such organic/inorganic polymeric coatings act as a protective layer for LCO against HF attack, although they could not promote stabilization of the LCO crystal structure under high voltage and high temperature conditions. On the other hand, the active inorganic material coatings (such as Al$_2$O$_3$, MgO etc.) deposited on the LCO using chemical routes and subsequent calcination results in the possible superficial doping of Al and Mg elements on the LCO surface (solid solution formation), and thereby, mitigate the structural degradation of LCO during cycling under adverse operating conditions.

These in situ and ex situ approaches of the chemical polymerization route have their own merits and demerits in their procedure and practical applications. There is a possibility of the unreacted precursors of the in situ chemical reaction could affect the properties of the final product and such feature hinders the scale-up production, however, this approach prevents the agglomeration of the host material particles and maintains uniform distribution along the polymer matrix. On the other side, the ex situ approach could scale-up the production of surface coated cathode materials, however, there is a problem associated with the uniform distribution of host particles in the dispersion of polymer matrix. Hence, strategic optimization in experimental procedure and selection of specific conducting/non-conducting polymers are required to realize the influence of such polymeric coatings on the electrochemical performance of the host cathode materials.

2.3. Deposition Techniques

2.3.1. Sputtering

Sputtering is a widely used process to deposit thin films of surface coating material onto a surface of the host material. The process starts with forming a gaseous plasma and then accelerating the ions (typically Ar) resulting from this plasma into target material (surface coating material), and the target material is gradually scraped away by the bombarding ions by energy transfer and is ejected in the form of neutral particles. These ejected neutral particles travel in a unidirectional until they come across with any contact. Thus, a thin film can be formed on the required host material. There are various types of sputtering techniques based on the energy source such as radio frequency (RF) magnetron, direct current (DC), and microwave (MW) etc. This energy source is required to sustain the plasma state when the plasma is losing energy during energy transfer with surroundings. This dynamic condition is created by optimized Ar gas flow into a pre-pumped vacuum chamber and allowing the chamber pressure to maintain a specific level and the live electrode is introduced into this low-pressure gas environment using a vacuum feedthrough.

Among the various types of sputtering techniques, RF magnetron sputtering is well-established and in use for numerous
commercial applications because of its benefits such as low-cost, easy control in the optimization of large-scale film deposition, and can be also used to sputter insulating materials (along with metals and alloys).[57] The operation procedure of sputtering techniques is same, however, the main difference between RF magnetron sputtering and traditional diode sputtering is the presence of a magnetic field at the target material (surface coating material) in a parallel orientation. The presence of magnetic field improves the confinement of the secondary electrons and thus enhances the plasma density (twice to that of traditional diode sputtering system). Due to above mentioned significant features of the RF magnetron sputtering; multiple reports have addressed the use of classes of a target material such as metal oxides, metal phosphates, and doping of metallic ions etc. to coat on the various host cathode materials, and revealed enhanced electrochemical performance. For instance, Ahn et al.[58] reported the improved electrochemical performance of LCO by cerium-phosphate (CePO₄) coating on it via RF magnetron sputtering. This improved performance was attributed to the increased ionic conductivity via inter-diffusion between the CePO₄ coating layer and LCO, besides coating layer itself acts as a solid electrolyte and impedes the degradation of LCO during electrochemical process. Similarly, nano size ZnO was coated on LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂ and showed improved rate capability with 166 mA h g⁻¹ discharge capacity at 3 C when compared to bare sample (125 mA h g⁻¹).[59] On the other hand, this sputtering was used to fabricate LCO thin films and Ti and Zr doped-LCO thin films, and doped-LCO thin films showed improved rate capability and cycle performance owing to combined effect of improved electrical conductivity from dopants (Ti and Zr) and the use of aqueous electrolytes in the present system.[60,61]

There are various merits and demerits of sputter deposition for their practical application. In sputter deposition technique, even the materials with very high melting points are easily sputtered; however, evaporation of these materials is difficult. The deposited films will have the same composition to that of the target material (surface coating material), but there could be some contamination issues associated with the uncontrolled direction of ejected atoms. Moreover, controlled growth of the layer-by-layer structure is practically difficult in these sputter deposition techniques when compared to pulsed laser deposition.

2.3.2. Chemical Vapour Deposition

Chemical vapour deposition (CVD) is a versatile material processing technique, with its applications of solid thin film coatings on the host materials, production of high-quality bulk materials and their composites using infiltration techniques. Typical experimental procedure includes, the substrate (or host material) is exposed to one or more volatile precursors and resulted in thin films of desired dimensions on the surface of the substrate through the reaction and/or decomposition of volatile precursors, however, also results in the impurity by-products on the thin films and are eliminated by gas flow through the reaction chamber.[62] Using CVD technique, surface coating materials can be deposited in different forms such as monocrystalline, polycrystalline, amorphous, and epitaxial. These CVD systems are classified based on the application, process and reactor used, and precursor and chemical reaction used. Namely, Atmospheric pressure CVD, low-pressure CVD, ultrahigh vacuum CVD, aerosol assisted CVD, direct liquid injection CVD, microwave plasma-assisted CVD, Combustion CVD, metalorganic CVD etc. With these various options of CVD, researchers in rechargeable LIBs have used CVD techniques for protective layer coating/surface engineering of electrode materials,[63–65] direct preparation of the composite electrode materials themselves,[66] template-assisted synthesis of electrode materials,[67] preparing artificial homogeneous solid-electrolyte interphase[68] etc. For example, metallic precursors were used to deposit LCO thin films on substrates using metalorganic CVD at the optimized deposition temperature (700 °C) and revealed appealing cycling stability, with 75% retention after 100 cycles, when compared to the samples deposited at 450 °C.[66] It is important to note that the deposition operating temperature also plays a key role in designing a final product with excellent electrochemical performance.

CVD has multiple applications due to various significant features mentioned above such as coating at any side of the substrate such as backside and even interior region of the porous materials. But, the deposition rate of general CVD is low, and may not be suitable for forming thick oxide coatings, which is a requirement for specific applications such as developing artificial SEI films on the electrode materials. In such cases, the laser can efficiently improve the deposition rate and thus used to form thick coatings.

2.3.3. Pulsed Laser Deposition

Pulsed laser deposition (PLD) is one of the most promising laser-based techniques for the deposition of the high purity thin films of complex oxide heterostructures, superlattices, and well-controlled interfaces. In this technique, as the name implies, the target material (surface coating material) is vaporized by short/intense laser pulses to form plasma in the vacuum chamber. Under optimized experimental conditions, the plasma consisting of vaporized target material deposits on the host material and forms a thin homogenous layer. The usual pulses used are of ultraviolet (UV) wavelength range 150 nm to 400 nm.[69,70] Various lasers have been used for PLD which could generate output power (~1 J cm⁻¹) that can eject the target material and thus the selection of laser is based on the type of target material. Some commonly use lasers in PLD are excimer lasers (e.g., KrF, ArF, XeCl) and solid state lasers (e.g., Nd-YAG, Ruby). There are various advantages of PLD which enable it to use for wide range of applications (coatings, fabrication of heterostructures etc.), such as the simple operation of technique, versatile in terms of choosing target material, fast process, and easily scalable. On the other hand, there are some disadvantages such as deposition of large particulates (micrometer size) on the film, such particles hinder the growth of successive layers and impede the electrical properties of the films. Further, having a narrow angular distribution of PLD limits its application in large area uniform thin films; however, both these problems were recently addressed by inserting a shadow
mask to block off the particles and designing both the target and substrate to rotate to facilitate larger uniform films.[71,72] This PLD process has been well recognized because of consistency in uniformity of film quality and dimensions.

