Advancements of Cathode Material for Rechargeable Lithium-Ion Batteries: Progress, Challenges, and Electrochemical Performance

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Received: March 29, 2025
Revised: May 21, 2025
Accepted: June 26, 2025

ABSTRACT

The increasing global need for efficient and environmentally friendly energy storage solutions has brought rechargeable lithium-ion batteries (LIBs) into the spotlight of technological advancement. A key element affecting LIB performance is the cathode material, which significantly influences factors including energy density, cycle life, rate capability, and overall stability. This review discusses recent developments in cathode material design, focusing on strategies that improve electrochemical performance. Traditional cathode materials like layered $LiCoO_2$ and spinel $LiMn_2O_4$ confront issues like capacity fading, structural deterioration, and inadequate performance at high currents. In response, researchers are now exploring advanced material designs, including core-shell structures, hierarchical porous frameworks, 3D interconnected networks, and surface-modified nanocomposites. These innovative structures provide various benefits, such as reduced lithium-ion diffusion distances, better structural stability during cycling, and enhanced electron transport kinetics. Additionally, the use of conductive coatings, dopants, and multifunctional binders has further boosted the electronic conductivity and structural robustness of cathode materials. New synthesis methods, including sol-gel processing, hydrothermal techniques, atomic layer deposition (ALD), and 3D printing, allow for precise control over morphology, composition, and nanoscale porosity. Electrochemical tests, including cyclic voltammetry (CV), Galvanostatic charge-discharge (GCD), and Electrochemical impedance spectroscopy (EIS), show that these new cathode designs consistently offer higher specific capacities, improved rate performance, and extended cycle life compared to traditional options. This review highlights the vital role of material design in boosting LIB performance and suggests future paths for creating high-capacity, durable, and safe lithium-ion battery systems. The findings presented here aim to steer next-generation energy storage technologies toward enhanced efficiency and sustainability.

Keywords: Cathode Material, Lithium-Ion, Electrochemical Performance, galvanostatic charge-discharge, sustainability

1.0 INTRODUCTION

Human progress is inherently linked to energy consumption, with global energy demands rising rapidly due to industrialization and population growth. Historically, these needs have been met predominantly by fossil fuels and nuclear power. However, the environmental repercussions of fossil fuel combustion, particularly greenhouse gas emissions contributing to global warming, alongside the finite nature of these resources, have intensified the search for cleaner, more sustainable alternatives. Transportation, primarily powered by

internal combustion engines, is a major contributor to CO_2 emissions and a significant driver of global energy consumption. Global energy demand is expected to exceed 700 quadrillion BTU by 2035 (2.19×10^{-14} Mtoe), underscoring the urgency for energy generation and storage technologies innovations(Byrne & Kurdgelashvili, 2011). While renewable energy sources like solar, wind, and tidal have shown promise, their intermittent nature necessitates reliable and efficient energy storage systems. Electricity, as a central component of energy use, demands advanced storage technologies to ensure consistent availability, particularly when generated from variable sources. In this review, LIBs have emerged as critical components for modern energy storage, powering devices ranging from portable electronics to electric vehicles. The performance of LIBs heavily depends on the cathode material, which governs energy density, cycling stability, and voltage. The journey began in the 1970s with Whittingham's use of TiS_2 as an intercalation host, followed by the introduction of lithium cobalt oxide ($LiCoO_2$) by Goodenough and Mizushima in the 1980s, which led to the first commercial LIBs (Whittingham & Yoshino, 2019). Despite $LiCoO_2$'s high conductivity, energy density, and favorable structural properties, its limitations, such as safety concerns and cost, have driven research toward alternative materials like nickel, manganese, and iron-based compounds (VS et al., 2024). As we confront the challenges of sustainable development and energy security, the evolution of high-performance, environmentally friendly, and long-lasting rechargeable batteries remains at the forefront of modern electrochemical research. Developing advanced cathode materials with improved capacity, safety, and stability is essential to enable the next generation of energy storage technologies.

2.0 HISTORY OF LITHIUM-ION BATTERIES

Early lithium battery designs utilized titanium disulfide (TiS_2) as the cathode and lithium metal as the anode. While TiS_2 performed well as a cathode, cycling tests revealed that lithium metal anodes experienced uneven dendritic growth, as depicted in Figure 1. Over the past two decades, the portable electronics industry has seen rapid growth, primarily driven by advances in LIB technology. LIBs have clear advantages over traditional battery systems, including lead acid, nickel-cadmium, and nickel-metal hydride, thanks to lithium's high electronegativity and low atomic mass (6.94 g/mol), which contribute to superior energy and power density(Ye, 2014). A major milestone in materials electrochemistry has been the innovation of LIBs. In 1991, Sony Corporation successfully launched commercial rechargeable LIBs with non-aqueous electrolytes. Their compact design, lightweight structure, long operational lifespan, high working voltage (around 4 V), and energy densities ranging from 150 to 250 Wh/kg made them the preferred energy storage solution for many rechargeable applications(Zhu et al., 2022). These properties revolutionized the design of portable electronics such as MP3 players, laptops, and mobile phones, driving the annual production of billions of LIBs. LIBs also offer cost-effective energy storage and delivery, making them essential for emerging applications like grid-integrated renewable power systems and environmentally friendly vehicles,

particularly hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs). The foundation for LIB technology dates back to 1912 when G.N. Lewis first explored lithium batteries, and the first non-rechargeable lithium cells entered the market in the 1970s(Itani & De Bernardinis, 2023). In 1980, rechargeable batteries using lithium metal anodes were developed, offering high voltage and capacity but facing serious safety issues due to instability. A pivotal advancement was using lithium ions in host intercalation compounds, which allowed for reversible lithium storage without significant structural degradation. In 1986, lithium intercalation into graphite was shown to possess promising electrochemical properties, shifting research focus toward safer lithium-ion systems instead of lithium-metal anodes.

