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Novel surface coating strategies for better battery materials

1 Lei Wen PhD

Associate Professor, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China

2 Xiaowei Wang MSc

PHD student, Institute for Superconducting and Electronic Materials, Australian Institute of Innovative Materials, University of Wollongong, Wollongong, Australia

3 Guo Qiang Liu PhD

Professor, School of Metallurgy, Northeastern University, Shenyang, China (corresponding author: liugq@smm.neu.edu.cn)

4 Hong Ze Luo PhD

Senior Researcher, Council for Scientific and Industrial Research, Pretoria, South Africa

5 Ji Liang PhD

Research Fellow, Institute for Superconducting and Electronic Materials, Australian Institute of Innovative Materials, University of Wollongong, Wollongong, Australia (corresponding author: liangj@uow.edu.au)

6 Shi Xue Dou PhD, DSc

Professor, Institute for Superconducting and Electronic Materials, Australian Institute of Innovative Materials, University of Wollongong, Wollongong, Australia

With the advancement of electrode materials for lithium-ion batteries (LIBs), it has been recognized that their surface/interface structures are essential to their electrochemical performance. Therefore, the engineering of their surface by various coating technologies is the most straightforward and effective strategy to obtain the desirable battery characteristics. Coating the electrode materials' surface to form a specifically designed structure/composition can effectively improve the stability of the electrode/electrolyte interface, suppress structural transformation, improve the conductivity of the active materials and consequently lead to enhanced cycle stability and rate capability of LIBs. However, due to the restrictions of conventional coating methods, it is still very hard to obtain a conformal and multifunctional coating layer. This paper focuses on recent advances and summarizes the challenges in the development of surface coating technologies for LIBs. Based on these factors, the new concepts of 'ultrathin conformal coating', 'continuous phase coating' and 'multifunctional coating' are proposed and discussed, followed by the authors' rational perspectives on the future development and potential research hot spot in the surface/interface engineering of LIB materials and systems.

1. Introduction

Lithium (Li)-ion batteries (LIBs) are the most widely used secondary power supply for portable electric/electronic devices due to their high energy density, negligible memory effect and low self-discharge. However, to meet the demands of various newly emerging energy storage applications, such as electric vehicles and intermittent energy harvest/storage systems (in particular renewable energy – for example, wind power, solar and hydraulic energy), the performance of LIBs needs to be pushed further to achieve even higher energy/power density, more stable and longer cyclability, faster charging/discharging rate and better safety.¹ Thus, the research and development of the new LIB materials and battery systems have attracted extensive attention. Unfortunately, none of these new materials/systems have been successfully deployed in the present commercial LIB market.² Lithium–sulfur (S) and lithium–air batteries are claimed as the most promising systems because of their much higher theoretical

specific energy density; however, they are still far from being ready for mass commercialization unless the several critical shortcomings are solved with suitable ease and cost parameters.³

The typical well-developed lithium-transition-metal-oxide-based cathode materials (e.g. lithium cobalt oxide (LiCoO₂), lithium manganese oxide (LiMn₂O₄) spinel, lithium nickel manganese cobalt oxide (LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂), lithium nickel cobalt aluminum (LiNi_{0.8}Co_{0.15}O₂) and lithium iron phosphate (LiFePO₄)) and graphite anode materials are still the dominant electrode materials for commercial LIBs. For these, the engineering of their surface (i.e. the interface between the material and the electrolyte after packaged in a cell) by various coating technologies is the most straightforward and effective strategy to obtain the aforementioned desirable battery characteristics. Based on their roles in a battery, the functionalities of surface coatings can be categorized into three main types, which are described as follows (Figure 1).

Figure 1. Functions of surface coating for LIB materials

The first functionality of the surface modification of electrode materials is to suppress the side reactions on their surface in the battery's operating environments. Due to the high working potentials, the cathode materials for LIBs usually suffer from transition-metal dissolution, phase transformation and electrolyte decomposition. Surface-coated cathodes have been demonstrated to be effective in blocking these surface processes and enhancing the electrochemical performance of the materials. For example, the electron-insulating but ion-conducting lithium carbonate (Li_2CO_3) has been selected as the coating material for a commercial lithium cobalt oxide cathode.⁴ Lithium carbonate is a well-known constituent for the conventional solid/electrolyte interface (SEI) layer, which can electrochemically protect the electrode. The magnetron-sputtered lithium carbonate layer can impede the formation of the primary SEI layer. With this protective coating, even when increasing the charging potential up to 4.7 V or elevating the operation temperature to 55°C, lithium cobalt oxide electrodes still deliver remarkably improved cycling stability, compared with bare lithium cobalt oxide. In another case, it was found that aluminum oxide (Al_2O_3) at the surface region of lithium cobalt oxide particles also leads to enhanced structural stability during cycling, and this is believed to originate from the suppression of the undesirable phase transition of lithium cobalt oxide from hexagonal to monoclinic phase.⁵

