The role of nanotechnology in the design of materials for Lithium-ion battery

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Abstract. With the growing market of electric vehicle (EV) in recent years, breakthroughs on components of the vehicle, especially the lithium-ion batteries (LIBs) recharging system, have been made by the introduction development of nanotechnology of the cathode and anode of the battery to have high energy and power density, low cost, stabilities, and improved capacity reservation performance. The current developments of the popular various cathode materials, LiCoO\textsubscript{2}, LiMn\textsubscript{2}O\textsubscript{4}, and high Ni-rich materials, and anode materials, nanostructured-Si, SnO\textsubscript{2}, and lithium titanium oxide, are discussed and reviewed with both advantages, and challenges, and potential improvement list. Progress in improving the characteristics of lithium-ion battery LIBs has been made due to nanotechnology’s microstructure modification. Further experiments development for on the material of LIBs of lithium-ion battery by modifying nanostructure need to be conducted and studied for EV recharging system to achieve the expected characteristics.

1 Introduction

Lithium-ion battery (LIB), as an advanced battery, has been widely discussed in recent years due to its comparably high energy density and power density, lightweight, long lifetime, fast-charging, high endurance, and cleanliness. Not only it dominates the rechargeable systems in portable electronics, but LIBs have also been introduced to electric vehicles and industries to act as a new source of energy to replace fossil fuels, which have a growing demand in recent decays. The structure and four essential components of a typical LIB are described in Figure 1.
Cathode materials, as one important part of LIBs, involve lithium cobalt oxide (Li$_x$CoO$_2$ or LCO), Lithium Iron Phosphate (Li$_x$FePO$_4$ or LFP), and few other compounds [1]. From recent research, Al doping is introduced to the Li$_x$CoO$_2$ materials to enhance cathode-electrolyte interphase formation and lower the transition metal redox energy level [2]. Graphite is commonly used as anode material in lithium-ion batteries for the last few decades. Its ring structure allows lithium ions to move inversely and fast between each layer. The formation of the solid electrolyte interphase (SEI) on the graphite surface in the redox reaction will protect the battery, resulting in a long lifespan. However, lithium dendrite formation due to Li-ion diffusion is detrimental to the battery since the cell can be short-circuited in certain conditions [3]. Li$_4$Ti$_5$O$_12$ is another anode material that is being used in grid energy storage. However, the high operating voltage and limited capacity make it challenging to have high energy density or power density, safe, lightweight, and low-cost characteristics. Considering electrolyte, organic liquid electrolyte and solid-state electrolyte are commonly used in batteries. But solid-state electrolyte is mainly focused on the future because it is more stable and safer. In recent decades, nanotechnology was applied into lithium-ion batteries, especially for anode, cathode, and even electrolytes, to improve the energy density and cycle performance.

One-dimensional nanochannels are used to reduce the particle size of LiFePO$_4$ to a critical value, which can greatly reduce the amount of trapped Li and reduce the effect of slow diffusion channels, to make full use of Li in the structure. Two-dimensional nanocoating is used to reduce the exposed electrochemically active surface area and improve cycle life. The spinel of lithium manganese oxide is a successful cathode material for commercial vehicles (Chevy Volt and Nissan LEAF). A three-dimensional nano diffusion network provides an effective mechanism for Li$^+$ removal and insertion during charging and discharging [3]. In addition, a lot of nanomaterials were applied to LIBs by designing the structure of materials into the nanoscale.