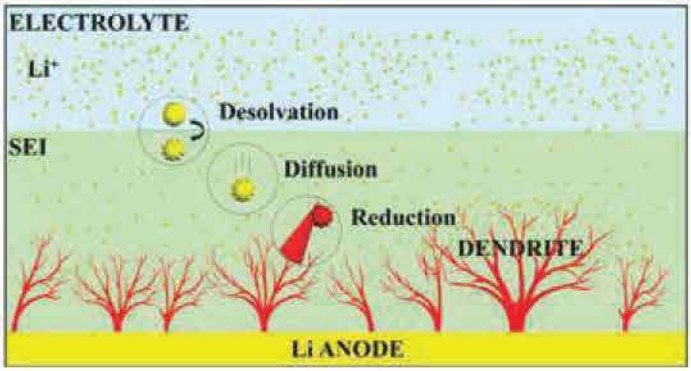

Figure 01: Lithium dendrite accumulation at the anode interface (Mishra & Patial, 2024).

3.0 WORKING PRINCIPLE FOR LIBS

LIBs generally consist of four key components, as shown in Figure 2a: a lithium-ion intercalation anode, a cathode, an electrolyte, and a separator. The fundamental operation of LIBs depends on the reversible movement of liathium ions (Li^+) between the anode and cathode host structures, along with redox reactions during charging/discharging cycles. During charging, Li^+ ions are extracted from the cathode, travel through the electrolyte and separator, and finally intercalate into the anode. In the discharge cycle, these ions travel back to the cathode. Simultaneously, electrons flow through an external circuit from anode to cathode during discharge, providing electrical energy, and in the reverse direction during charging. This reversible electrochemical process is a hallmark of solid-state chemistry and illustrates LIBs' capacity for charge storage. Three key processes occur during battery operation: solid-state diffusion of Li^+ ions, charge transfer at the electrode electrolyte interface, and ion transport within the electrolyte. While the energy conversion efficiency of LIBs is influenced by several variables, it is strongly dependent on the structural and chemical properties of the electrode, electrolyte, and separator materials. To enhance LIB performance, improving

energy storage capability, conversion rate, and overall device efficiency is crucial, as these factors are directly linked to the underlying electrochemical reactions. Among all the components, electrode materials, particularly cathodes, are central to LIB development, especially in addressing the growing demands of the electric vehicle (EV) market. Notably, current cathode materials often lag behind anode materials in terms of specific capacity. As illustrated in Figure 2b, cathode materials represent the heaviest component by weight in a LIB cell. Furthermore, the overall storage capacity of LIBs largely depends on both the quantity and the rate at which Li^+ ions can be extracted and reinserted into the cathode. This underscores the cathode's critical role relative to the other cell components. According to the Argonne National Laboratory's Battery Performance and Cost (BatPaC) model, cathode materials such as $[Li_{1.05}(Ni_{4/9}Mn_{4/9}Co_{1/9})_{0.95}O_2]$ are nearly twice as expensive as commonly used anode materials like graphite. This cost disparity arises from the cathode's influence on key battery parameters, operating voltage, rate capability, and energy density, constrained by its inherent theoretical capacity and thermodynamic properties. Consequently, there is a pressing need to develop cost-effective, high-performance cathode materials to advance LIB technologies and meet the evolving requirements of the EV sector.

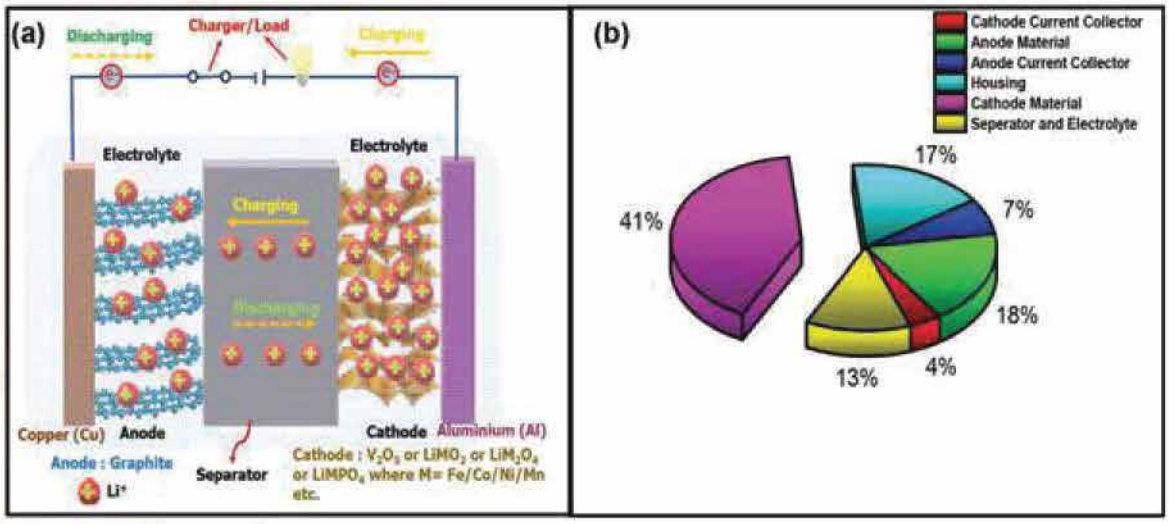

Figure 02: a) Fundamental working principle of charge/discharge processes in LIBs. b) Mass allocation among the various components of lithium-ion batteries (Kotal et al., 2022).