For anode materials, it is generally accepted that the side reactions (e.g. the decomposition of electrolytes) between electrode/electrolyte interfaces play a major role in the capacity fading of LIBs during cycling. Due to this, an SEI layer forms on the graphite anode surface during the operation of LIBs.⁶ It has been known that this SEI layer has a significant contribution on the irreversible initial capacity loss, rapid self-discharge, unstable cycle life, low rate capability and poor safety of LIBs.⁷ Therefore,

it is necessary to coat a dense pyrolytic carbon layer on the surface of the graphite anode to impede SEI formation, improve interface stability and increase the first-cycle coulombic efficiency.^{8,9} Another typical anode is the zero-strained lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) anode material, on whose surface the electrolyte will gradually decompose to release gases (e.g. carbon dioxide (CO_2), carbon monoxide (CO) and hydrogen (H_2)) due to its high interfacial activity.^{10,11} To improve its interfacial stability, a series of surface coatings has been applied, including pyrolytic carbon coating,¹² aluminum fluoride (AlF_3) coating¹³ and oxide coating,¹⁴ which was used to protect the active surfaces and hinder gas formation.

Another function of the surface coating on the electrode materials is to improve their structural integrity during the prolonged cycling, particularly for high-capacity materials. More or less, volume variation of electrode materials occurs during the cycling. For example, graphite shows about 10% volume change, whereas a tin (Sn) alloy anode shows up to 200% and a silicon (Si) anode can reach as high as 400%, resulting in a very fast capacity decay.¹⁵ Applying a layer of rigid carbon and/or elastomeric polymer on the surface of these high-capacity silicon and tin-based anode materials will prevent them from collapsing and thus significantly improve their cycling performance.^{16,17} For example, Wang *et al.*¹⁸ reported that the cycling performance of a silicon anode can be significantly improved by coating a self-healing polymer on its surface. This concept is also applicable to other battery systems with similar issues. In a lithium–sulfur cell system, the massive volume expansion of sulfur cathode (up to 80%) and polysulfide dissolution during the cycle result in the rapid fading of capacity. The cycling performance of lithium–sulfur batteries can be significantly improved by coating carbon, nitride or a polymer on the sulfur surface.^{19–21}

Moreover, surface coating of electrode materials can also improve their ion/electron conductivity, which is essential for their rate performance. It has also been noticed that most LIB electrode materials have very poor electrical conductivity (e.g. lithium iron phosphate and lithium titanate are almost insulators).^{22,23} In this regard, surface coating of the electrode active materials with a conductive layer is an economical and feasible solution that can effectively improve the electronic and/or ionic conductivity of pristine materials. For example, high-electron-conductivity carbon, conductive polymer and nitrides have been coated on the surface of lithium iron phosphate²⁴ and lithium titanate^{25,26} materials, leading to a significantly improved high rate performance of these materials.

Briefly, coating treatments can significantly improve the performance of electrode materials for LIBs. Currently often-used coating technologies include chemical methods (e.g. coprecipitation, surface nitration/carbonization, chemical vapor deposition and sol–gel method) and physical methods (e.g. atomic layer deposition (ALD) deposition and mechanical mixing). Surface coating techniques have been widely used in the LIB industry. Well-commercialized surface-coated LIB materials include carbon-coated graphite anode, carbon-coated lithium iron phosphate and lithium titanate materials and oxide-coated lithium cobalt oxide and lithium nickel cobalt aluminum materials.

Despite the various coating methods that have been developed or even applied to commercial LIB materials, there are still several critical issues that remain challenging. These mainly include three aspects. The first one is the control of coating uniformity: it is very difficult to get a uniform, dense and highly conformal coating layer by traditional wet-chemical or mechanical coating methods, and the uncoated sections will be exposed to the electrolyte, causing undesirable performance decay of LIBs.²⁷ This is also associated with the difficulty of precisely controlling the coating thickness: the thickness of the coating layer by the conventional methods (up to tens of nanometers) is generally too thick, which will impede lithium-ion transportation and cause deteriorated battery performance, particularly at high rates.²⁸ The second issue is the lattice mismatch between the electrode material and the surface coatings, which may result in the detachment of the coating layer from the bulk materials during repeated cycling. The third challenge is the hardness of obtaining a multipurpose coating that comes with two or more functionalities, as most of the current coating technologies provide only a monofunctional coating.

Aimed at these issues, future surface coating techniques are expected to endow LIB materials with higher stability, durability and rate capability. Figure 2 shows technological trends and possible applications of future surface coating techniques for LIB materials. Specifically, the following aspects – namely, *ultrathin conformal coating*, *continuous phase coating* and *multifunctional coating* – are particularly feasible for tackling these issues. They may attract the focus of research and become potential hot spots.