These significant features of PLD lead its application in surface engineering of electrode materials for LIBs. For example, Iriyama et al.[73] reported deposition of magnesium oxide (MgO) film on the PLD-deposited LCO films. It is evident from the electrochemical properties, that PLD coating of MgO significantly improved the interfacial kinetics of Li-ion diffusion rate between LCO and the electrolyte. PLD was not only used for surface engineering of the electrode materials, but also the fabrication of solid electrolyte. Solid-state thin-film batteries were reported with amorphous solid electrolyte Li$_{2.2}$V$_{0.54}$Si$_{0.46}$O$_{3.4}$, which was prepared by PLD technique from Li$_2$CO$_3$, SiO$_2$, and V$_2$O$_5$. The ionic conductivity of the Li$_{2.2}$V$_{0.54}$Si$_{0.46}$O$_{3.4}$ is evaluated to be 2.5 × 10$^{-7}$ S cm$^{-1}$ at 25 °C with activation energy of 0.54 eV.[74] Thus, it is evident that PLD is one of the competitive techniques used to fabricate various components in the LIBs.

2.3.4. Atomic Layer Deposition

Atomic layer deposition (ALD) or atomic layer epitaxy (ALE) is a vapour phase self-terminating thin-film deposition technique and has been established since the 1970s. It is most significant and powerful deposition technique that can be used to deposit a wide range of materials such as metals, metal oxides, metal nitrides, metal sulphones, and compound materials. Even though there are various other techniques such as sputtering, CVD, physical vapour deposition (PVD), and electrodeposition, which can be used for surface engineering and coating of the materials used in various applications, they are not as facile as that of ALD. For example, conductive surfaces are required for electrodeposition to deposit coatings, whereas ALD can deposit coatings on conductive and insulating materials/surfaces. Moreover, ALD is self-terminating thin-film deposition technique which can terminate gas-solid surface reactions and effectively controls the thickness and dimensions of the coating over a large scale. The critical factors involved in the deposition technique are substrate (or host material) type, deposition operating temperature, and precursor materials. The substrate should have enough reactive sites to originate ALD. The operating temperature (usually in the range of 100–250 °C) should be optimized considering the parameters of reducing the physical sorption of precursor constituents and decomposition of precursor materials. The precursors should be feasible to produce enough amount and concentrations of gaseous phase vapours to saturate all the adsorption sites on the substrate. Hence, ALD is considered to be unique deposition technique with atomic scale deposition with low operating temperatures and well control in the thickness and dimensions of the coating films. Specifically, in LIBs, the ALD technique has been used in various functionalities, such as conductive and non-conductive surface coating of active materials (anode and cathode), and their as-prepared electrodes (see Table 1). For example, surface coatings should minimize the rate of undesirable surface/side reactions associated with SEI layer formation and Li-ion diffusion, and enhance the ionic conductivity of the electrode material. Further, coatings should be mechanically stable to facilitate large volume expansions in the case of conversion type electrodes.[75,76]

Recently, there have been various research directions in the application of ALD for surface engineering of LIB electrode materials: ALD coating of (i) electrode materials (anode and cathode) with one or more target materials, (ii) solid electrolytes, and (iii) as-prepared electrodes before assembling cells (Table 1). For instance, Cheng et al.[77] reported systematic ALD based Al$_2$O$_3$ and TiO$_2$ coatings on the as-prepared LCO electrode at an as low operating temperature of 120 °C. ALD coated samples showed better cycling performance than bare samples because of developing better interfacial kinetics during cycling. Together with the influence of ALD, it is important to essential criteria that the metal oxide with the higher band gap energy (> 3.9 eV) would be better to facilitate thin film deposition on LCO. In the similar lines, ALD coating of Al$_2$O$_3$ on both anode and cathode material, significantly improved the cycling stability of lithium-ion full-cell based on the natural graphite and LCO as anode and cathode respectively.[78] On the other hand, there have been various reports on ALD coating on the particles of electrode active materials and on the separator films.[79-81] In these cases, it is important to establish a mechanism to interface between ALD coating material and the host. The following section discusses a possible research in those directions.

3. Research Strategies

There have been various research directions in the surface engineering of LCO cathode material for LIBs as represented in Table 2. The surface engineering strategies include simple heat-treatment of host material under optimized experimental conditions, the individual or combined effects of a surface coating of host material with foreign organic/inorganic based insulating/conducting materials, and superficial/atomic-level doping of foreign elements into the host material. There have been varied classes of surface coating hybrid materials based on single, binary, and ternary- metallic elements, and their choice are based on its compatibility (both physically and electrochemically) with the host material, and its interfacial stability with the electrolyte and the separator used in the particular battery system. Furthermore, there are various other innovative surface coating techniques such as coating with polymeric materials, ionic conductors, and glassy-electrolyte thin films, together with in situ coating through the electrolyte additives. This section illustrates various examples from literature and our own research results in each case of surface engineering and establishes the influence of such strategies in improving the electrochemical performance of LCO at adverse conditions.

3.1. Simple Heat-Treatment of Bare LiCoO$_2$

Initially, Dahn et al.[82] proposed that the simple grinding and successive heating or moisturizing could be enough for enhancing the specific capacity and capacity retention even at 4.5 V charge cut-off voltage, without any surface coating approach. However, it is important to note that the capacity
degradation is not only because of undesirable side reactions of LCO with the electrolyte, but also structural instability from the Co$^{4+}$ dissolution that is initiated from the surface. These phenomena can be directly observed in the cycling or storage tests at 60 °C over weeks. Accordingly, it is essential to introduce the hybrid surface treatment approaches to resolving these problems: metal oxide coating and surface doping in which the selected elements are heavily located to minimize the reversible capacity. Later, Lee et al. \cite{83} reported that under controlled step-wise heating conditions, could be able to develop spinel phase Li$_{x}$Co$_{2}$O$_{4}$ on the surface of the LCO. Unfortunately, there is no evidence of long-term cycle and rate performance for practical applications, although, such spinel phase Co$_{2}$O$_{4}$ formation could reduce the oxygen evolution from the layered lithium transition metal oxides over cycling. Besides, the simple addition of amorphous YPO$_4$ and Al$_2$O$_3$ with LCO were proved to be successful in better cycling stability.\cite{84} However, under careful examination and our practical experience, we believe simple heating and mixing strategies could not sustain for long-term and adverse applications as they break down to understand and explain in detail interfacial mechanism between the LCO and the electrolyte.