4. 0 CATHODE MATERIALS FABRICATION TECHNIQUES

4.1 Sol-Gel Method

The sol-gel technique is a wet-chemical method used to build coatings by hydrolyzing and condensing metal alkoxides or inorganic salts, which form a gel-like network that is then dried and calcined to produce the final material (Mishra & Patial, 2024). This approach allows for precisely incorporating dopants, providing excellent control over chemical composition, particle size, and surface properties. Common materials like Al_2O_3, TiO_2, and ZrO_2 are often used as cathode coatings to improve cycling stability and minimize unwanted reactions with the electrolyte. Key advantages of the sol-gel process include its low processing temperature, adaptability to complex shapes, and ability to produce functional and hybrid coatings.

4.2 Solid State Synthesis

Solid-state synthesis involves heating and mixing solid precursors to form durable coatings through reaction and diffusion processes(Jangid et al., 2024). This high-temperature method is widely used to produce chemically stable and long-lasting coatings. Materials such as doped oxides, phosphates, and ceramics, like $LiNi_{0.5}Mn_{1.5}O_4$ and $LiFePO_4$, are particularly well-suited for cathode applications using this technique. The method offers several advantages, including cost-effectiveness, scalability for mass production, and strong mechanical and thermal stability. However, precise control of temperature and reaction time is essential to avoid unwanted phase transitions or non-uniform coatings.

4.3 Hydrothermal Synthesis

Hydrothermal synthesis involves the use of high pressure and temperature within a sealed reactor to produce crystalline coatings (Zhu et al., 2022). This method is commonly applied to fabricate precise and well-defined metal oxide or phosphate coatings. Utilizing water as the solvent offers advantages such as high crystallinity, controlled particle growth, and an environmentally friendly process. However, it is time-consuming and is limited to materials that can withstand extreme pressure conditions.

4.4 Atomic Layer Deposition (ALD)

ALD is a vapor-phase technique that prepares thin, uniform coatings with atomic-level precision by introducing precursors in a self-limiting, step-by-step process (Leskelä & Ritala, 2002). Since only one monolayer is deposited per cycle, this method allows for excellent control over film thickness and uniformity. ALD is commonly used to coat cathode materials like NMC ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$) and $LiCoO_2$ with compounds such as Al_2O_3, $LiAlF_4$, and MgO. This technique enhances high-voltage and thermal performance, improves the stability of the cathode-electrolyte interface, and ensures pinhole-free coatings. However, due to its high cost and slow deposition rate, ALD is best suited for specialized applications that demand exceptional precision.

4.5 Electrochemical Deposition

This method involves the direct deposition of coating materials onto the cathode surface from an electrolyte solution under the influence of an electric field. It is commonly used to apply conductive coatings such as metal oxides, phosphates, or carbon layers. The technique is effective for coating complex surface geometries and yields thin, uniform films with high precision. However, it demands precise control over deposition parameters and the use of specialized equipment.

4.6 Freeze Drying Method

This process starts with freezing a precursor solution, followed by vacuum drying to remove the solvent through sublimation. The resulting material is porous, lightweight, and has a high surface area. It is used to fabricate hierarchical layered cathodes or nanostructured coatings that promote better ion diffusion and conductivity. This method enables the production of lightweight cathodes with improved electrochemical performance while maintaining active surface area and being environmentally friendly. However, its limitations include challenges in scaling up and the need for precise freeze-drying conditions to ensure uniformity.

5. 0 LAYERED LITHIUM TRANSITION METAL OXIDES

5.1 Primary Layered Transition Metal Oxides ($LiMO_2$, M=Co, Ni and Mn)

Lithium cobalt oxide ($LiCoO_2$), lithium nickel oxide ($LiNiO_2$), and lithium manganese oxide ($LiMnO_2$) are three commonly used intercalation materials for cathodes in rechargeable LIBs. Among these, $LiCoO_2$ is highly prevalent due to its easy handling and straightforward fabrication process. It can be easily synthesized using both chemical and solid-state methods.