Figure 2. Future surface coating techniques and their relative impact on the materials' characterizations

2. Ultrathin conformal coating

Conventional coating technologies are normally incapable of precisely controlling the thickness and morphology of the coated layers. As a result, battery performance is frequently unstable, particularly between different batches of products. The newly developed ultrathin conformal coating technologies are particularly advantageous in this and other aspects. First, a uniform and ultrathin coating can create an ultrathin layer that fully isolates the electrode materials from the electrolyte but allows the lithium ions and electrons to penetrate easily without significantly increasing the impedance. Second, a conformal coating layer on granular materials will exactly resemble the morphology of the particle and possess a pinhole-free structure, so that electrode degradation can be largely decreased in the battery.

By far, a number of technologies have been developed for this task, such as ALD, magnetron sputtering and kinetic control coating. Recently, the ALD technology has attracted great interest as a novel tool for modifying electrode properties by way of ultrathin surface coating. ALD is a surface-controlled process, in which the deposition of films is dictated by alternative self-terminating and gas–solid surface reactions.²⁹ By the ALD method, atomic scale ultrathin coatings (usually in several nanometers) with excellent uniformity, flexibility and conformity can be easily obtained. The thickness of the deposited layer can be controlled by adjusting the ALD cycles. In contrast, the coatings produced by conventional chemical methods are usually in the range of several hundreds of nanometers thick. Coatings obtained from ALD mainly include oxides (e.g. aluminum oxide, zirconium dioxide (ZrO₂), titanium dioxide (TiO₂) and zinc oxide (ZnO)) and nitrides (e.g. titanium nitride (TiN)). The most widely used ALD coating material is aluminum oxide, which uses trimethylaluminum and water as the precursors.³⁰ For example, conformal and nanometric aluminum oxide coatings on nanosized lithium cobalt oxide

cathode material, which is prepared by ALD, effectively increases the voltage window and rate performances compared to uncoated micro- and nanosized particles.³¹ ALD has also been used to deposit zirconium dioxide on lithium titanate anode material to improve its electrochemical performance, resulting in higher specific capacity, better cycling and rate performance.³² Lithium-ion-conducting solids, such as lithium aluminate (LiAlO_2), have also been coated on the surface of lithium nickel cobalt aluminum or graphite materials by ALD. Due to its fast lithium-ion transport kinetics, this novel lithium-ion conductor provides a thin but stable barrier against the side reactions without compromising the lithium-ion transfer at the interface.³³

However, one of the major drawbacks of the ALD method is its high cost and extremely low efficiency, which is unsuitable for mass production. As aforementioned, although various wet-chemical methods have been widely used to coat LIB materials, it is still a huge challenge to form an ultrathin and uniform layer on the surface of materials, due to the fast kinetics of the common wet-chemistry methods. Therefore, it is necessary to develop a highly controllable chemical coating process to obtain the desired ultrathin layer with a relatively high yield. For example, by carefully controlling the kinetics during the precipitation of aluminum phosphate (AlPO_4), a core-shell-structured $\text{LiCoO}_2@/\text{AlPO}_4$ can be obtained and the thickness of the aluminum phosphate coating can be tuned from 10 to 90 nm.²⁸ In another case, iron (III) phosphate (FePO_4) particles were coated with a very thin layer of polyaniline through an in situ polymerization method, and this composite was subsequently transformed into lithium iron phosphate with an ultrathin and semigraphitic carbon shell (1–2 nm) by pyrolysis in the presence of lithium salts.³⁴

Compared with conventional coating techniques, these ultrathin coating processes can uniformly and conformally coat the surface of the electrodes with precise control of the composition and thickness. These ultrathin layers will modify only the surface of the electrode materials, and the change in materials' bulk properties will thus be minimized.³⁵

3. Continuous phase coating

In order to improve the cycling performance of the electrode materials, various oxides (e.g. aluminum oxide, magnesium oxide (MgO), zinc oxide, MPO_4 (M = cobalt (Co), iron (Fe), nickel (Ni)) and zirconium dioxide), fluorides (e.g. ammonium fluoride (NH_4F) and aluminum fluoride) and binary oxides (e.g. lithium aluminate, lithium pyrophosphate ($\text{Li}_4\text{P}_2\text{O}_7$), yttrium aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$) and magnesium aluminate (MgAl_2O_4)) have been utilized as the coating layers, which are mainly expected to prevent electrolyte decomposition under high potentials. However, a huge volume change mismatch upon lithiation/delithiation frequently exists at the interface between the coating and the pristine materials, which leads to a weak interface bonding between these two phases and the easy detachment of the coatings during the cycling. For example, a manganese (Mn)-rich coating was prepared on a nickel-rich cathode material (Li

($\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$), which was supposed to improve its specific capacity and safety characteristics.³⁶ However, during the cycling, the nickel-rich bulk core shrank, whereas the outer layer expanded, causing inner cracks at the interface sections and deteriorated performance. Fundamentally, this volume change mismatch and poor bonding strength are caused by the diffusion-induced stresses among the nickel, cobalt and manganese atoms at the interface between the bulk and the outer layer during the high-temperature heat treatment.