Firstly, nanosized Transition-metal oxides (TMOs) are considered promising anode materials because of their high reversible capacity over 800mAh g$^{-1}$ and excellent rate, cycle performances. However, low conductivity and large volume expansion create great damage to TMOs as anode materials, which causes structural defects, decreasing the lifespan of the battery. To effectively solve these problems, it is very important to arrange the structure of materials by accurately controlling the nanostructures [4]. It is beneficial to improve electron transfer, shorten ion diffusion length, and adapt to volume changes in the cycle process by using customized carbon nanostructures and reduced TMS nanoparticles [5]. The latest research on LIBs cathode materials relies heavily on the use of nanocomposite materials and nano-thick coatings to optimize ion and electron conduction pathways, preventing unwanted and irreversible side reactions [6]. High Ni-rich material, the nanostructured oxide, is a successful strategy that effectively reduces the diffusion time from Li$^+$ surface to core and provides better rate capability. Silicon was applied to the anode by designing kinds of the nanostructure, like silicon nanowires or silicon nanoflower. Although nanostructured oxide...
improves the performance of anode materials, it still has big challenges on capacity retaining of the anode materials during cycling. Therefore, the reasonable design of nanomaterials is the key to determine its overall performance [7]. Nanotech has improved the efficiency of electron injection and removal and the performance under high current density, which tried to reduce the influences brought by the covalent bond framework in polyanions of lithium iron phosphate [8]. By decreasing the particle size of LiFePO₄, the electrochemical behavior of the battery will be improved. For the research of anode materials, some ions inevitably dissolve in the electrolyte and then deposit on the surface of the electrode, affecting the chemical performance of the battery, for example, the manganese ions in lithium manganese anode materials, besides, an anode that uses LiNi₁₋ₓ₋₀·₅MnₓCo₀·₅O₂ [9]. Liu and Chen found that the chemical reaction between the nickel-rich electrode and electrolyte can reduce the reversible capacity of the battery and increase the internal impedance of the battery by analyzing the composition of the final product, thus affecting the safety of the battery [9]. On the one hand, nanostructured coatings provide isolation between anode and electrolyte, thus preventing the materials from dissolving. On the other hand, nanocoating prevents the chemical reaction between the electrode and electrolyte, thus improving the safety and chemical performance of the batteries.

In this Review, we discuss recent advances in high energy Li-based battery materials for electric vehicle (EV) applications by nanotechnology. We first review the application of nanotechnology in cathode and anode materials of LIBs. We target materials that are either already commercialized or under development, which we believe in have the greatest potential to meet the high-energy requirement for EV applications.

2 Nanotechnology enables Li-ion cathode materials

Lithium cobalt oxide (LiCoO₂) is one of the most common cathode materials. Its high specific energy makes LiCoO₂ a popular choice for mobile phones, laptops, and digital cameras. The layered structure of cathode material promotes lithium ions to move from the anode to the cathode during discharge and flow in the opposite direction during charge. As a widely used electrode material, LiCoO₂ has the following advantages: (1) Excellent electrochemical performance. (2) Excellent processing performance. (3) High tap density, which helps to improve the volume-specific capacity of the battery. (4) Stable performance, good consistency. However, LiCoO₂ is rarely used in traction batteries. In the condition of overcharge, the excess lithium ions on the anode would still move to the cathode. As anode can’t fully accommodate lithium ions, lithium ions would form metal lithium. The lithium metal is called Li dendrite. Once the dendritic crystal is formed, diaphragm piercing may occur, which will lead to an internal short circuit to cause safety concerns on application.

2.1. Nanostructured LiCoO₂

Since the introduction of LIBs into the market of portable electronics, many efforts had been devoted to developing nanostructure design to reduce the particle size of LiCoO₂ by using solid-state reactions [10] and solution-assisted methods [11~14], thus improving the performance of LiCoO₂. Gu Yuanxiang’s work [15] showed that nanofibers can achieve rapid solid diffusion and improve the short diffusion distance of Li+. However, due to its high cost and structural instability at high potential, we focus on how nanotechnology has enabled the development of LiCoO₂ materials. Researchers in Japan have come up with a solution different from the insertion of an artificial SEI [16~17]. Nanodot BaTiO₃ [18] was used to support LiCoO₂ cathode, thus improving its charge ability and cyclability shown in Figure 1. With nanodot BaTiO₃, the battery has a lower interfacial resistance between the cathode and electrolyte. High current density created by high dielectric constant material will create strong Li⁺ paths at non-solid electrolyte interface covered regions. Thus, high chargeability and cyclability can be provided.
Figure 1. (a) Discharge capacities as a function of C-rate, which increases from low 1C to ultrahigh 100C in a five-repeated measurement sequence for each C-rate. Black, blue, and red circles correspond to Bare, Planar BTO, and Dot BTO, respectively. (b) Nyquist plots of Bare and Dot BTO before and after charge at 1C. Black open circle, black solid circle, red open circle, and red solid circle correspond to Bare before charge, Bare after charge, Dot BTO before charge, and after Dot BTO after charge, respectively. (c) Discharge capacities of Bare at 5C, Dot BTO at 5C, and Dot BTO at 50C repeating 800 times. (d) Schematic of lithium intercalation and de-intercalation in Bare and Dot BTO thin films at a low C-rate and ultrahigh C-rate. Copyright Nano Letters 19.3 (2019): 1688-694. Web.

