Proceedings of CONF-MCEE 2027 Symposium: Sustainable Geomaterials and Materials Chemistry for Construction and Environment
DOI: 10.54254/2755-2721/2027.MD38637

Using Nanotechnology for Electrode Materials in Lithium-Ion Batteries

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Abstract. Nowadays, lithium-ion batteries (LIBs) are widely used in portable electronics, electric vehicles, and grid-scale energy storage systems. However, the commercial graphite anode has almost reached its theoretical capacity limit of 372 mAh g^{-1}, and conventional cathode materials still face problems such as low specific capacity and unstable electrode-electrolyte interfaces, which limit the cycle life and safety of the batteries. Nanotechnology can provide useful ways to deal with these problems, because it shortens the diffusion path of lithium ions, buffers the volume strain during charge and discharge, and stabilizes the interfacial chemistry between electrode and electrolyte. This paper reviews the recent development of nanotechnology in both cathode and anode materials. For cathode materials, elemental doping can stabilize the crystal lattice and improve ion transport, surface coatings can reduce the dissolution of transition metals and side reactions with the electrolyte, and morphology control can further shorten diffusion paths and improve rate capability. For anode materials, carbon coating, porous structures, and one-dimensional nanowires can relieve volume expansion and make the solid-electrolyte interphase more stable. This review also discusses several key challenges, such as nanoparticle agglomeration, side reactions at the interface, and manufacturing cost, and gives some prospects for future multi-scale synergistic design.

Keywords: Lithium-ion batteries, nanotechnology, cathode materials, anode materials

1. Introduction

Lithium-ion batteries (LIBs) have been widely used in portable electronic devices, electric vehicles, and large-scale energy storage systems due to their high energy density, high operating voltage, and long cycle life. Driven by the global transition toward carbon neutrality and the rapid expansion of the new energy vehicle market, the performance requirements for LIBs regarding energy density, cycle life, safety, and cost continue to rise. The widely adopted graphite anode, however, has a theoretical specific capacity of only 372 mAh g^{-1} and can no longer satisfy the demand for high-energy-density battery systems. Conventional cathode materials such as $LiFePO_4$, $LiCoO_2$, and ternary NCM generally deliver practical specific capacities below 200 mAh g^{-1}. Meanwhile, LIBs still suffer from unstable electrode-electrolyte interfaces, low initial Coulombic efficiency, rapid capacity fade, and inadequate thermal safety.

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Nanotechnology provides a promising route to address these limitations. When electrode materials are reduced to the nanoscale, the lithium-ion diffusion path is significantly shortened, the number of electrochemically active sites is increased, and the stress caused by volume changes can be buffered by the free surfaces of nanostructures. In addition, the electrode-electrolyte interface can be engineered through surface coating or morphology control. In recent years, researchers have studied various topics, such as doping and coating modifications for cathode materials, carbon coating and porous structure design for anode materials, and nanoscale manufacturing methods like mechanical milling. These studies cover different size scales, from atomic-level doping and mesoscale coating to macro-level electrode structure design. This paper reviews the recent progress of nanotechnology in cathode and anode materials, and also discusses the basic working mechanisms, existing challenges, and future research directions.

2. Nanotechnology in cathode materials

2.1. Elemental doping modification

Elemental doping is an important approach to improving the electrochemical performance of layered cathode materials. Meng et al. prepared Ti^{4+}-doped $LiNi_{0.75}Mn_{0.25}O_2$ by a high-temperature solid-state method using TiO_2 as the dopant. Ti^{4+} doping did not change the phase composition or morphology, but significantly improved cycling stability and rate capability. At an optimal Ti^{4+} molar fraction of 1.5%, the capacity retention after 50 cycles increased from 87.87% to 95.42%, and the discharge specific capacity at 4C increased from 66.47 to 104.00 mAh g^{-1}. The mechanism is that Ti^{4+} strengthens the transition-metal–oxygen (TM–O) bond, suppresses transition-metal dissolution and oxygen loss during cycling, and widens the lithium-ion extraction/insertion channels while lowering internal resistance [1].

Transition-metal ion doping can also exert synergistic effects. Han et al. investigated Cu^{2+} doping in $LiMn_{0.6}Fe_{0.4}PO_4$ (LMFP) and found that Cu^{2+} simultaneously improved electronic conductivity, lithium-ion diffusion coefficient, and structural stability, i.e., a trifunctional synergistic enhancement. The $LiMn_{0.6}Fe_{0.39}Cu_{0.01}PO_4$@C electrode delivered discharge specific capacities of 160.3 and 121.2 mAh g^{-1} at 0.1C and 2C, respectively, and retained 92.5% of its initial capacity after 200 cycles at 1C. First-principles calculations confirmed that Cu incorporation lowers the lithium-ion diffusion barrier, and in-situ XRD analysis demonstrated excellent structural reversibility. These results indicate that doping modifies the lattice at the atomic scale, providing a general strategy for enhancing the cycling and rate performance of high-nickel and polyanion cathodes [2].