### 3.2. Coating with Metal Oxides, Metal Fluorides, and Metal Phosphates

This section deals with metal oxides, metal fluorides, and metal phosphates as surface coating materials for LCO. The classes of surface coating materials include single-element based materials, binary and ternary hybrid materials. It is noteworthy that our notation of single-element material is the material with

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<td>Spinel Li$<em>{2}$Co$</em>{3}$O$_{4}$ formation</td>
<td>165 mA h g$^{-1}$ after 45 cycles at 0.5 C, 4.5 V and 140 mA h g$^{-1}$ at 3 C</td>
<td>[83]</td>
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<tr>
<td>YPO$_4$ and Al$_2$O$_3$ addition</td>
<td>Al$_2$O$_3$:180 mA h g$^{-1}$ after 40 cycles, YPO$_4$: 170 mA h g$^{-1}$ after 50 cycles at 0.1 mA cm$^{-2}$, 4.5 V</td>
<td>[84]</td>
<td></td>
</tr>
<tr>
<td>Single-element based coating materials</td>
<td>Al$_2$O$_3$</td>
<td>165 mA h g$^{-1}$ after 70 cycles at 0.5 C, 4.4 V</td>
<td>[10]</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>168 mA h g$^{-1}$ after 70 cycles at 0.5 C, 4.4 V</td>
<td>[15]</td>
<td></td>
</tr>
<tr>
<td>AlPO$_4$</td>
<td>145 mA h g$^{-1}$ after 20 cycles at 1 C, 4.3 V</td>
<td>[16]</td>
<td></td>
</tr>
<tr>
<td>AlF$_3$</td>
<td>155 mA h g$^{-1}$ at 40 mA g$^{-1}$, 4.6 V</td>
<td>[2]</td>
<td></td>
</tr>
<tr>
<td>CeF$_3$</td>
<td>160 mA h g$^{-1}$ at 40 mA g$^{-1}$, 4.6 V</td>
<td>[2]</td>
<td></td>
</tr>
<tr>
<td>MgF$_2$</td>
<td>130 mA h g$^{-1}$ after 50 cycles at 0.2 mA cm$^{-2}$, 4.25 V, 45 °C</td>
<td>[25]</td>
<td></td>
</tr>
<tr>
<td>Binary hybrid materials</td>
<td>ZrTiO$_4$</td>
<td>130 mA h g$^{-1}$ after 130 cycles at 0.1 C, 4.4 V</td>
<td>[95]</td>
</tr>
<tr>
<td>MgAl$_2$O$_4$</td>
<td>125 mA h g$^{-1}$ after 160 cycles at 0.1 C, 4.4 V</td>
<td>[96]</td>
<td></td>
</tr>
<tr>
<td>SrAl$_2$O$_4$ garnet</td>
<td>180 mA h g$^{-1}$ after 30 cycles at 0.2 C, 4.6 V</td>
<td>[98]</td>
<td></td>
</tr>
<tr>
<td>MgAl$_2$O$_4$ garnet</td>
<td>140 mA h g$^{-1}$ at 0.4 C, 4.4 V</td>
<td>[99]</td>
<td></td>
</tr>
<tr>
<td>ALD based AlW$_x$F$_y$ films</td>
<td>162 mA h g$^{-1}$ after 50 cycles at 20 mA g$^{-1}$, 4.4 V</td>
<td>[27]</td>
<td></td>
</tr>
<tr>
<td>Mg and P based</td>
<td>Full-cell: 120 mA h g$^{-1}$ and energy density of 1.5 W h cc$^{-1}$ at 10 C, 100 mA h g$^{-1}$ after 100 cycles at 1 C, 4.35 V, 60 °C</td>
<td>[10]</td>
<td></td>
</tr>
<tr>
<td>Ternary hybrid materials</td>
<td>La$_2$O$_3$/Li$_2$O/TiO$_2$</td>
<td>160 mA h g$^{-1}$ after 250 cycles at 1 C, 4.4 V</td>
<td>[103]</td>
</tr>
<tr>
<td>SrO/Li$_2$O/La$_2$O$_3$/Ta$_2$O$_5$/TiO$_2$</td>
<td>100 mA h g$^{-1}$ after 900 cycles at 1 C, 4.2 V</td>
<td>[104]</td>
<td></td>
</tr>
<tr>
<td>Lithium metal oxides/phosphates</td>
<td>Li$_2$ZrO$_3$</td>
<td>138 mA h g$^{-1}$ after 50 cycles at 1 C, 4.5 V, 145 mA h g$^{-1}$ at 3 C</td>
<td>[87]</td>
</tr>
<tr>
<td>Li$_3$CoPO$_4$</td>
<td>100 mA h g$^{-1}$ after 100 cycles at 5C, 4.5V, 55 °C</td>
<td>[105]</td>
<td></td>
</tr>
<tr>
<td>LiAlO$_2$</td>
<td>165 mA h g$^{-1}$ after 20 cycles at 0.1 C, 4.35 V</td>
<td>[106]</td>
<td></td>
</tr>
<tr>
<td>LiNi$<em>{0.3}$Mn$</em>{0.2}$O$_2$</td>
<td>Pouch-type full-cell: 148 mA h g$^{-1}$ and energy density of 2 W h cc$^{-1}$ after 100 cycles at 1 C, 4.47 V</td>
<td>[This work]</td>
<td></td>
</tr>
<tr>
<td>LiCoPO$_4$</td>
<td>153 mA h g$^{-1}$ after 50 cycles at 1 C, 4.5 V</td>
<td>[31]</td>
<td></td>
</tr>
<tr>
<td>Li$_3$PO$_4$</td>
<td>140 mA h g$^{-1}$ after 100 cycles at 4.5V, 50 °C</td>
<td>[112]</td>
<td></td>
</tr>
<tr>
<td>Polymers</td>
<td>Polyacrylonitrile</td>
<td>171 mA h g$^{-1}$ after 60 cycles at 0.7 C, 4.5 V</td>
<td>[113]</td>
</tr>
<tr>
<td>Ionic conductors, glassy-electrolyte thin films</td>
<td>Li$<em>{1.3}$Al$</em>{0.3}$Ti$_{1.7}$ (PO$_4$) and Mg doping</td>
<td>175 mA h g$^{-1}$ after 100 cycles at 1 C, 4.5 V; 173 mA h g$^{-1}$ at 3 C</td>
<td>[114]</td>
</tr>
</tbody>
</table>
only one metallic element (that actively involves directly/indirectly in promoting electrochemical properties of LCO), binary hybrid materials consist of at least one transition metal element and one or more electrochemically active/inactive elements, and henceforth with ternary hybrid materials.

3.2.1. Single-Element Based Coating Materials

The research concepts of a surface coating of host material were started with the significant research outcomes originated from the doping of simple transition/post-transition metallic elements such as Ag, Al, La, Mg etc. into the LCO,[85–87] and results in the stabilization of layered structure with simultaneous forming of electrochemically active/inactive by-products. For example, La doping into LCO resulted in the formation of rhombohedral LaCoO$_3$ and, tetragonal and ion-conducting La$_2$Li$_0.5$Co$_0.5$O$_4$ phases, together with rhombohedral LiCoO$_2$.[85] However, simple doping of the foreign element could not solve the long-term problems associated with stabilization of the solid electrolyte interphase (SEI) layer formation and Co$^{4+}$ dissolution over cycling due to continuous contact of the electrolyte with the surface of the LCO. Besides, Cho and co-workers have performed early studies of surface coating LCO with metal oxides such as Al$_2$O$_3$, ZrO$_2$, and TiO$_2$ etc., and enhanced capacity retention of LCO even at a cut-off voltage 4.4 V vs Li/Li$^+$. [10,15,88] Similarly, there have been various reports on different metal oxides as potential surface coating candidates for LCO. The enhanced performance was presumed due to the possible formation of stable interfacial solid-solution thin layer LiM$_{x}$Co$_{1-x}$O$_2$ (M = Al, Zr, Ti etc.) between surface coating metal oxide and LCO. Nevertheless, further XRD analyses on these metal oxide coated LCO samples revealed no evidence of solid solution layer, and alternatively, the enhanced capacity retention could be attributed to the removal of moisture based residuals such as LiOH, Li$_2$CO$_3$ on the surface of LCO while re-heating during coating process, and further surface coating layer mitigates the HF formation during side reaction of LiPF$_6$ with water. Moreover, the coating layer impedes the amount of the electrolyte decomposition and tends to the formation of stable SEI layer on the LCO surface.[89,90]