5.1.1 Lithium Cobalt Oxide (LCO)

Since 1980, layered LCO has been the main commercial cathode material for rechargeable LIBs, attracting significant interest. LCO features an ordered layered structure with the R3m space group. The first-generation LIBs consisted of graphite as the anode, LCO as the cathode, and an electrolyte blend of dimethylene carbonate (DMC), ethylene carbonate (EC), and $LiPF_6$. During charging, lithium ions (Li^+) migrate from the LCO cathode through the electrolyte to the graphite anode, while electrons travel externally from the cathode to the anode. During discharge, both Li^+ ions and electrons move in the opposite direction. Although LCO has a theoretical capacity of 274 mAh/g due to the complete transfer of Li^+ ions, its structure becomes unstable at high levels of delithiation, especially when more than half of the lithium is removed (i.e., when x exceeds 0.5) (Antolini, 2004). The upper cut-off potential of LCO is about 4.2 V (Li/Li^+), resulting in a practical capacity of approximately 140 mAh/g. In contrast, the expense and toxicity of cobalt pose

6.1 Nickel Layered Oxide ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$)

Lithium-insertion compounds are valued for their high-rate capability, chemical stability, cost-effectiveness, and security. $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NCM) is a prominent layered oxide cathode material known for its improved structural stability at greater voltages, better environmental compatibility, reversible capacity, inexpensive, and high thermal stability. However, traditional bulk micro-sized cathode materials limit electrochemical performance and do not meet battery requirements. Therefore, researchers have focused on altering the morphology and size of electrode materials. Nanostructured materials have surmounted the limitations of bulk size, enhancing the electrochemical performance of NCM. Various nanostructures, for example, nanoparticles, hollow spheres, nanowires, and porous materials, have been developed to improve particle-particle contact and optimize particle size, ultimately enhancing rate capability. NCM, with its hexagonal α-$NaFeO_2$ structure, features a 2D architecture that facilitates Li-ion diffusion along the a or b axis. The Li-ion diffusion tunnels run parallel to the layers, comprising planes like (010), (100), (110), and (001)(Xu et al., 2017). The planes, involving corner-sharing NiO_6, CoO_6, and MnO_6 units, are electrochemically inactive as they do not provide an effective path for Li^+ ion transport. However, NCM nanostructures that expose the (Jangid et al.) active facets can significantly enhance electrochemical performance. Li et al. synthesized NCM nanoplates with facets using ethylene glycol under continuous stirring at 85 °C for 8 hours(Li et al., 2014). The material was dried overnight at 120 °C, then preheated at 450 °C and calcined at 800-900 °C for 8–16 hours. Ethylene glycol played a crucial role in forming the material and acted as a chelating agent. The synthesized NCM nanoplates' morphology and size were confirmed using transmission electron microscopy (TEM), while high-resolution TEM (HRTEM) revealed the crystallographic features of the material, as shown in Figures 3(a, b, c, and d). The CV analysis of NCM nanoplates, as shown in Figure 3(e and f), conducted between 2.5 - 4. 5 V at a scan rate of 0.1 mV/s, showed a redox peak between 3.6 and 4.0 V, indicating effective Li- ion movement and electron migration. NCM prepared at 850 °C for 12 hours exhibited the smallest potential gap of 0.18V, suggesting fast redox reactions and electron transfer during Li- ion intercalation/deintercalation. The CV symmetry reflects excellent reversibility of the charge/discharge process. Additionally, charging/discharging tests as Figure in 3 (g and h) at 0.1 C revealed that NCM at 850 °C for 12 hours demonstrated the highest discharge capacity of 207. 6 mAh/g with 93. 1% Coulombic efficiency (CE). After 50 cycles, the discharge capacity remained at 180.3 mAh/g, indicating an 89. 4% capacity retention as shown in Figures 3(i and j). The cyclic performance for the boost in the current density of 1C is shown in Figure 3(k and l). The NCM nanoplates also displayed superior performance at higher current densities, with capacities of 169.8, 160.5, and 149.3 mAh/g at 2.5, and 7C, correspondingly, as shown in Figures 3 (m and n). Despite these improvements, similar to $LiCoO_2$ (LCO), NCM experiences rapid capacity fading during cycling. This issue has prompted the exploration of new materials to further enhance performance.