2.2. Surface coating modification

Surface coating constructs a protective layer on cathode particle surfaces, suppressing side reactions between the electrolyte and active material. Jiang et al. coated NCM811 with different amounts of nitrogen-doped carbon using a rheological method with dopamine hydrochloride as the carbon source. An appropriate nitrogen-doped carbon layer formed a uniform protective shell, and the introduced N atoms anchored Ni atoms and suppressed Li^+/Ni^{2+} cation mixing. Excessive coating, however, reduced Ni^{3+} to Ni^{2+} and aggravated cation mixing. The NCM811-CN0.75 sample exhibited the best performance, reaching 151.6 mAh g^{-1} at 10C and retaining 82.2% capacity after 300 cycles at 5C [3].

Atomic layer deposition (ALD) enables nanoscale conformal coatings. Barthwal et al. deposited a conformal ZnF_2 layer on $Li(Mn_{0.6}Fe_{0.4})PO_4$ by ALD. Under harsh high-voltage cycling conditions

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(2.5–4.5 V, 1000 cycles at 1C and 5C), the capacity retention of LMFP@ZnF_2 was more than 22% higher than that of the uncoated cathode. Post-test analysis revealed that the ZnF_2 coating promoted the formation of a thin, uniform, inorganic-dominated cathode-electrolyte interphase (CEI) enriched in F, Li, and P, preserved the Mn/Fe stoichiometry, and mitigated particle pulverization. In contrast, the uncoated cathode formed an organically enriched CEI with poor stability. This strategy is particularly valuable for high-voltage, cobalt-free cathodes [4].

2.3. Morphology control and crystal-plane engineering

Beyond doping and coating, morphology control can optimize lithium-ion diffusion. Li et al. addressed the intrinsically low electronic conductivity (~10^{-16} S cm^{-1}), slow lithium-ion diffusion, and Jahn–Teller distortion-induced structural collapse of Li_2MnSiO_4 by a hydrothermal method using CTAB as a crystal-growth regulator. The synthesized nanoneedle Li_2MnSiO_4 was approximately 200 nm long and 30 nm wide. Theoretical calculations indicate that lithium ions migrate along the a and c axes with the lowest energy barriers; the nanoneedle morphology shortened the exposure distance of the corresponding crystal planes, yielding a discharge specific capacity of 217.3 mAh g^{-1} at 0.1C. This work demonstrates that nanostructure and crystal-plane engineering can optimize ion transport from a crystallographic perspective, offering a new route for low-conductivity cathode materials [5].