In addition, it is necessary to note that the different species of coating layers prompts (e.g., Al$_2$O$_3$ vs AlPO$_4$) various features in the electrolyte decomposition, and is clear evidence of improving electrochemical performance by surface engineering. For instance, Cho’s group proposed AlPO$_4$ as a competing coating candidate for the better thermal stability of LCO aimed at addressing thermal runaway problem. The thermal stability of uniformly AlPO$_4$ coated LCO sample was tested via overcharge safety tests by initially charging coated and bare samples to 12 V and maintained for 2 h. Surprisingly, coated-LCO maintained better thermal stability with surface temperature (of pouch cells) of only ≈60 °C when compared to bare pouch-cells (≈500 °C) as shown in Figure 3.[16] Such a high temperature has been attributed to short-circuit of the cell and exothermic reaction corresponding to the oxygen evolution (during electrolyte decomposition with LCO surface). Contrary to the metal oxide coatings, the improved thermal stability in AlPO$_4$ coating is also associated with the strong P=O bond and the strong covalency between the polyanion (PO$_4$) and the Al$^{3+}$ ion in AlPO$_4$.[88] Further microstructural analyses revealed that the AlPO$_4$ reacts with LCO to form a Li$_3$PO$_4$ layer and Al-doped Li$_{1-x}$Co$_{1-x}$O$_2$.[91] Hence, in-depth investigation of interfacial phenomena between the surface coating material and host, and their influence on the electrochemical and thermal

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Figure 3. The flowchart demonstrating the reason of thermal runaway and AlPO$_4$ was employed as a coating material on LiCoO$_2$ to overcome the problem. The section of this figure is reproduced and adapted with permission.[16,88] Copyright 2003, Wiley VCH and Copyright 2013, American Chemical Society.
properties could be special research direction. Moreover, such phosphate based coatings were proved to enhance the thermal stability of various other layered and spinel structured cathode materials.[92,93] In the similar lines, it is also important to consider the choice of the electrolyte that is more compatible with ALPO₄ and other surface coating materials. For example, most recently, X-ray photoelectron spectroscopy (XPS) study revealed that ALPO₄ promotes the formation of metal fluoride layer on the LCO surface with both electrolytes (LiPF₆ and LiClO₄ salts), the film formed with LiClO₄ developed more impedance when compared to LiPF₆ salt, as the origin of fluorine for film formation on coated cycled electrodes is from LiPF₆ salt (in LiPF₆ based electrolyte) and PVDF (in LiClO₄ based electrolyte).[94]

On the other hand, metal fluorides were well-studied as coating materials for LCO.[2,25-27] Although, the metal fluorides were successful in improving the electrochemical performance, there is a possible decomposition of the electrolyte with metal fluorides and results in the formation of uncontrollable film on the surface of LCO and by-products such as HF, LiF etc. at high cut-off voltages (> 4.3 V vs Li/Li⁰), which limit their practical applications due to safety concerns. For instance, the major limitation of the potential candidate AlF₃ is that it is wide-band gap dielectric and thus electrically insulating.[27]

### 3.2.2. Binary Hybrid Materials

Owing to the significant contribution of transition/post-transition metals such as Al, Mg, Zr, Ti etc., Fey's group proposed various binary hybrid materials based on these elements to take benefits of their individual ions, such as MgAl₂O₄ (Al³⁺ and Mg²⁺), ZrTiO₄ (Zr⁴⁺ and Ti⁴⁺) etc. For instance, the binary material ZrTiO₄[95] revealed the formation of solid solution thin film LiₓM₀.₅(Coₓ−₀.₅)O₂⁺₀.₅ (M = Zr and/or Ti) (as suggested by Cho et al.[21]) due to possible substitution of foreign tetravalent ions into interstitial Co⁴⁺ sites. On the contrary, during heat-treatment for the preparation of MgAl₂O₄ coated LCO,[96] the possible interfacial phases are LiAl₄CoO₇, LiMgCoO₄, and their combinations. These phases are different to that of ZrTiO₄, due to the possible substitution of Al³⁺ into Co⁴⁺ sites, and Mg²⁺ requires Co⁴⁺ of equal amount to neutral charge and are originates from oxidation of Co⁴⁺. Fortunately, the origin of more Co⁴⁺ ions can improve the electronic conductivity of coated-LCO particles, and thus electrochemical performance is evident from various reports. For instance, ZrO₂, TiO₂, and ZrTiO₄ coated LCO samples showed eight, five, and ten times enhancement in their cycling stability when compared to bare LCO in the voltage range of 2.75–4.4 V vs Li/Li⁰.[95,97] Hence, we believe binary materials are advantageous over their individual materials, because together with the forming of solid-solution thin film, Mg²⁺ ions induce enhanced conductivity and Al³⁺ ions stabilize the layered structure of LCO over cycling. Considering the advantages of binary materials, various groups have proposed binary hybrid materials based on oxides and fluorides coated on LCO such as, 3LaAl₂O₃:Al₂O₃ garnet, Y₃Al₅O₁₂ garnet, and ALD based Al₆F₄ films etc.[27,98,99] The ALD based Al₆F₄ films on LCO showed enhanced cycle life and rate capability due to the combined effects of AlF₃ chemical inactiveness and high electrical conductivity of tungsten.[27] The similar dual coating strategy was applied to some other layered structures. Thus, in designing surface coating material, it is important to explore the merits and demerits of the individual metallic/non-metallic elements in the compound/composite and their feasibility in the improvement of electrochemical and thermal properties of LCO for long-term practical applications.