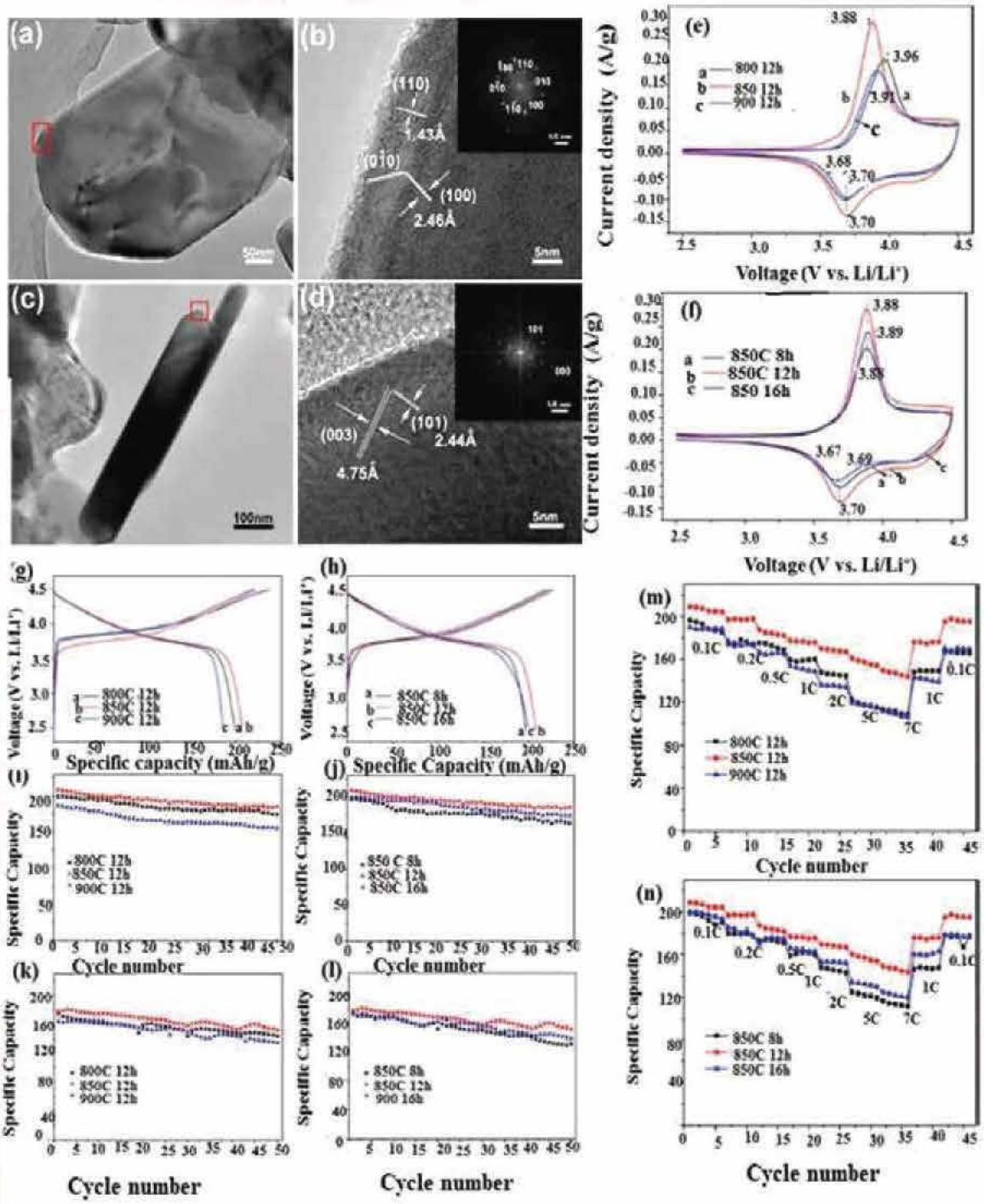

Figure 03: (a, c) TEM images showing the front and side views of NCM particles sintered at 850 °C for 12 hours. (b, d) HRTEM images and corresponding Fast Fourier Transform (FFT) patterns of the front view

shown in (a) and side view along the c-axis shown in (c). (e, f) CV curves of NCM nanoplates synthesized at varying (e) sintering temperatures and (f) sintering durations. (g, h) GCD profiles at 0.1C over a voltage window of 2.5–4.5 V. (i, j) Cycling performance at 0.1C and (k, l) cycling stability at 1C. (m, n) Rate capability of NCM nanoplates at different (m) sintering temperatures and (n) sintering times, measured across a voltage range of 2.5 – 4.5 V and current densities ranging from 0.1C to 7C (Li et al., 2014).

7.0 STRUCTURAL TUNING OF LAYERED LITHIUM TRANSITION METAL MATERIALS

7.1 Double-Layer Coating

Yoon-Sung et al. demonstrated enhanced cycling performance and thermal stability in LIBs by applying a dual-layer coating to the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM) cathode(Yoon-Sung et al., 2015). This dual coating comprised Al_2O_3 nanoparticles and a conductive poly(3,4-ethylenedioxythiophene)-block-poly(ethylene glycol) (PEDOT-co-PEG) copolymer, as illustrated in Figure 4(a). Al_2O_3 nanoparticles (2– 4 nm) were mixed with NCM through ball milling for 4 hours to prepare Al_2O_3-coated NCM (Al-NCM). The Al-NCM powder was then dispersed in a 0.5% PEDOT-co-PEG/methyl pyrrolidine solution and stirred at 60°C for 4 hours. The resulting dual-layer coated NCM (dl-NCM) was filtered and dried at 100°C. For comparison, a single-step coating was also carried out to produce the conductive polymer-coated NCM (cp-NCM). TEM images (Figure 4 b–e) confirmed the uniform surface coatings. Bare NCM (Figure 4b) indicated no coating, while cp-NCM presented a smooth conductive polymer layer. Al-NCM displayed a rough coating layer 18–38 nm thick (Figure 4d), while dl-NCM had a smoother dual-layer surface (Figure 4e). Electrochemical testing revealed that the pristine NCM delivered an initial discharge capacity of 170.1 mAh/g, decreasing slightly to 163.3 mAh/g after 100 cycles at 0.5C (Figure 4f). Although Al-NCM illustrated minimally reduced initial capacity due to increased interfacial resistance, cp-NCM and dl-NCM exhibited enhanced capacity retention and improved cycling behavior, attributed to improved interfacial conductivity. Q. Ran et al. further explored a novel surface modification strategy by combining gradient phosphate polyanion doping with a polyaniline (PANI) coating(Ran et al., 2019). The composite, denoted P-NCM@Li_3PO_4-PANI, was prepared in two steps: (1) phosphate (PO_4^{3-}) gradient doping followed by in-situ Li_3PO_4 formation via reaction with Li-residues; and (2) wet coating with PANI polymer. The coating was characterized using TEM, HRTEM, and selected area electron diffraction (SAED), as shown in Figure (4 i–p). Figure 4(m) revealed lattice fringes corresponding to the (011) plane of Li_3PO_4 (0.355 nm spacing), and SAED patterns confirmed the crystalline nature of Li_3PO_4 and amorphous PANI coatings. Electrochemical measurements demonstrated that surface modifications did not significantly alter voltage profiles (Figure 4q), indicating that the gradient doping and coatings preserved the structural integrity of the material. Coulombic efficiencies were 81.4% for pristine NCM, 75.6% for phosphate-doped NCM (P-NCM), and 77.1% for P-NCM@Li_3PO_4-PANI, with slight reductions attributed to increased interfacial impedance and decreased active material content. Nonetheless, the rate capability of P-NCM@Li_3PO_4-PANI was superior, as shown in Figure 4r, due to improved electronic