3. Nanotechnology in anode materials

3.1. Carbon-based and carbon-coated nanoanodes

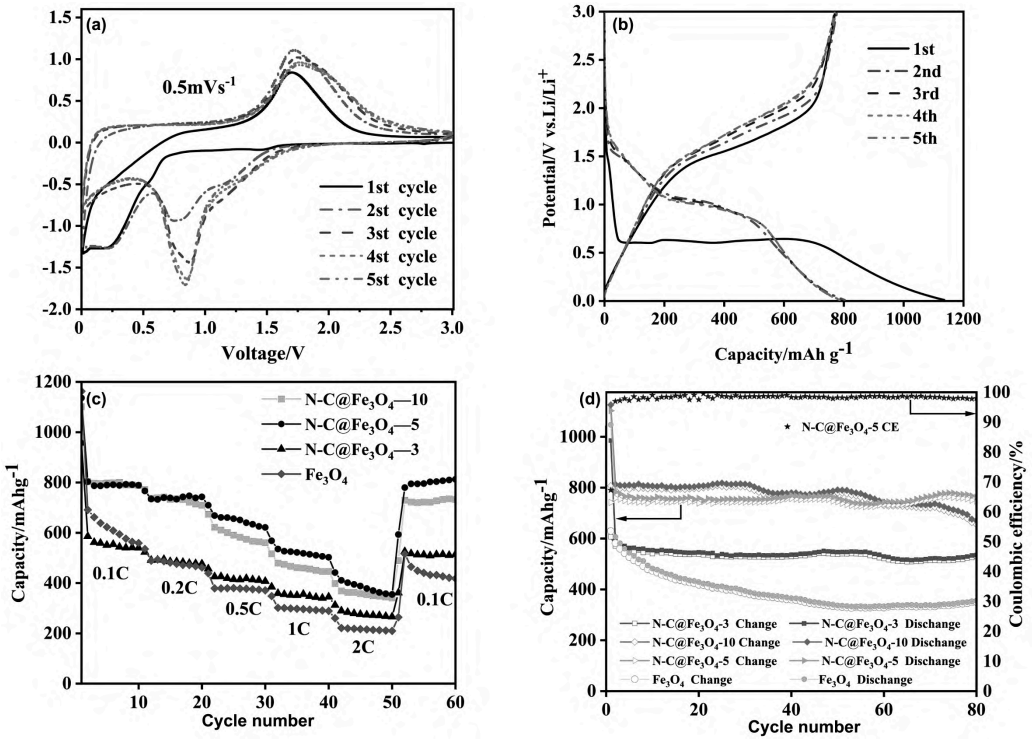


Figure 1. Electrochemical performance of the N-C@Fe_3O_4 electrode: (a) cyclic voltammetry curves; (b) charge–discharge profiles; (c) rate capability; (d) cycling stability and Coulombic efficiency [6]

DOI: 10.54254/2755-2721/2027.MD38637

Transition-metal oxide (TMO) anodes offer high theoretical capacity, but their volume expansion/shrinkage during cycling tends to cause pulverization. Carbon coating is an effective solution. Sui et al. used edible ice jelly, a biomass carbon source, complexed with ferrous oxalate hydrogel and subjected to one-step high-temperature pyrolysis to prepare nitrogen-doped ice-jelly-carbon-coated Fe_3O_4 composites (N-C@Fe_3O_4). As shown in figure 1, the carbon layer effectively prevented agglomeration of Fe_3O_4 nanoparticles, improved electronic conductivity, and stabilized the solid-electrolyte interphase (SEI). When the current density is turned back from 2 A g^{-1} to 0.1 A g^{-1} (Figure 1c), the reversible capacity goes back to 812.72 mAh g^{-1}, which shows good rate reversibility. Among all samples, the N-C@Fe_3O_4-5 one showed the best performance, and it still kept 762.74 mAh g^{-1} after 80 cycles at 0.1 A g^{-1}. In the rate test, the discharge capacities were 788, 747, 621, 502, and 370 mAh g^{-1} at 0.1, 0.2, 0.5, 1, and 2 A g^{-1}, respectively. The good rate performance is mainly because of the pseudocapacitive contribution [6].

For silicon anodes, the porous carbon framework can not only hold the volume expansion but also provide a conductive network. Zhang et al. used pre-oxidized polyvinylpyrrolidone (PVP) as the framework, and glucose or sucrose as the carbon source, then they made Si@PVP/glucose and Si@PVP/sucrose porous silicon-carbon composite electrodes by microelectronic printing. The Si@PVP/glucose electrode had more uniform pores and smaller cracks after cycling, which means it can better resist the expansion stress. Its first-cycle specific capacity was 1655 mAh g^{-1} at 0.1 A g^{-1}, and after 100 cycles it still kept 1095 mAh g^{-1}, giving a capacity retention of 97.4%. The Si@PVP/sucrose electrode kept 970 mAh g^{-1} after 100 cycles, with a retention of 91.0%. The porous structure gives enough space for silicon to expand, so it can reduce the pulverization and damage of the electrode [7].

3.2. Silicon-based nanoanodes

Silicon has a theoretical specific capacity as high as 4200 mAh g^{-1}, which is about ten times that of graphite. It also has a proper working voltage (~0.2–0.3 V vs. Li/Li^+) and rich resources, so it is considered the most promising anode material for the next generation. However, during lithiation, silicon will expand by more than 300%, and this will cause the electrode structure to collapse, make the SEI form and break again and again, lead to irreversible loss of active lithium, and make the capacity drop quickly. As a result, the initial Coulombic efficiency becomes low and the cycle life becomes short [8].

Mechanical milling is a solid-state processing method, and it is simple, scalable, and the structure can be easily adjusted. Li et al. reviewed the recent progress of using mechanical milling to control the structure and performance of silicon-based anodes, including how to prepare nanosilicon, how to design silicon–carbon composites, how to build silicon–metal or metal silicide systems, and how to do in-situ coating. By milling, the particle size, morphology, and structure can be controlled accurately, so the structural stability is improved without using complex and harsh conditions. But there are still some problems, such as uneven composites, hard to control the milling energy input, and the interfacial reaction mechanisms are not fully understood [9].