Although, aforementioned coating methods have been proven to effectively reduce the side reactions and HF attack because of reduced direct contact area between the electrolyte and cathode material even beyond 4.4 V (vs Li/Li⁰). However, these coatings led to increased charge transfer resistance upon cycles, thereby decreasing rate capability. More importantly, upon charged states, and further no evidence of improved electrochemical performance in full-cell has been reported both at elevated temperatures and high cut-off voltages.[8,32,45] These results are due to uneven coating layer and even at higher cut-off voltages, structural instability from the Co⁴⁺ dissolution that is initiated from the surface. These phenomena can be directly observed in the cycling or storage tests at 60°C for weeks. Accordingly, it is essential to introduce the hybrid surface treatment approaches to resolving above problems: metal oxide coating and surface doping in which the selected elements are heavily located to minimize the capacity loss. Hence, we have recently designed thermally stable (50% reduced heat generation to bare-LCO, Figure 5i) novel cathode with surface coating strategy of the simultaneous presence of MgO nanoparticles and super-ficial doping of Mg and P on the surface of LCO particle (MP-LCO) by using simple, scalable, and low-cost wet method and calcination process as shown in Figure 4a. Hereby, we describe complete microstructural analyses of MP-LCO and its relationship with the better electrochemical performance. Figure 4e,d shows the high-resolution transmission electron microscope (HR-TEM) images of bare and MP-LCO from selected regions in Figure 4b,c respectively. The selected regions (h and i) in Figure 4e are corresponding to layered and mixed phases in bare-LCO, respectively (respective FFT patterns in Figure 4h,i). The origin of mixed phase is attributed to a cation-mixing layer of ~5 nm is evident for bare-LCO associated with occupying of Co in Li sites, and is more when compared to MP-LCO (<2 nm) (Figure 4g). The reduction in the cation-disordered phase could be attributed to the possible relocation of Co in its initial sites along with partial occupation of Mg²⁺ in Li sites on the surface and atomic site doping of P⁵⁺ in O sites during re-calcination of LCO for surface coating. This is further confirmed from the significant intensities of Mg 1S and P 2p XPS peaks over the etching of MP-LCO particle (see Figure 4i). On the other hand, Figure 4f is a high-resolution image of the marked area in Figure 4d showing the presence of nanoparticle islands. To further understand the atomic scale structural evolution at the various regions on the surface of MP-LCO, two regions are selected in Figure 4d (marked as f and g). HAADF-STEM images were collected in the selected regions (f and g) and represented as Figure 4f,g. The two regions (j and k) in Figure 4f are corresponding to rock-salt MO (space group $Fm\bar{3}m$, could be MgO) and layered phases, respectively and is evident from their
FFT patterns (Figure 4j,k, respectively). Notably, the existence of relatively thin cation disordered (cubic rock salt) phase could enhance the structural and electrochemical stability of cathode materials at the fully charged state, thus nano-size pillar affected surface acts as a protective layer during electrochemical cycling.\cite{100}

By using the lithium half-cell, we can estimate the volumetric energy density of the MP-LCO, comparing with other high capacity cathode materials such as LiNi0.85Co0.13Al0.02O2 (NCA) and Li1.17(Mn0.6Ni0.2Co0.2)0.83O2 (OLO) (Figure 5a,d). Based upon maximum obtainable electrode density of the electrode and voltage profiles, LiCoO2 showed the highest value of 2.80 W h cc\(^{-1}\), while NCA and OLO showed 2.57 and 2.10 W h cc\(^{-1}\), respectively at 0.1 C. The MP-LCO exhibited improved cyclic stability at 60 ºC with a capacity retention of 86.5% after 100 cycles, excellent rate capability with a discharge capacity of 145 mA h g\(^{-1}\) at 10 C in lithium half-cells, which is \(\approx\)25 times higher than bare-LCO as shown in Figure 5b,f. Such an inferior cycling and rate performance of the bare-LCO cathode can be assigned to the structural degradation (formation of micro-cracks initiated from surface to the core of particle as shown in the Figure 5g) at elevated temperatures together with adverse cut-off voltages, significant side reactions on the surface (see Figure 5h), and Co dissolution into the electrolyte because of HF attack, are evident from our post-mortem analyses using focused-ion beam (FIB), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and also confirmed from the literature.\cite{101,102}

3.2.3. Ternary Hybrid Materials

Though the metal oxide coatings showed enhanced capacity retentions, these coatings tend to enhance impedance over cycling, thereby decreasing the cycle and rate capabilities. Hence, there is a problem associated with the ionic charge transfer at the interface between the electrolyte and the surface of cathode particle. Lanthanum titanate perovskite, La2/3-xLi3xTiO3, is considered to be one of the potential sources for high Li-ion conductivity of \(\approx 10^{-3} \text{ S cm}^{-1}\) at room temperature. Inspired by such perovskite structures, Hong’s group proposed La2O3/Li2O/TiO2 and SrO/Li2O/La2O3/TiO2/TiO2 as thin film surface coating materials for LCO, and reported to enhance cycling stability because of the fast ion conductivity of compounds like Li0.35Sr0.5La0.05Ta0.35 Ti0.65 O3 and its ability to facilitate Li-ion diffusion across the electrolyte and the cathode.\cite{103,104} However, still there is a severe capacity drop even for coated samples, and we believe such perovskite coatings are limited to the surface (of LCO) and could not stabilize the LCO layered structure via doping and/or cation-mixing. Therefore, extensive studies are essential in the direction of microstructural influence of surface coating samples on the layered structure of LCO.
3.3. Coating with Lithium Metal Oxides/Phosphates

Pristine cathode materials suffer from the HF attack from electrolyte decomposition, dissolution of metal ions, and thus formation of thick SEI layer that spends a major amount of Li-ions, and even severe at high cut-off and temperature conditions. Simple metal oxides/phosphates coatings enhanced the capacity retentions, however, decreased rate capability due to increased impedance over cycling (because of insulating nature of inactive metal oxides towards Li-ions). Therefore, it is necessary to increase the Li-ion conductivity by the surface coating of LCO with lithium-based metal oxides/phosphates, which possess high Li-ion conductivity and provides facile Li-ion diffusion across the SEI. Accordingly, there have been various reports on lithium metal oxide coated LCO.\textsuperscript{[87,105,106]} Though there is an improvement in the electrochemical performance of LCO to some extent, but could not sustain for the harsh conditions such as high cut-off voltage and temperatures, and could be attributable to the chemical instability of the surface coating materials. Recently, Oh et al.\textsuperscript{[107]} proposed a novel strategy in the surface coating of Ni-rich layered oxide material with chemically activated Li-rich layered oxide and AlF\textsubscript{3} (Figure 6a,c). Such Li-rich layered oxide is chemically stable and acts as a protection layer in the heterostructure cathode, and revealed excellent rate and cycle capabilities at 25 and 55 °C as shown in Figure 6d,e.