and ionic conductivity from the PANI layer. Zhang et al. mentioned in-situ fabrication of Ni-rich $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ coated with Li_3PO_4. The NCM@Li_3PO_4 composite exhibited enhanced reversible capacity, rate capability, and long-term stability. Such surface engineering strategies, including doping and coating, significantly influence the bandgap, cation ordering, and charge distribution, thereby boosting the electrochemical performance of NCM cathodes(Zhang et al., 2020). With the rising demand for electric vehicles (EVs), LIBs require cathode materials with intense energy/power density, excellent cycle life, and fast-charging capabilities. While commercial cathodes like $LiCoO_2$, $LiNiO_2$, and $LiMnO_2$ face limitations in energy density, lithium-rich layered oxides such as $Li_{1+x}Mn_{1-x-y}M_yO_2$ ($0 < x < 1$; M = transition metals) have emerged as promising alternatives, offering capacities >250 mAh/g and energy densities up to 900 Wh/kg. However, challenges such as irreversible capacity loss, voltage fading, and low-rate performance persist. These issues are primarily caused by phase transitions (layered-to-spinel), formation of dislocations, and the evolution of unstable redox couples during cycling. To address these challenges, extensive efforts are being directed toward surface-modified Li-rich cathodes, such as $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$, which exhibit improved capacity and cycling stability.

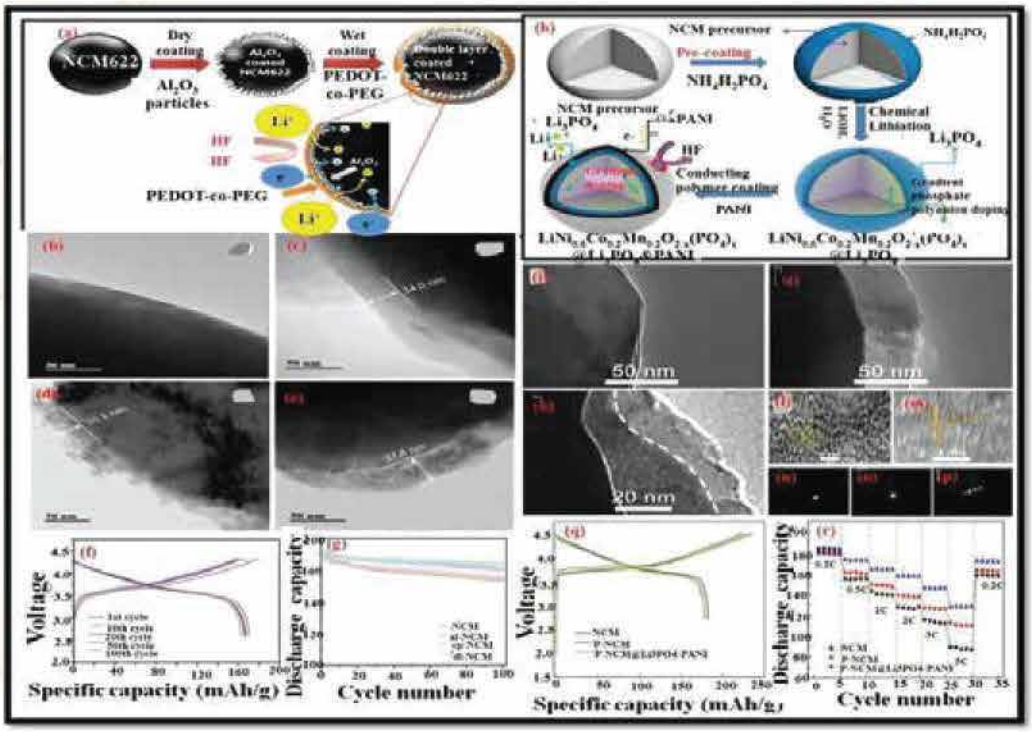

Figure 04: (a) Graphical illustration of single and dual-layer coatings of Al_2O_3 and PEDOT-co-PEG, TEM images of (b) pure NCM, (c) conductive polymer-coated NCM (cp-NCM), (d) alumina-coated NCM (al-

NCM), and (e) dual-coated NCM (dl-NCM), (f) voltage curves of the dl-NCM electrode, (g) discharge capacities of Li^+ ion cells assembled with pure NCM and surface-modified NCM electrodes. (h) Representation for the preparation of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_{2-x}$@$Li_3PO_4$-PANI (P-NCM@$Li_3PO_4$-PANI), TEM images of (i) pure NCM, (j) P-NCM, (k) P-NCM@Li_3PO_4-PANI samples, HRTEM images of (l) NCM, (m) Li_3PO_4 layer, selected area (electron) diffraction (SAED) patterns of (n) PANI coating, (o) Li_3PO_4 coating layer, (p) P-NCM, (q) initial charge/discharge plots, and (r) Differentiation of rate performance (2.7 - 4.5 V)(Li et al., 2018; Yoon-Sung et al., 2015).

