

Nanostructured Electrodes: Transformative Pathways for High-Performance Lithium-Ion Batteries

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Abstract:

The worldwide shift to renewable energy and electrified transport/grid systems intensifies demand for lithium-ion batteries (LIBs), yet inherent limitations persist in energy density, structural integrity over cycles, and cost. Conventional electrodes like layered oxide cathodes and graphite anodes are limited by inadequate specific capacity, significant volume variation, and interfacial instability. This review emphasizes the impact of nanotechnology on electrode performance. Diverse nano-structuring designs—nanoparticles, nanowires, nanotubes, nanosheets, porous/hollow nanostructures—for advanced cathodes (e.g., layered metal oxides, olivine phosphates) and anodes (e.g., silicon, tin, transition metal oxides) are methodically assessed. Nanoscale engineering via morphology control, surface modification, and compositing enhances ionic/electronic transport while mitigating volume expansion, stabilizing electrode-electrolyte interfaces, and reinforcing structural integrity. Despite substantial improvements in capacity, cycle life, and rate performance, challenges include elevated surface area accelerating parasitic reactions, compromised volumetric energy density from densification hurdles, slurry processing complexities, and economic constraints. Future progress necessitates balancing electrochemical enhancements with scalable manufacturing, cost efficiency, and sustainable end-of-life management for advanced LIBs.

Keywords: Lithium-ion battery; nanotechnology; electrode materials.

1. Introduction

Driven by the global transition to sustainable energy and electrified transportation, lithium-ion batteries

(LIBs) have gradually become the dominant energy storage technology because of the advantages of high energy density, high power density, long cycle life, decreasing cost trajectory, and versatility. Substantial

governmental policy support has accelerated this transformation, evidenced by measures like the US Inflation Reduction Act (IRA) of 2022 linking tax credits to domestic production and mineral resources, the EU's Critical Raw Materials Act (2023), and China's ongoing „New Energy Vehicle“ subsidies [1, 2]. Annual global LIBs demand will

surpass 2.7 terawatt-hours by 2030, a near tenfold increase from 2023, to meet the rapid expansion of the demand for electric vehicles (EVs) and grid storage (Fig. 1) [3]. Societal decarbonization pressures have further intensified the demand for high-performance safe and sustainable batteries.