In order to avoid this, the volume change mismatch between the coating layer and the bulk phase should be minimized. Compared with a heterogeneous phase coating, it is more desirable to form a continuous phase coating with a gradually evolved crystal structure that has a similar volume change during charging/discharging processes. For example, a nanofunctional and full-gradient approach has been developed to prepare a nickel-rich lithium transition-metal (manganese and cobalt) oxide material, in which the manganese concentration gradually increases but the nickel and cobalt concentration decreases linearly from the center to the surface.³⁷ These gradient materials have a continuously and gradually converted crystal structure, which significantly reduces the volume change mismatch between the coated phases and pristine materials. This strategy has also been applied to coat spinel lithium manganese oxide by a concentration-gradient layer with a continuously increasing nickel content to form finally a surface layer of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$. Due to the same crystal structure of lithium manganese oxide and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, this material is homogeneous without any apparent gaps/cracks between the inner core and the outer coating. The final coated materials thus show excellent capacity stability even at 55°C, in which condition a traditional lithium manganese oxide material inevitably fails.^{38,39}

Briefly, what makes continuous phase coating interesting for LIB development is that such coating strategy can significantly maintain the integrity of materials under electromechanical stress, particularly on the particle levels. Furthermore, it also helps improve the surface coverage of the coatings on materials due to their similar gradient composition.⁴⁰

4. Multifunctional coating

An ideal coating should meet many requirements, which mainly include (a) high electronic conductivity, (b) high ionic conductivity, (c) the ability to protect materials from acid attack (e.g. hydrofluoric acid (HF) formed from the decomposed electrolyte) and (d) good flexibility. Nevertheless, it is extremely difficult for a single coating layer to meet these requirements fully, due to the complicated physical and chemical processes inside LIBs. For example, a carbon coating has good electrical conductivity but lacks ionic conductivity. Although an oxide coating can significantly improve the stability of the electrode materials at high potential, its electronic conductivity is often very low. Despite that, a polymer coating can effectively buffer the volumetric variation of silicon or other alloy anode materials; these coatings usually show low ionic and/or electronic conductivity.

To deal with these issues, the multiphase coating method could be a potential solution. In one case, lithium iron phosphate cathode materials were coated with a mixture of lithium phosphate (Li_3PO_4) and carbon, which resulted in an improved rate capability compared with carbon-coated lithium iron phosphate. In this architecture, lithium phosphate and carbon possess excellent ion and electronic conductivity, respectively. Consequently, the resultant lithium phosphate/carbon hybrid coating showed much decreased interfacial impedance.⁴¹ In another study, a graphene/aluminum oxide hybrid coating was introduced to prepare silicon composite anode materials. Crystalline silicon particles were firstly deposited onto graphene sheets by using liquid chlorosilane as silicon source. Then, an aluminum oxide layer was directly deposited on the silicon–graphene composite. In this configuration, graphene was used as a flexible buffer to neutralize the huge volume expansion of silicon particles. At the meantime, the side reactions between the electrode and electrolyte were suppressed by the aluminum oxide layer. Consequently, this design results in a remarkable enhancement in the initial efficiency and reversible capacity.⁴²

5. Conclusion and perspective

Consumers are constantly demanding lighter, safer and space-effective LIBs. Such demands will continue to generate numerous research activities toward the development of electrode materials. Among different modification methods, surface coating plays an important role in the modification of LIB materials, which significantly improves the cycling and rate performance of LIBs and shows potential applications for the newly emerged lithium–sulfur or lithium–air/oxygen (O_2) systems. Application of surface coating in LIB materials has three aspects: (a) the coating layer acting as a protecting phase to enhance the stability of the materials, (b) buffer volume expansion during charging/discharging processes and (c) improvement of electronic/ionic conductivity. However, due to the restrictions of conventional coating methods, it is still very hard to obtain a conformal and multifunctional coating layer. Therefore, in order to achieve the desired functionalities, it is necessary to design and control precisely the structure and chemical compositions of the interface between the coating phases and the pristine materials. The future of the new coating technology will focus on ultrathin, uniform, continuous and multifunctional coating and other combinations to integrate their merits. Thus, diversified coating methods need to be developed, such as ALD and kinetics-controlled wet-chemical methods. Although there are still many problems to solve, the ubiquitous applications of surface coating technologies with low cost and convenience are very much anticipated in the near future. Ultimately, the performance of these coated materials will completely exceed that produced by the conventional coating process.

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