One-dimensional nanostructures can directly help buffer the volume change. Li et al. grew Sn-doped silicon nanowires (SiNWs) from stable silica at 250 ¹C, using a modified aluminothermic reduction method based on a solid–liquid–solid (SLS) mechanism. During growth, the reduced silicon atoms move freely in the molten salt and mix with the pre-reduced Sn, and when the Si concentration in the Sn–Si alloy reaches supersaturation, single-crystal SiNWs start to grow, with about 3.0 at% Sn doping. When used as a lithium-ion battery anode, the Sn-doped SiNWs showed an initial Coulombic efficiency of 85.4%, and after 500 cycles at a high current density of 4 A g^{-1}, it

DOI: 10.54254/2755-2721/2027.MD38637

still kept a reversible capacity of 1133 mAh g^{-1}. The nanowire structure can provide a fast axial path for electron transport, and its free radial surfaces can also take in the volume strain caused by lithiation [10].

4. Challenges and outlook

4.1. Nanoparticle agglomeration and interfacial side reactions

The introduction of nanomaterials brings new challenges while improving performance. Nanoparticles have high specific surface area and high surface energy, leading to agglomeration during electrode fabrication and cycling, which reduces the effective reaction area and disrupts the conductive network. Meanwhile, the enlarged surface area intensifies side reactions at the electrode-electrolyte interface, causing excessive SEI growth, continuous electrolyte consumption, and degraded initial Coulombic efficiency and cycling stability. Feng et al. systematically reviewed strategies for regulating the LIB interface, noting that stable interfaces must be constructed through multi-level approaches including binder and conductive agent optimization, electrolyte and additive design, electrode double-layer engineering, heterostructure and surface coating design, and separator optimization. Nanotechnology must therefore be combined with interfacial engineering to fully exploit its size advantage [11].

4.2. Manufacturing, cost, and scale-up barriers

Cost and scale-up are central obstacles for nanoanode materials. Taking nano-SiO_2 as an example, its theoretical specific capacity reaches 1965 mAh g^{-1}, and it is abundant, low-cost, and easy to synthesize, making it a promising alternative to silicon. However, its intrinsically low electrical conductivity limits electrochemical activity, and the irreversible Li_2O and lithium silicate formed during the first lithiation significantly lower the initial Coulombic efficiency; volume change, although smaller than that of silicon, remains non-negligible. Nanomaterial fabrication often requires complex processes such as templating, chemical vapor deposition, or sol–gel methods, leading to high synthesis cost and poor batch-to-batch consistency, which conflicts with the low-cost, large-scale production required for commercialization [9, 12]. Future directions include intelligent milling and data-driven process optimization to improve homogeneity and controllability; multi-scale synergistic design to simultaneously balance capacity, lifetime, safety, and cost; and engineering validation in practical battery systems.

5. Conclusion

Nanotechnology has demonstrated remarkable effectiveness in both cathode and anode materials for lithium-ion batteries. On the cathode side, elemental doping stabilizes the lattice framework at the atomic scale and suppresses transition-metal dissolution and structural collapse; surface coatings construct protective layers that inhibit electrolyte side reactions; and nanoneedle-like morphology control shortens lithium-ion diffusion paths. These three methods improve cycle stability and rate performance from different aspects, namely the lattice, the interface, and the ion diffusion process. On the anode side, carbon coating and porous structure design can well hold the volume expansion of transition-metal oxides and silicon, stop particles from agglomerating, and keep the SEI film stable; mechanical milling and solid–liquid–solid growth also provide practical ways to make and optimize silicon-based nanoanodes at a larger scale.

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However, there are still some problems for real applications, such as nanoparticle agglomeration, more side reactions at the interface, and high manufacturing cost. The large surface area of nanoparticles is good for ion transport, but it also causes uncontrolled side reactions and makes the SEI grow too thick, so these problems need to be solved by better interface design and electrolyte optimization. Besides, many nanoscale fabrication methods have complex synthesis steps and vary from batch to batch, which makes it hard to use them in industry. In the future, more attention should be paid to multi-scale design that combines atomic-level doping, mesoscale coating and morphology control, and macroscale electrode structure, together with data-based process improvement and smart manufacturing. If specific capacity, rate performance, cycle life, safety, and cost can be balanced at the same time, nanotechnology will help make practical high-energy-density lithium-ion batteries, and these batteries can meet the growing needs of electric vehicles and grid-scale energy storage in the future.

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