2.2. Nanostructured LiMnO$_2$

Although LiCoO$_2$ has great cycle performance and discharge ability, it still has disadvantages on high cost and great harm to the environment. In addition, lithium manganese oxide [19] (Li-Mn-O) has lower cost and lighter environmental problems than LiCoO$_2$. Among all kinds of Li-Mn-O compounds, layered orthorhombic LiMnO$_2$ (o-lmo) is attracted much attention because of its high theoretical capacity (285 MAH / g) [20]. According to the literature, the cycling performance of o-lmo is mainly affected by: (1) Manganese is dissolved in the electrolyte solution by the disproportionation reaction of $2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+}$ (electrolytically soluble) + Mn$^{4+}$ (2) the high oxygen activity on the electrode surface leads to the evolution of O$_2$ at the electrode/electrolyte interface, especially at high temperature; (3) Structural transition from o-lmo to spinel phase during electrochemical cycling [21]. To overcome the above shortcomings, the study of nanotechnology is devoted to design the core-shell structure of orthorhombic LiMnO$_2$@Li$_2$CO$_3$ (o-LMO@Li$_2$CO$_3$) nanoplate array cathode made by Li$_2$CO$_3$ coating and nanosheet array structure [22], which is prepared by solid conversion of Mn$_3$O$_4$ nanoplates. The prepared o-lmo @ Li$_2$CO$_3$ nanosheet array cathode showed high specific capacity, superior high-rate performance, and good cycle stability even at high temperatures (60 ℃).

Figure 2. SEM images of the o-LMO@ Li$_2$CO$_3$nanosheet array electrode at different magnifications. Copyright ACS Applied Materials & Interfaces 2016 8 (25), 16116-16124

2.3. Nanostructured Ni-rich cathode materials

Therefore, the layered material LiCoO$_2$ has a limited practical capacity (∼155 mAh g$^{-1}$), and research has, therefore, been devoted to developing cheaper alternatives with higher energy densities and higher rates. A great interest focuses on NMC materials with higher nickel content. They can provide higher specific capacity within the same voltage window and further decrease dependence on scarce, geographically concentrated, and expensive cobalt. With the high fraction of Ni in the Li[Ni$_x$Co$_y$Mn$_z$]O$_2$ (NCM) and Li[Ni$_x$Co$_y$Al$_z$]O$_2$ (NCA) cathodes [23], the capacity and energy density of the
battery increases significantly, and the cost is greatly decreased. Katharina Marker et al. developed NCM 811 and adopted operando synchrotron X-ray diffraction (XRD). Ex situ solid-state NMR spectroscopy provides new insights into the structural changes and lithium dynamics of NMC811 during electrochemical charge and discharge [24]. As reported by Liu and co-workers, the internal crack for single-crystalline heterostructure cathodes created using nanotechnology is extremely small compared to the polycrystalline cathodes [25]. Electrolyte penetration is also prevented since the cracking is slight and starts from inside. Based on the prediction figure 1 by Choi and co-workers, the future of advanced Ni-rich cathodes requires help from nanotechnology to reach its full limit.

3 Nanotechnology enables Li-ion anode materials

LIB anode materials can be divided into three groups: (1) graphite and titania; (2) alloy and de-alloyed Si and Si composites; (3) metal oxides, metal sulfides. In this section, we focus on those materials that have been commercialized or are close to commercialization.

3.1. Nanostructured Lithium titanium oxide

Lithium titanium oxide (LTO) of spinel structure has been developed to reach high power density and capacity retention [26]. Combined with LiCoO₂ cathode, the power density for a 2V LTO anode cell developed by Norio Takami and co-workers can reach 4000W kg⁻¹ for 10s pulse with great safety performance and 1 min fast charging [28]. Further study of LTO modified by Ag-Cu particles was conducted by Krajewski and co-workers, which LTO as anode material showed 19 mAh g⁻¹ at 10 C current rate with a 12.5% increase in specific capacity retention characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) [28]. The development of the LTO anode demonstrated the important role of nanotechnology in improving specific capacity, charge time, and capacity retention rate; and experimenting with the battery's anode.