Annual lithium-ion battery demand by application

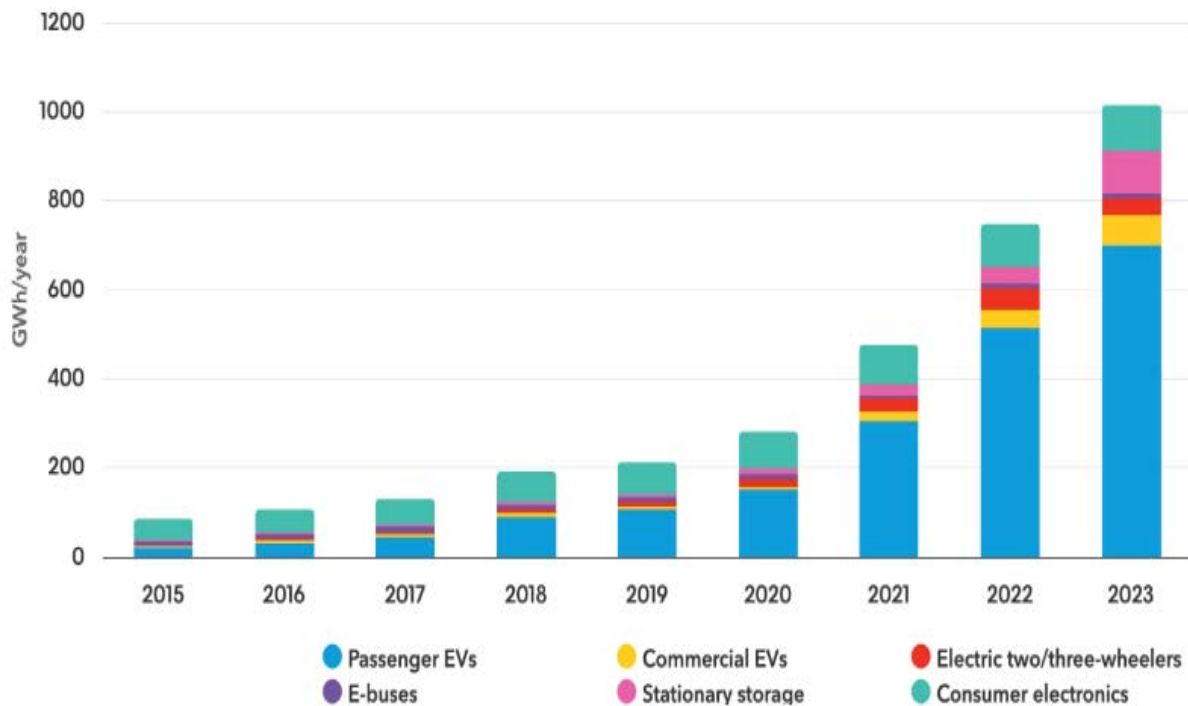


Fig. 1 The worldwide consumption trend of lithium-ion batteries since 2015 [3]

LIBs function through lithium-ion movement between cathode and anode. Commercialized LIBs typically utilize layered transition metal oxides (e.g., NMC: $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, LCO: LiCoO_2 , NCA: $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$) or olivine structures (LFP: LiFePO_4) as cathodes, with graphite remaining the primary anode choice due to stability and cost-effectiveness [4]. However, conventional cathodes exhibit limitations in specific capacity, rate capability, and instability of the structure when cycling, especially at the high voltages needed for greater energy density. Graphite anodes approach their theoretical capacity limit (~ 372 mAh/g) and present safety issues such as lithium dendrites during rapid charging [4]. These fundamental barriers impede achieving the necessary energy density, power density, charging speed, longevity, and safety for

next-generation applications like long-range EVs and large-scale renewable integration. Consequently, developing electrode materials capable of exceeding these intrinsic performance limits constitutes a significant scientific challenge.

Nanotechnology provides a transformative approach to addressing these limitations. Engineered nanomaterials, featuring dimensions typically between 1 and 100 nanometers, possess fundamentally distinct properties from their bulk equivalents. Key benefits include significantly shortened diffusion paths for Li^+ ions and electrons, enabling rapid charging and discharging; Enhanced reaction kinetics from increased electrode-electrolyte contact area; Improved strain tolerance during lithium insertion/extraction, reducing mechanical degradation and extending

cycle life, particularly vital for high-capacity materials like silicon; And access to novel reaction mechanisms enabled by nanoscale dimensions, potentially unlocking higher capacities [5]. Integrating nanotechnology into LIBs electrodes has emerged as a major research focus, demonstrating substantial potential for overcoming conventional material limitations and advancing battery performance boundaries.

This review focuses on the critical role of nanotechnology in transforming LIBs electrode performance. Diverse nanostructures design strategies were investigated, including nanoparticles, nanowires, nanotubes, nanosheets, porous/hollow architectures for state-of-the-art cathodes (e.g., NMC, LFP) and anodes (e.g., silicon, tin, transition metal oxides, novel carbon nanostructures beyond graphite). Fundamental mechanisms where nanoscale engineering—through morphology, size control, surface modification, and compositing—addresses key challenges were examined: improving ionic/electronic conductivity, buffering volume expansion, stabilizing electrode-electrolyte interfaces and enhancing structural integrity. Synthesis strategies for critical nanomaterials and the inherent trade-offs concerning scalability, cost, complexity, and electrochemical performance are explored. Persistent issues associated with nanomaterial electrodes are addressed, including high-surface-area-induced side reactions, potential volumetric energy density reduction from densification issues, slurry processing difficulties, long-term nanoscale stability concerns, and economic viability. Finally, the development trend of the next-generation of high-performance LIBs was prospected.