In similar lines, we have surface-treated LCO with optimized proportion (1 wt%) of Li-based Mn-rich layered structure (LiNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{2}). The LiNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{2} (LNMO) material is having high capacity values and structurally stable, in which Ni\textsuperscript{2+} and electrochemically inactive Mn\textsuperscript{4+} ions contributes to the electrochemistry and structure stabilizing, respectively, during Li-ion intercalation/de-intercalation, thereby no question of Mn dissolution.\textsuperscript{[108]} The thermally stable surface-coated LCO (LNMO-LCO) was microstructurally analyzed using TEM, STEM, and electron energy loss spectroscopy (EELS) to understand the influence of LNMO on the surface and the layered structure of...
LCO (see Figure 7). The origin of ≈5 nm thick cation-mixing layer (Figure 7f) is possible due to cation mixing between Li and Co in LCO, and resulted in mixed, rock-salt (space group \( Fm\overline{3}m \)), and layered phases (see FFT patterns, Figure 7c–e), whereas, the thickness of the cation-mixing layer was reduced to ≈1 nm (Figure 7j), and is mainly due to the native site occupancy of Co, partial doping of \( \text{Ni}^{2+} \) and \( \text{Mn}^{3+} \) in Li and Co sites, respectively, during further calcination process while surface treatment resulting in clean layered phase (FFT pattern, Figure 7i). Importantly, the presence of relatively thin cation-mixing layer and thus nano-size pillar influenced surface of LNMO-LCO could act as a safeguarding film and improve the structural stability and electrochemical performance of fully charged state cathode materials.\(^{100}\) Nevertheless, the thickness of the cation-mixing layer should be as low and optimal to have better Li-ion diffusion rate and thereby rate capability. The electronic structure (oxidation states) of transition metals in LNMO-LCO, that could contribute to enhanced electrochemical performance, was confirmed from EELS on the selected region (Figure 7k) and resulted in EELS peaks (Figure 7l) corresponding to O K-edge, Mn L-edge, and Co L-edge at energy ≈517 eV, ≈618 eV, and ≈759 eV, respectively, during the second scan at 2 nm depth (first scan corresponding to conductive coating for TEM analysis and was ignored). In the initial scan, the Co L-edge constitutes of two peaks namely \( L_1 \) and \( L_2 \) at ≈759 eV and ≈774 eV, respectively corresponding to vacant Co 3d states. It is well known that the variation in the ratio of the intensity of \( L_1 \) and \( L_2 \) peaks was related to the oxidation state of the cations in the material, for example, a smaller intensity ratio \( L_1/L_2 \) represents the higher oxidation state of the cation corresponding to that L-edge peak.\(^{109,110}\) Therefore, to examine the variation in the oxidation state of Co, we have performed EELS scan for every 2 nm from the surface to 20 nm depth of the particle (marked in Figure 7k). Notably, the intensity of Co L₂-edge peak was increased after two initial scans and is a good insight of resulting in the higher oxidation state of Co as 4+ in co-existence with Co³⁺, which could improve electric conductivity by electron hopping mechanism between Co sites.\(^{111}\) Figure 7m shows the behaviour of \( L_1/L_2 \) intensity ratio vs the distance inside of the particle; it is imperative that over 6 nm, the intensity ratio was gradually decreased and constant in the region 16–20 nm. This implies that there is variation in the oxidation state of Co from 3+ to 4+ over the particle, co-existence of Co³⁺ and Co⁴⁺, and this Co⁴⁺ oxidation state could be attributed to the charge compensation with dopant Mn³⁺ ions. Hence, we believe such strategic surface coating could improve electrical conductivity and electrochemical performance of LCO at the high voltage and temperature operations.

Half-cells based on both samples bare-LCO and LNMO-LCO were tested electrochemically in the voltage range of 3.0–4.55 V. The initial reversible capacity for bare-LCO and LNMO-LCO were 213 and 215 mA h g⁻¹ with a respective Coulombic efficiency of 97.7% and 98.7% at 25 °C. Along with the increase in the initial discharge capacity owing to the presence of Ni as a surface coating and doping element, LNMO-LCO sample exhibited better rate performance when compared to that of bare-LCO as shown in Figure 8a. Importantly, LNMO-LCO delivered a discharge capacity of 212 mA h g⁻¹ at 0.1 C (1 C = 210 mA g⁻¹) and capacity retention of 153 mA h g⁻¹ at 7 C, and much higher to that of bare-LCO (85 mA h g⁻¹ at 7 C). Consequently, resulted in the significant improvement in specific energy density for LNMO-LCO samples when compared to bare-LCO (see Figure 8b) and could be attributed to the increase in electric conductivity was resulting from the co-existence of Co⁴⁺ along with Co³⁺ during doping of Ni and Mn. Furthermore, the cycling stability test was conducted at 60 °C (Figure 8c), the LNMO-LCO sample showed improved initial capacity (207 mA h g⁻¹) and capacity retention (70.5%) with a
discharge capacity of 146 mA h g$^{-1}$ after 200 cycles, when compared to bare-LCO (49.2% capacity retention). The same trend was observed in the cases of working voltage decay and specific energy density (see Figure 8d,e). It is usual case of increased capacity fading at elevated temperatures due to severe metal ions dissolution into the electrolyte and resulting in the formation of relatively thick SEI layers on the cathode and anode, thereby developing impedance in the cell and deteriorates the electrochemical mechanism. The cycle and rate performance data represents the combined positive effect of Ni and Mn-based surface coating material with superficial doping of Ni and Mn elements at the surface, and resulting cation-mixing layer on the particle surface to regulate the thicker SEI layer formation and undesirable structural transformations of the cathode material. The excellent performance of LCO after surface treatment is further confirmed by post-mortem analyses (FIB and XPS) and in situ XRD. The cross-sectional FIB image of bare-LCO particle (Figure 8f, after cycling at 60 °C) shows lengthy crack along the radial direction of the particle and are mainly attributed to the electrochemical/mechanical stresses and huge volume expansions during Li-ion intercalation/de-intercalation, thereby impedes the electrochemical performance of bare-LCO. Such cracks are significantly reduced in case of LNMO-LCO, due to successful superficial doping of Ni and Mn ions into LCO (see etching profile of XPS, Figure 8g) and resulted in the reduced volume changes at the crystal structure level, is evident from the in situ XRD analysis and comparison of c and a parameters variations during charging and discharging at 0.02 C (see Figure 9). However, further studies in the direction of the full-cell assembly with these materials are required to realize their compatibility in the practical applications and are the part of next section.

On the other hand, lithium metal phosphates are also considered as potential candidates for the surface coating of LCO and improved electrochemical performance, and most importantly, thermal stability was enhanced. The main reasons are as mentioned above, high Li-ion conductivity of lithium metal oxides/phosphates and thermally stable due to the presence of P=O bond.$^{[31,88]}$ For instance, Li$_3$PO$_4$ was coated on LCO$^{[112]}$ and showed excellent rate and cycle performance. Li$_3$PO$_4$ is not only having high ionic conductivity ($\approx 10^{-8}$ S cm$^{-1}$) but also excellent high-voltage and temperature stability and is revealed from their cycle and rate performance at both room temperature and 50 °C in the voltage range 3.0–4.5 V vs
Li/Li\(^+\). Such Li\(_3\)PO\(_4\) could be considered for coating (via simple spraying/ALD) on the as-fabricated electrodes under optimized levels, which could reduce the surface passivation and overall impedance of the cell. Moreover, such phosphate coatings are proved to be thermally stable in pouch cells under harsh conditions even at high charge cut-off voltage of 4.5 V vs Li/Li\(^+\).\(^{[88]}\)

### 3.4. Coating with Polymeric Materials, Ionic Conductors, and Glassy-Electrolyte Thin Films

Other research directions in the surface coating of LCO include polymeric materials, ionic conductors, glassy-electrolyte thin films etc. as surface coating materials. Though, various studies report the improvement in conductivity of LCO by coating with conductive/semi-conductive polymers such as PPy,\(^{[45]}\) polyacrylonitrile (PAN),\(^{[113]}\) PI-PVP,\(^{[53]}\) etc., but limited for practical applications due to severe safety problems associated with polymers. On the other hand, Li\(_{1.1}\)Al\(_{0.9}\)Ti\(_{1.7}\)(PO\(_4\))\(_3\) (LATP)\(^{[114]}\) and lithium phosphorous oxynitride (LiPON)\(^{[115]}\) were used as coating materials to increase Li-ion conductivity, however, either of the materials hardly showed improved long-term performance at high cut-off voltage. In the case of LATP, there is severe capacity fading over 100 cycles without Mg doping, although, enhanced cycling stability by simple doping of Mg into LCO together with LATP coating.\(^{[114]}\) This illustrates the importance of careful choice of coating material that could stabilize LCO layered structure along with protecting its surface during the electrochemical process. Besides, electrolyte with multifunctional additives which could form stable in situ artificial SEI layer on the cathode and improve oxidation stability of the electrolyte, have drawn much research attention to realize high energy density Li-ion cells at the high cut-off voltage (>4.3 V vs Li/Li\(^+\)). The various electrolyte additives (at optimized proportions of stabilizing SEI) that are used for LCO-based LIBs include 2,2'-Bis[4-(4-maleimidophenoxy) phenyl]propane (BMP), biphenyl (BP), trimethyl boroxine (TMB) etc.\(^{[116,117]}\) For example, 0.5% w/v BMP additive facilitated optimized thickness of SEI layer and enhanced the high voltage cycling stability, however, these additives could stabilise SEI but could not influence the stability of LCO layered structure.\(^{[117]}\) Hence, we believe the combination of a surface coating of LCO and usage of the electrolyte additives could achieve high energy density Li-ion cells with better cycle and rate performance. The following section describes the realization of the impact of surface coated-LCO in the full-cell configuration with electrolyte additives.