3.2. Nanostructured Si and composites

The development of a high capacity of anode materials for future lithium-ion batteries is required to solve the low energy density of existing batteries. Silicon is an anode material with ultra-high specific capacity (theoretical capacity 4200 mAh/g), more than ten times the capacity of traditional carbon materials. However, in the process of charging and discharging, pure silicon will have a huge volume change (volume expansion rate of 300%) by resulting in powder, which will affect the safety of the battery. On the other hand, pure silicon has a low electrical conductivity, making it difficult to improve the high-current charge-discharge capacity of lithium-ion batteries. To achieve better cycle life performance, a nanostructured-Si with a conformal carbon coating has been proposed. However, the whole composition process is costly, complex, and time consuming. To solve the above problems, a new synthesis method [29] has been proposed to increase the cycle life of Si. In this process, the nanostructured Si would be first transformed into Mg₂Si. Under low partial vapor pressure, Mg₂Si would decompose into Si and Mg vapor, thus reacting with CaCO₃, a conformal C nanolayer could be formed on the newly formed nanostructured Si. The reversible capacity of the Si electrode prepared by this method would remain 764.6 mA h g⁻¹ after 500 cycles, while its original reversible capacity is 1359.7 mA h g⁻¹ at 4 A g⁻¹ shown in Fig 4. A nanostructured Si/SiOC composite anode with volume-change-buffering microstructure [30] has been proposed to mitigate the effects of volume changes. The capacity showed 800 mA h g⁻¹ at the current density of 100 mA g⁻¹, and with approximately 100% capacity retention after 100 cycles.
3.3. Nanostructured Tin oxides and composites

There are many metal oxides and metal sulfides candidates that have been investigated as potential anode materials for LIBs. SnO\textsubscript{2} is considered one of the most promising anode materials for lithium-ion batteries because of its theoretical capacity to reach 8.4 Li\textsuperscript{+}. However, a large volume change of SnO\textsubscript{2} can cause particle pulverization \cite{31}. Various nanotechnologies have been actively applied in tailoring these materials for better electrochemical performance in LIBs. Amorphous SnO\textsubscript{2} (\textalpha-SnO\textsubscript{2}) thin films, which are conformally coated on the surface of reduced graphene oxide (rGO) by atomic layer deposition (ALD), showed higher capacity than the theoretical value. Due to the extra interface charge storage, it is caused by the high specific surface area of \textalpha-SnO\textsubscript{2}/rGO nanocomposites \cite{32}. Besides, some papers reported SnO\textsubscript{2} and carbon composites made by graphene nanoribbons (GNRs) and tin oxide (SnO\textsubscript{2}) nanoparticles (NPs) as anode material for LIBs to overcome the volume change of SnO\textsubscript{2} \cite{33}. Furthermore, fluorine-doped SnO\textsubscript{2}@Graphene can load F-SnO\textsubscript{2} nanoparticles on the surface of reduced graphene oxide sheets more uniform and higher by enhancing the electron transfer lithium-ion diffusion in the composite \cite{34}. In addition, rGO/Fe\textsubscript{3}O\textsubscript{4}/SnO\textsubscript{2} ternary nanocomposite can enhance the cycle performance by maintaining almost 100% in the first 100 cycles with the exceeding 700 mAhg\textsuperscript{-1} in its specific capacity \cite{35}.

4 Conclusion and outlook

Advances in Li-ion batteries are likely to continue to be strongly supported by the innovations from nanotechnology. We expect that the rational design of nanomaterials will play a critical role in the development of high-energy-density Li-ion batteries, even the long-range EVs. This review summarized some recent research progress of nanostructured cathode materials for lithium-ion batteries, including LiCoO\textsubscript{2}, LiMn\textsubscript{2}O\textsubscript{4}, and high Ni-rich material. First, the charging-discharging process of LiCoO\textsubscript{2} cathode is discussed in detail, and the advantages and drawbacks of LiCoO\textsubscript{2} are listed. The nanostructured LiCoO\textsubscript{2} and LiCoO\textsubscript{2} with nanodots technique are reviewed. With these two methods, the cycle life of LiCoO\textsubscript{2} cathode material batteries can be highly improved. Second, the mechanism of LiMn\textsubscript{2}O\textsubscript{4} is discussed. To solve problems like the dissolution of Mn and its change in the structure during the charge/dischARGE process, a nanoplate array method using LiCoO\textsubscript{2} is reviewed. In the case of current Ni-rich cathodes, to accomplish both structural and thermal stability, nanotechnology is involved in changing the structure and make modifications to the cathode to make it has good performance on capacity preservation after many cycles.

As for the anode side, to solve its huge volume change
problems, a nanostructured-Si with a conformal C coating has been proposed, so the safety of the battery and capacity could be increased by adopting the nanotechnology. The composites which are made by graphene nanoribbons (GNRs) and tin oxide (SnO) nanoparticles (NPs) can buffer the volume change of SnO during the cycle. To fulfil the high-power demand, the LTO of the spinel structure is discussed due to its high-performance anode materials for LIBs. It is believed that future work should focus on the relationship between composite structure and electrochemical performance by comprehensive research of structure design.

References