2. Challenges and Bottlenecks in Lithium-Ion Batteries

LIBs with higher performance for next-generation applications are facing major scientific and engineering challenges. Critical constraints such as energy density limitation, volume-change-induced structural instability, and cost issues together hinder the commercialization process.

2.1 Energy Density Limitation

Energy density - described as the amount of energy stored per mass or volume unit - is critical for extending electric vehicle range and portable electronics runtime. Commercial LIBs using layered oxide cathodes (e.g., NMC, NCA) and graphite anodes are nearing theoretical capacity limits [3]. The energy density bottleneck originates from inherent constraints in conventional electrode materials. For example, high-capacity lithium-rich layered oxides ($x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$) exhibit severe voltage fade, ox-

ygen release, and poor cycling stability, limiting practical capacity well below theoretical values [6]. Silicon (Si) offers an order-of-magnitude higher theoretical capacity (3579 mAh/g for $\text{Li}_{15}\text{Si}_4$ vs. 372 mAh/g for graphite), but rapid capacity decay hinders practical application. Traditional nanostructures, such as nanoparticles, reduce pulverization yet exhibit poor initial Coulombic efficiency (ICE) and lower volumetric energy density, primarily resulting from excessive solid-electrolyte interphase (SEI) formation and densification issues [7]. High-nickel ($\text{Ni} > 80\%$) NMC cathodes operating at voltages >4.3 V vs. Li^+/Li require complex surface coatings and electrolyte additives to address instability and reactivity, increasing complexity and cost [8]. These compromises also suppress practical energy density. The protective layers required for high-voltage cathodes introduce inert components, decreasing overall cell energy density by 10-20 %. Simultaneously enhancing specific capacity and operating voltage of nanoscale cathode and anode materials while ensuring long-term stability and high ICE remains a significant challenge for substantial energy density improvements.

2.2 Volume Expansion

The insertion/extraction process of lithium ions during charge/discharge cycles inherently causes volume changes in electrode materials, a critical bottleneck for next-generation high-capacity anode nanomaterials like Si and tin (Sn) and certain high-capacity cathodes. Full lithiation of Si to $\text{Li}_{15}\text{Si}_4$ induces $\sim 300\%$ volume expansion, generating immense mechanical stresses [9]. Particle pulverization results from repeated expansion and contraction, loss of electrode electrical contact, and continuous SEI layer cracking/reformation. Unstable SEI consumes lithium ions and electrolyte, accelerating capacity fade and increasing impedance [10]. Nanostructure enhances mechanical durability in electrodes but increases irreversible electrolyte decomposition and SEI growth due to high surface area, depleting lithium and electrolyte [6]. Substantial volume changes in Si nanomaterials also cause overall electrode swelling/contraction, risking delamination from current collectors, conductive network disruption, and long-term cycling challenges to cell engineering and packaging integrity [11]. Therefore, mitigating volume expansion requires more complex nanomaterial design (e.g., yolk-shell structures, conductive matrix confinement), advanced binders, and stable electrolyte formulations.

2.3 Cost and Commercialization Barriers

Reducing costs while simultaneously enhancing performance and sustainability are essential for the widespread use of LIBs in grid storage and electric vehicles. High

costs stem from the type and processing of materials: the cathode material containing cobalt, such as NMC and NCA, accounts for ~40 % of cell costs due to the scarcity and price fluctuation of cobalt [12]. Low/Co-free cathodes (e.g., high-Ni NMC, Li-rich Mn-based) face stability/rate capability/synthesis challenges hindering commercialization. Silicon-based anode nanomaterials increase the costs via precise synthesis (e.g., chemical vapor deposition for Si nanowires, magnesiothermic reduction for porous Si), and are more expensive than graphite due to the high cost of additional conductive additive/advanced binders [13]. Moreover, specialized electrolyte systems for high-energy electrodes also increase the cost [14]. In addition, manufacturing scalability poses hurdles: nanomaterial deposition/handling, uniform high-content electrode coatings, and quality control exceed graphite production complexities [15]. Underdeveloped recycling infrastructure for metal recovery and nanomaterial composites adds lifecycle costs and environmental concerns [13].