8.0 OLIVINE {LITHIUM IRON PHOSPHATE ($LIFEPO_4$)}

Olivine-type materials used in LIB cathodes are typically represented as $LiMPO_4$ (where M = Fe, Co, Ni, Mn), with $LiFePO_4$ being the most widely used due to its inexpensive, non-toxicity, thermal stability, and excellent cycle life(Shiratsuchi et al., 2009). Although cathodes like $LiMnPO_4$, $LiNiPO_4$, and $LiCoPO_4$ operate at higher voltages (4.1–4.8 V) than $LiFePO_4$ (3.5 V), they generally have lower capacities. Introduced by Goodenough in 1997, $LiFePO_4$ features an olivine structure with a strong polyoxyanionic framework, which stabilizes oxygen and ensures safety even at high charge states. However, its low electronic conductivity (~10^{-9}–10^{-10} S/cm) and gradual lithium-ion diffusion limit its rate performance compared to layered and spinel cathodes. To address these drawbacks, researchers have employed strategies like particle size reduction, doping with foreign atoms, surface coatings, and carbon-based nanofillers such as carbon nanotubes, graphene, and 3D-mesoporous carbons. These nanomaterials enhance conductivity through their high surface area and favorable morphology, significantly improving the electrochemical behavior of $LiFePO_4$. Carbon coating, in particular, is considered one of the most effective and conventional approaches to boost its performance in energy storage applications.

9. 0 IMPACT OF THE CATHODE-ELECTROLYTE INTERACTION ON THE PERFORMANCE OF LI-ION BATTERIES

Next-generation lithium-ion batteries operating at higher voltages (up to 4.8 V) require robust and stable cathode electrolyte interphases (CEIs) due to the intensified interfacial reactions between cathode materials and electrolytes(Kazzazi et al., 2021). CEIs form spontaneously during charge/discharge cycles through complex surface redox reactions, as cathode materials typically nucleophilic and Lewis basic interact with the oxygen atoms of electrolyte components. When the LUMO of the cathode lies below the HOMO of the electrolyte, oxidation reactions occur, resulting in the development of CEI layers rich in organic compounds as shown in Figure 5a. Ni-rich layered oxide cathodes, though advantageous for their high energy density and low cost, suffer from structural instability due to Ni^{2+} migration into Li sites, oxygen loss, and intergranular cracking, which lead to parasitic reactions, thickened CEI, increased impedance, and capacity

fade. To address these challenges, different strategies have been developed, such as atomic layer deposition (ALD), polymeric coatings (e.g., aromatic polyamides), cation doping (e.g., Al^{3+}, Cr^{3+}, Mg^{2+}), and surface coatings (e.g., Al_2O_3, TiO_2, SiO_2, sulfated ZrO_2), all aimed at suppressing side reactions, improving structural stability, and enhancing lithium-ion mobility. ALD produces conformal layers without altering the cathode structure, while polymers provide flexible, uniform protection against electrolyte degradation, as shown in Figure 5b. Cation doping minimizes cation mixing, adjusts lattice parameters, and strengthens M–O bonds, thereby enhancing structural integrity and electrochemical performance. Additionally, electrolyte additives like FEC and $LiPO_2F_2$ form LiF-rich CEIs that stabilize the interface but lose effectiveness once decomposed, prompting the use of high-concentration electrolytes to maintain durable CEIs derived from salt decomposition. Li-free coatings offer further advantages by avoiding transition metal redox changes, with materials like Al_2O_3, TiO_2, and sulfated ZrO_2 effectively reducing cation mixing and parasitic reactions. These multifaceted approaches aim to construct chemically and mechanically stable CEIs to ensure the longevity and high performance of advanced lithium-ion batteries.