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**Figure 8.** a) Discharge capacity with an increasing of C-rate vs cycle number, b) specific energy of bare-LCO and LNMO-LCO from Figure 8a (specific energy was calculated using 1\(^{st}\) cycle at each C-rate), c) cycle performance of bare-LCO and LNMO-LCO at 60 °C, and d, e) trend of working voltage and specific energy over cycling at 60 °C, respectively. The voltage range is 3.0 to 4.55 V vs Li/Li\(^+\). f) Cross-sectioned ex situ FIB images of bare-LCO and LNMO-LCO particles after 200 cycles at 60 °C and g) XPS depth profiles of Ni 2p and Mn 2p peaks of LNMO-LCO sample with increasing of Ar\(^+\) etching time up to 2000 seconds.
4. Realizing Impact of Surface Coated – LiCoO₂ in the Full-Cell Configuration

The electrochemical performance of the surface-coated LCO samples (in the half-cell configuration) seems to be appealing and is evident from our earlier reports and literature, however, apart from the inherent properties of active material, the capacity degradation in the half-cell could also be mainly attributed to Li metal and the electrolyte in the case of high loading density.[118] Hence, coin-type full cell was designed and assembled using bare-LCO, MP-LCO as cathodes and natural graphite (NG) as anode in the (negative/positive) N/P ratio of 1.05 and was evaluated in the voltage range 3.0–4.35 V. The rate capability tests were performed with constant current (CC, 0.1 C) – constant voltage (CV, 0.05 C) mode during charging and CC mode with respective C-rates during discharge (1 C = 160 mA g⁻¹). The discharge capacity and energy density of the MP-LCO are 160 mA h g⁻¹ and ≈ 2.2 W h cc⁻¹, respectively, at 0.1 C with the capacity retention and energy density of 70.9% and 1.4 W h cc⁻¹ at 10 C, respectively, even at aggressive cut-off voltage of 4.35 V vs NG and follows the same trend for working voltage (Figure 10a–c). On the other hand, the bare-LCO suffered from the severe capacity and energy density fading at high current rates and making it almost impossible for practical applications. Furthermore, excellent cycling stability is evident from the capacity retention of MP-LCO (51%) is twice when compared to bare-LCO (28%) after 200 cycles at 60 °C (see Figure 10d). This full-cell data is in good agreement with that of half-cell as shown above (Figure 5a–f).

To the next level of research standards for industry applications, we have designed and assembled pouch-type full-cells (see inset of Figure 11a) with bare-LCO, LNMO-LCO as cathodes (loading level: 18 ± 0.1 mg cm⁻²) and NG as anode (loading level: 9 ± 0.2 mg cm⁻²) in the N/P ratio of 1.03 ± 0.2 and was evaluated in the voltage range 3.0–4.47 V with customized electrolyte 1.15 M LiPF₆ in EC:DMC:DEC (3:4:3 v/v) + 1% VC + 0.5% TMSB. To achieve high energy density of electrodes, we have used minimal proportions of electrochemically inactive materials (polymer binders and conductive additives) and thus the ratio of active material, conductive additive (or SBR in anode), and binder is 94:3:3 and 97:1.5:1.5 for cathode and anode, respectively. The formation cycle (Figure 11a) was performed by charging to 4.47 V with 0.1 C CC and 0.05 C CV modes and discharging to 3.0 V at 0.1 C CC modes (1 C = 180 mA g⁻¹). The reversible capacity of bare-LCO and LNMO-LCO is 179 and 180 mA h g⁻¹, respectively and the sudden drop (marked) while charging is attributed to the degassing step which could promote the long-term electrochemical performance by extracting gas formed during charging.[119] Interestingly, the surface-coated LCO (LNMO-LCO) not only enhanced capacity values but also cycle, rate capabilities and energy density. The LNMO-LCO cell showed improved discharge capacity and energy density of 145 mA h g⁻¹ and 1.95 W h cc⁻¹ at 2 C (Figure 11b,c), respectively when compared to bare-LCO (133 mA h g⁻¹, 1.7 W h cc⁻¹) at 2 C. In addition, though at a high loading level of active material (18 mg cm⁻²), LNMO-LCO delivered a high energy density of 2.42 W h cc⁻¹ and excellent cycle performance with capacity retention of 84% after 100 cycles at 4.47 V charge cut-off and 25 °C (Figure 11d,e). The high-temperature (at 45 °C, Figure 11f) also reveals improved performance of LCO by surface treatment, capacity retention of 83% with a discharge capacity of 150 mA h g⁻¹ after 50 cycles. This improved electrochemical performances and energy density of LNMO-LCO based Li-ion full-cells even at high loading level of electrodes, elevated temperatures, and high charge cut-off 4.47 V are in agreement with half-cell performance (Figure 8a–e), could be attributed to the high conductivity, chemical stability, and surface protection features of Ni and
Mn-based layered-structure hybrid surface coating. Simultaneously, the influence of full-cell design considerations, assembly techniques, and customized electrolytes (with additives) on the long-term cycle and rate capabilities cannot be ignored.

5. Conclusions and Critical Opinions

This progress report reviews the past and recent advancements in the surface engineering of LiCoO$_2$ for its better electrochemical performance at high operating temperature and cut-off voltage. We have also demonstrated our new outcomes on novel surface coating strategies for LiCoO$_2$, together with the importance of full cell studies (with high loading mass of electrodes) are mostly highlighted. Though, LiCoO$_2$ is commercially prominent in various portable applications, the practical reversible capacity ($\approx$ 140 mA h g$^{-1}$) and long-term cycle and rate capabilities are limited and mainly attributed to the high-voltage crystal structural deformation. The earlier work by Dahn’s group proposed that the poor high-voltage performance of LiCoO$_2$ is attributed to unknown moisture species on the surface, but not due to the crystal structural deformation, and further simple heating is enough for better electrochemical performance without any surface coating. However, from literature and our previous experimental evidences proved that the only simple heat-treatment could not sufficient to improve LiCoO$_2$ high-voltage performance, but systematic coating (with optimized level) on the surface of LiCoO$_2$ and their mechanical stability and chemical association with the host (bulk of LiCoO$_2$) and the electrolyte do certainly influence on the high operating temperature and voltage performance by reducing phase transitions and micro-cracks formation initiated from surface to the core. Hence, the ultimate goal is of developing novel hybrid surface protection layer to realize high-energy and high-voltage Li-ion cells even at adverse operating conditions such as high loading mass of electrodes, fast charge-discharge current rates, and the elevated temperatures.