3. Application of Nanotechnology in Lithium-Ion Batteries

Nanotechnology utilizes materials at the 1-100 nanometer scale to circumvent inherent constraints within lithium-ion batteries. Engineered nanostructures—including nanoparticles, nanowires, nanotubes, nanosheets, and porous or hollow forms—boost ion diffusion rates, alleviate mechanical stress during volume fluctuations, and fortify electrode-electrolyte interfaces such as SEI layers. This methodology enables innovative reaction pathways while tackling critical issues for cathodes (NMC, LFP) and anodes (silicon, tin, transition metal oxides), markedly enhancing electrical conduction, structural robustness, and cycle life.

3.1 Nanostructured Cathodes

Conventional cathode materials like layered oxides and lithium-rich manganese oxides (LRMO) face intrinsic limitations in specific capacity, structural stability at high voltages, and voltage fade. The stability and reaction kinetics of the cathode can be enhanced by nanoscale engineering of tailored architectures, surface modifications and composite design.

3.1.1 Layered metal oxides

High-nickel cathodes (Ni > 80 %) are essential for boosting energy density but suffer from severe interfacial degradation and microcrack formation above 4.3 V vs. Li⁺/Li. The core-shell/gradient structure nanomaterial composed of Ni-rich cores and Mn/Al-rich shells (or concentration gradients) minimizes direct electrolyte contact with the

highly reactive core surface at high voltages, thus improving the stability of high-nickel cathodes. This approach significantly suppresses transition metal dissolution and parasitic reactions. For instance, a gradient NMC90 cathode featuring a protective Al₂O₃ coating demonstrated exceptional stability, exhibiting only 5 % capacity loss over 200 cycles, directly tackling the energy density limitation by enabling stable high-voltage operation [16]. In addition, replacing polycrystalline agglomerates with single-crystal nanoplates structure can eliminate grain boundaries, which are the primary site for microcrack initiation during cycling. This design drastically improves mechanical integrity and cycling stability. Single-crystal LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ nanoplates showcased remarkable capacity retention of 99 % after 500 cycles at 1C rate, directly addressing the structural instability challenge [17]. Meanwhile, LRMOS offer high capacity (>250 mAh/g) through anion redox, but suffer from severe voltage decay and oxygen release. Ajayi et al. modified the LRMOS surface with integrated spinel-like nanodomains. These nanodomains exhibit an atomic configuration analogous to spinel compounds like LiMn₂O₄, serving to thermodynamically stabilize the oxygen lattice framework. They effectively suppress deleterious phase transformations and minimize oxygen release during electrochemical cycling. Additionally, the nanodomains improve oxygen redox reversibility by establishing stable migration pathways and reaction environments for participating oxygen anions. Thus, surface-modified Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂ immediately addressed the voltage fade issue that restricts practical energy density by delivering a high capacity of 280 mAh/g with negligible voltage decay below 0.2 mV each cycle [18].

3.1.2 Olivine phosphates

While inherently stable and cobalt-free, olivine phosphates (e.g., LFP) suffer from low intrinsic electronic and ionic conductivity, limiting its rate performance. The solution is to adopt nano-scale conductive coating to enhance the surface conductivity. Coating LFP nanorods with graphene significantly improves electron transport across the electrode. This nanostructured composite achieved a high capacity of 165 mAh/g even at demanding 5C discharge rates, directly addressing the rate capability limitation for grid storage applications [19].