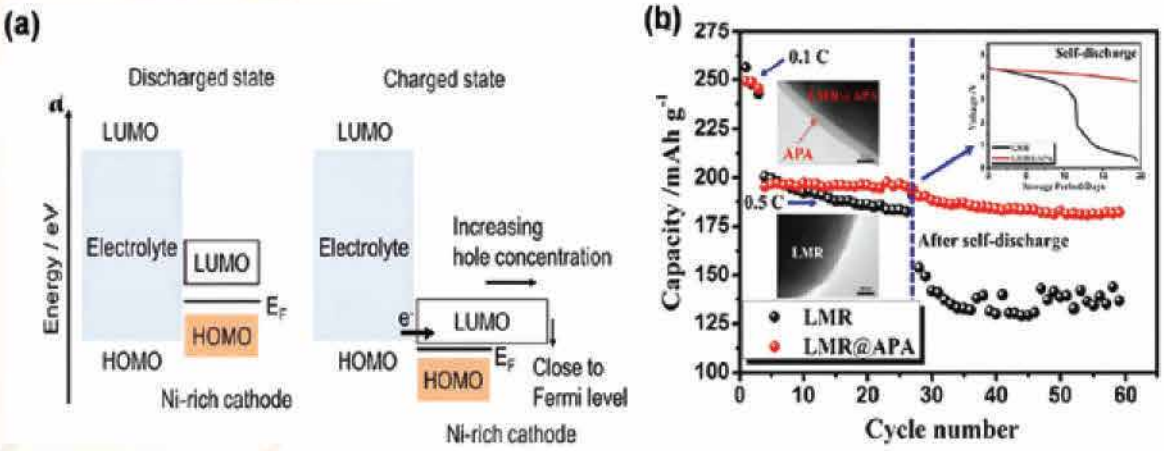

Figure 05: (a) Illustration of electrolyte oxidation and decomposition occurring at the cathode surface and (b) TEM image showing the APA-coated LMR cathode along with its cycling performance(Takahashi et al., 2020; Ye et al., 2021).

10.0 CHALLENGES AND TRADE-OFFS

While architectural innovations in cathode materials have led to notable improvements in electrochemical performance, several challenges continue to hinder their large-scale application in lithium-ion batteries. One major issue is the scalability of complex nanostructured designs, which often rely on intricate processes like templating, etching, and multi-step synthesis. These methods, although effective at the lab scale, are difficult to standardize and reproduce on an industrial scale, leading to inconsistencies in material quality and

increased production costs. Additionally, many advanced cathode architectures, such as core–shell or highly porous structures, require expensive precursors and precise control over morphology, making them costly to produce. This complexity in synthesis must be addressed with scalable, cost-effective methods to ensure commercial viability. Another critical concern is interface instability and structural degradation during battery cycling. Volume changes in cathode materials can disrupt the interface with the electrolyte, causing reduced ionic conductivity and long-term capacity loss. Furthermore, certain high-energy-density materials are susceptible to phase transitions, which can compromise both stability and performance. Environmental and safety concerns also arise, particularly with materials that involve toxic or scarce elements like cobalt or nickel. These not only raise sustainability issues but also pose risks such as thermal runaway or electrolyte leakage under mechanical or thermal stress. Overcoming these challenges will require a balanced approach that combines performance with scalability, safety, and environmental responsibility, paving the way for the practical implementation of next-generation lithium-ion batteries.

11.0 EMERGING TRENDS AND FUTURE PROSPECTS

The design of cathode materials for LIBs is rapidly evolving due to the growing demand for higher energy densities, increased safety, and longer cycle life in portable electronics, electric vehicles, and grid storage systems. One of the most emerging advancements in this field is the integration of artificial intelligence (AI) and machine learning (ML) into the discovery and optimization of materials. These tools can analyze vast datasets to predict novel cathode compositions with superior electrochemical performance, identify optimal particle sizes and morphologies, and significantly accelerate the research process by reducing reliance on traditional trial-and-error methods. Another transformative development is the use of 3D printing technology for fabricating advanced electrode architectures. This technique allows for precise control over microstructures, enabling the design of cathodes with hierarchical porosity, interconnected networks, and enhanced surface area, all of which contribute to better ion transport and capacity retention. Furthermore, hybrid and composite cathode systems, particularly polymer–inorganic hybrids, are gaining attention due to their ability to combine the electrical conductivity and stability of inorganic materials with the mechanical flexibility and processability of polymers. These hybrid structures not only enhance performance but also improve the structural integrity and safety of batteries during charge-discharge cycles. In addition, solid-state electrolytes (SSEs) are being explored as safer alternatives to liquid electrolytes, offering the potential for higher energy densities. However, ensuring compatibility between SSEs and advanced cathode materials, especially under high voltage conditions, remains a significant challenge. Future research must focus on the development of stable interfaces to facilitate efficient ion transport and minimize interfacial resistance. Collectively, these emerging trends AI-driven design, 3D-printed architectures, hybrid cathode systems, and

solid-state integration are expected to redefine the landscape of lithium-ion battery technology and pave the way for next-generation energy storage solutions with enhanced performance, safety, and sustainability.

12.0 CONCLUSION

In recent years, significant advancements in cathode material architecture for LIBs have been made, focusing on the development of novel nanostructures, surface modifications, and hybrid composites to enhance electrochemical performance. Innovations such as nano-structuring, hierarchical designs, core–shell architectures, and doping strategies have all shown promise in improving capacity, rate capability, and cycle life. Additionally, emerging techniques like 3D printing and AI-driven material optimization are accelerating the discovery of new materials with tailored properties. However, key challenges remain, including scalability, synthesis complexity, and interface instability, which must be addressed to ensure these advanced architectures can be efficiently integrated into commercial battery technologies. Looking ahead, the next generation of LIB cathodes will require a delicate balance between achieving high energy densities, maintaining long-term safety, and ensuring environmental sustainability. This will involve optimizing the interplay between materials science, electrochemistry, and manufacturing processes. As such, interdisciplinary research linking chemistry, materials science, and electrochemical engineering will be crucial for overcoming current limitations and realizing the full potential of advanced cathode architectures. By combining innovative design strategies with cutting-edge technologies, future LIB cathodes will play a central role in meeting the growing demands of energy storage applications, contributing to the improvement of safer, more efficient, and sustainable energy systems.

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