The simple doping of LiCoO$_2$ with Al, Mg, and Ti or surface coatings such as metal oxides/phosphates/fluorides have been reported at $>$4.3 V cut-off. The first led to improved structural stability but was effective only below 4.35 V (vs Li), conversely reduced the reversible capacity. On the other hand, the later coating methods have been proven to effectively reduce the side reactions and HF attack because of reduced direct contact area between the electrolyte and cathode material even beyond 4.4 V (vs Li). However, these coatings led to increased charge transfer resistance upon cycles, thereby decreasing conductivity. Further hybridizing the surface engineering of LiCoO$_2$ with combined surface protection and doping strategies provide improvements in electrical/ionic conductivity and structural stability, thereby long-term cycle and rate performance at harsh conditions. Accordingly, our recent work on wet chemical route-based surface treating LiCoO$_2$ with simultaneous cation-mixing layer and Ni, Mn superficial doping, originated from Li-based Ni, Mn layered structure showed high energy density 3.2 W h cc$^{-1}$ at 0.1 C and improved cyclic stability (in half-cell) at 60 °C with a capacity retention of 70.5% after 200 cycles at 4.55 V cut-off, and excellent rate capability with a discharge capacity of 153 mA h g$^{-1}$ at 7 C, which is $\approx$2 times higher than bare-LiCoO$_2$. We realized from our post-mortem analyses and in situ XRD patterns, the
mechanistic behaviour of the novel hybrid surface coating layer can mitigate the undesired side reactions and structural volume expansions/degradations of LiCoO2 at the elevated temperatures and high current operations.

In addition to the better electrochemical performance of surface-coated LiCoO2 in half-cells, demonstration of their performance in full cells is required for practical applications. In the present work, Mg and P (MP) coated LiCoO2 and Li(Ni,Mn)O2 (LNMO) coated LiCoO2 showed respectable full-cell electrochemical performance. For instance, the MP-coated LiCoO2 with loading density of 3.6 g cc$^{-1}$ exhibited excellent rate capability with a capacity of 112 mA h g$^{-1}$ at 10 C, which is $\approx$14 times higher than bare-LiCoO2 at 4.35 V cut-off, improved cycle life at 60 °C and high energy density of $\approx$1.4 W h cc$^{-1}$ (400 W h kg$^{-1}$) at 10 C. Notably, surface-coated LiCoO2 showed better thermal stability with reduced exothermic heat flow at 4.45 V cut-off (vs Li metal). On the other hand, LNMO-coated LiCoO2 pouch-type full-cells with a high loading level of cathode material (18 mg cm$^{-2}$) showed enhanced capacity retention of 83% with a discharge capacity of 150 mA h g$^{-1}$ after 50 cycles at 4.47 V, 45 °C. Besides, various parameters such as active electrode areas of the cathode and anode, negative to positive (N/P) ratio, degassing step, and charging-discharging conditions, etc. need to be considered while designing a full-cell to realize high energy density Li-ion cells. Yet, Li-ion full-cells with high energy density and high voltage would be mostly dependent on preparing competitive high voltage and capacity cathode materials. Hence, it is prerequisite to develop novel strategies for surface coating materials by considering their compatibility with the electrolyte/electrolyte additives and the bulk of host (LiCoO2) even at the high charge cut-off voltage. For instance, Kraytsberg et al.$^{[120]}$ successfully coated MgF$_2$ on as-prepared spinel LiMn$_{1.5}$Ni$_{0.5}$O$_4$ powder using the ALD technique, and this strategy enhanced the electrochemical performance of the spinel cathode material, even at the high cut-off voltage of 4.7 V (vs Li) and high operating temperature (45 °C), by mitigating the possible undesirable side reactions of electrode material with the electrolyte, as the ALD-based MgF$_2$ film acts as a protective layer. Such ALD-based coating strategies could be employed for LiCoO2 and other cathode materials to achieve high energy density under adverse operating conditions. Not only surface treating of LiCoO2 (or other cathode materials) as-prepared powders with various coating methods but also it is advantageous to consider the re-coating of as-prepared surface-coated electrodes, which could enhance the interfacial stability between the surface of coated-cathodes and the electrolyte to promote the long-term cycle life of Li-ion cells. For example, from our preliminary data (not shown here), we have observed 2ALD coating or simple hand spraying of Al$_2$O$_3$ on LNMO-coated LiCoO2 as-prepared electrodes showed ultra-stable cycle life even at a high cut-off voltage (4.55 V vs Li). Putting together a strategical surface modification of electrode materials and the surface treatment of their high loading electrodes, customized electrolyte system, and optimized full-cell design; it is presumed to develop high energy and high voltage Li-ion cells for the next-generation practical applications.

6. Experimental Section

Synthesis of MP-LCO: MP-LCO was prepared by using simple solution process as illustrated in Figure 1. 0.8 g of magnesium acetate (99 wt% assay, Sigma-Aldrich) was dissolved in 40 g of absolute ethanol (99 wt% assay, OCI, Korea) with a mild heating at 65 °C under isothermal bath. Then, 0.18 mL of H$_3$PO$_4$ (85 wt% assay, Sigma-Aldrich) was
added to above solution and resulted in the formation of white sol. Then, this white solution was kept for 20 min under vigorous stirring. 100 g of bare LiCoO2 was slowly added to the resultant solution and vigorously mixed for 1 h at 65 °C. The mixture was transferred into the silicon bath at 110 °C and boiled with stirring until the solvent was fully evaporated. The remained powder was transferred into a drying oven at 120 °C for 1 h. Finally, the resulting powder was annealed at 600 °C for 5 h under air condition with a heating rate of 5 °C min⁻¹ in a box furnace.

Synthesis of LNMO-LCO: LiNi0.5Mn0.5O2 coated LiCoO2 was prepared using the sol-gel method. Add stoichiometric proportion of lithium acetate, nickel acetate, and manganese acetate (Sigma-Aldrich, South Korea) to approximately 70 mL of distill water (corresponding to 1 wt% LiNi0.5Mn0.5O2). The above solution was stirred for a few minutes till precursors are completely dissolved and slowly added 20 g of LiCoO2. The resultant solution was further stirred at room temperature for 30 min (to completely miscible LiCoO2 with precursor solution) and then further stirred under isothermal bath at 120 °C for 4 h to evaporate the solvent and formation of a gel. The thus obtained partially dried powder/gel was dried in drying oven at 110 °C for 2 h. Completely dried precursor powder was transferred to box furnace for calcination process at 750 °C for 3 h in air atmosphere. The calcined powder was ground well followed by a sieving process. Thus obtained 1 wt% LiNi0.5Mn0.5O2 coated LiCoO2 powder.

Electrodes Fabrication for The Half cell Configuration: The electrodes were composed of 94 wt% active material, 3 wt% super P as a conductive additive, and 3 wt% poly(vinylidene fluoride) (PVDF) as a binder. The electrochemical properties were characterized by assembling coin-type samples were 7 ± 0.2 N/P capacity ratio and operated 2.5 cm with a 1.03 ± 0.5% TMSB. The electrode

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