3.2 Nanostructured Anodes

High-capacity anode materials like silicon and tin oxides promise significant energy density gains but face catastrophic failure due to massive volume changes (>300 %) and consequent unstable SEI layers. Nanostructures are paramount for their viability. For transition metal oxides

anodes, surface modifications or encapsulation may be an effective measure to overcome the inherent sluggish kinetics and structural deformation.

3.2.1 Silicon-based anodes

Torres et al. encapsulates Si nanoparticles (“yolk”) within a conductive carbon shell (“shell”), with engineered void space in between. The void accommodates Si expansion during lithiation, preventing shell fracture. The stable carbon shell, in turn, supports a consistent SEI layer. This structure demonstrated a high capacity of 1,950 mAh/g, an ICE of 92 %, and retained 88 % capacity after 200 cycles, directly solving the dual problems of pulverization and unstable SEI [20]. In addition, Si designed as a vertical nanowire array structure can greatly improve the battery performance. Growing Si nanowires directly on the current collector (e.g., copper) eliminates the need for polymeric binders and provides direct electrical pathways and room for expansion. Arrays sustained 98 % capacity retention at 2C rates, highlighting the kinetic advantages and structural resilience of this nano-architecture [21].

3.2.2 Tin-based anodes

Tin oxide (SnO_2) offers good capacity (~ 790 mAh/g) but suffers from volume changes (~ 260 %). Confining SnO_2 nanosheets onto nitrogen-doped carbon nanotubes provides mechanical support against volume changes, enhances conductivity, and can hinder unwanted species migration. This composite delivered 790 mAh/g at 1 A/g with minimal decay (0.05 % per cycle), demonstrating effective volume change management [22]. In addition, Sn/SnO_2 @C core-shell structures were formed by embedding Sn/SnO_2 heterostructures into a carbon matrix, which leverages the beneficial properties of both Sn (conductivity and kinetics) and SnO_2 (higher capacity). The carbon matrix provides confinement and conductivity, while the core-shell interface enhances lithium-ion adsorption kinetics, reducing charge transfer resistance by 60 %.

3.2.3 Transition metal oxide

Transition metal oxides, such as TiO_2 and MnO , offer good safety but often suffer from slow kinetics or structural distortion. Modifying TiO_2 -B nanowires with lithium-ion conductive metal-organic frameworks (e.g., UiO-66-NH_2) creates fast ion transport channels on the surface. This enabled the anode to maintain 90 % capacity at ultra-high 10C rates, overcoming kinetic limitations. Moreover, confining MnO nanoclusters (< 5 nm) within graphene layers physically restricts the detrimental Jahn-Teller distortion occurring during cycling. This strategy doubled the cycle life compared to bulk MnO , directly addressing structural instability [23].

4. Conclusion

In summary, this review systematically examines nanotechnology’s essential function in overcoming LIBs electrode performance limitations. Nanoscale particles, wires, and porous/hollow frameworks significantly improve ion and electron mobility while accommodating volume changes and stabilizing electrode-electrolyte interfaces. Structural designs like core-shell formations in high-nickel cathodes inhibit surface deterioration; Yolk-shell configurations in silicon anodes provide pulverization resistance; Nano-coated olivine phosphates enhance electrochemical kinetics. These approaches collectively resolve critical cathode and anode challenges, substantially extending cycle durability and increasing energy storage capacity. Nanoscale engineering fundamentally advances LIBs technology by enabling unprecedented reaction pathways and material architectures that surpass conventional material constraints. Future investigations require equilibrium among electrochemical gains, manufacturing scalability and economic viability, prioritizing affordable nanomaterial synthesis techniques, optimized electrode compaction, preserving energy density, long-term nanostructural stability assessments and sustainable recycling integration. Exploration of combined nano-architectures and multifunctional surface modifications simultaneously boosting multiple performance indicators remains vital for developing subsequent generations of high-energy safe and ecologically sound LIBs.

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