

Application of different types of nanocoatings in lithium-ion batteries

Jiatong Bo*

Manchester Metropolitan Institute, Hubei Unibersity, Wuhan, China

*Corresponding author: 21904474@stu.mmu.ac.uk

Abstract. Nowadays, nanocoating has been highly regarded because of its performance dramatically surpassing traditional materials. The nanocoating has various unique characters such as surface effect, small size effect and quantum effect. With the growing of population of world and industrial process, batteries have been increasingly vital in a variety of domains, especially in electric vehicles. Lithium-ion batteries (LIBs) stand out from the crowd among those batteries because of its high energy density and long cyclic lifespan. This research will discuss the application of nanocoating in LIBs. Nanocoating has the potential to enhance the safety and cyclic lifespan of Li-ion batteries. Furthermore, it could promote electrical conductivity and restrain the volume expansion. It also could improve safety character and energy density. This research summarizes the use of different nanocoatings in LIBs and analyze the performance of these nanocoatings. This research is expected to provide a new perspective for the development of new nanocoatings for application in LIBs.

Keywords: Nanocoatings; lithium-ion batteries; electrochemical performance.

1. Introduction

Nanotechnology have developed dramatically, which widely used in different fields, such as medicine, material science and biology. The definition of nanotechnology is also changing with research deeply continuing. Nanomaterials have unique properties compared with bulk materials because of its small size. Nanotechnology is concerned with how to apply it in daily life and industrial production [1, 2]. In recent years, nanotechnology is never a new concept for every career, which it can be seen as a general-purpose technology [3].

With nanotechnology rapidly developing, various themes of it have been used in different fields. For example, wound dressing and pregnancy test are used in health and fitness, and stain resistant cushions are applied in home and garden. Nanocoating is one of the main domains, which is a technique for functionalizing nanomaterials for incorporation into polymer coatings [4]. Various performance of nanocoating surpass the traditional materials, such as higher hardness and wear resistance, increased corrosion resistance, self-lubricity and self-cleaning power. Due to above mentioned performance, nanocoating offers numerous applications [5, 6], such as machinery environments. In addition, it can be used in the food packaging sector to offers antimicrobials and antioxidant properties [7].

With the growing of the world's population and industrial process, the need of energy increasingly rises. Batteries as a vital energy storing device are essential to fulfill ever-growing demand of energy. Various renewable energy such as wind power and solar power may be unstable or intermittent, so batteries could store these energies to use without special conditions. Electric vehicles have been seen as an effective solution to decrease the emission of greenhouse gases. The progress of battery technology is the key part of electric vehicles popularization. Especially, LIBs have been highly regarded because of its high energy density and long cyclic lifespan. Although batteries fields have developed rapidly, new generation batteries still have some obvious disadvantages such as poor stability. In addition, even silicon anodes also have its downsides with high volume expansion during charge and discharge [8].

To improve these drawbacks, nanocoating has been used in batteries massively due to its above-mentioned performance. A number of reports have appeared, introducing some nanocoating applying in battery fields, but a review dedicated to summarize nanocoating used in anode material, cathode

material, solid-state electrolyte and circuit board is still missing. This research would consider to summarize these a variety of nanocoating on LIBs and contrast of the difference between them.

2. The use of nanocoating in LIBs

2.1. Carbon nanocoatings

Nanometer-thin carbon coatings made from a citrate precursor can enhance the performance of LIBs by firmly adhering to substrate particle surfaces [9]. Carbon nanocoatings are used as “electrochemical wiring”, which could establish efficient electron and ion conduction pathways in nanoparticle-based electrodes [10]. By applying this into active materials, it could achieve improving electronic conductivity, preserving electrode material, enhancing structural stability by constructing a path for electron movement. Carbon nanocoatings are prepared by sol-gel method and subsequent firing in an inert atmosphere [11]. The preparation of carbon nanocoating on the battery has improved the electrical conductivity obviously. When the carbon content reached at about 5 wt%, the conductivity plateau value is higher than uncoated one. Compared to non-coated materials, a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ active material with carbon nanocoatings, the capacity is mainly up to 2 times because of a decrease in polarization. In addition, carbon coated material could maintain reversible capacity than non-coated one. The capacity of non-coated material would diminish from 140 mAh/g to 40 mAh/g, but carbon coated one could maintain its capacity. In addition to acting as an electrically conductive medium, the carbon coating can be used as a mechanical and/or (electrical) chemical protective layer to protect the underlying active material. Electronic conductivity and ionic permeability are improved by optimizing the thickness and carbon content of the coating. The continuous coating could be prepared by controlling active particle size [11]. However, this method could only be suitable up to high temperature and not sensitive to reductive atmosphere. There have been some probabilities that using the electron-conductive polymers [12, 13].

2.2. Diatomite-derived nanosilicon

Silicon has used as a high capacity anode material for LIBs. However, traditional carbothermic reduction production spends much money and energy [14]. There is a method to efficiently convert silica-based frustules within diatomite (DE) into nanosilicon (nanoSi). The silica structure in DE combining with common salt (as a heat absorber) could be converted to nanosilicon by magnesiothermic reduction. The converted nanosilicon particles maintain the original porous structure of diatomite, which could benefit with penetration of electrolyte and volume expansion. After 50 cycles, the specific discharge capacity of the nanosilicon anode still maintain 1102.1 mAh/g. After 50 charge-discharge cycles and high areal loading, the Coulombic efficiency was consistently around 100% and >80% capacity retention was preserved. It can perform high silicon utilization at high current density. The nanosilicon anode, using PAA as a binder, maintains a specific high discharge capacity even at high current densities of 4C. In addition, nanosilicon anode has a good capacity retention rate from 67.4% to 98.3%.

2.3. Rutile-TiO₂ nanocoatings

There are various intrinsic characters of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ which leads it receiving attention [15]. Higher Li-insertion voltage prevents electrolyte reduction on electrode surfaces and the formation of the SEI layer. This material is a zero-strain insertion material, which can be used to react reversibly in either direction during lithium insertion/extraction. However, the process is hindered by kinetic issues, low electrical conductivity, and a low lithium diffusion coefficient. To tackle this problem, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheets was prepared. The performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheets (LTO NSs) with nanocoating outdistance than pristine LTO NSs. The electrochemical performance test revealed that all samples demonstrated a high specific capacity at a high rate. At a high charge-discharge rate (10 C), the sample can perform 100 cycles with little capacity attenuation. At charge and discharge rates of 5 C and 20 C, the LTO-RT-600 sample showed little attenuation after 100 cycles, maintaining its

capacity at 168 mAh/g and 149 mAh/g, respectively. Additionally, at extremely high rates of 60 C, the LTO-RT-600 can still provide more than 10 times capacity of uncoated LTO-600. The charge transfer resistance of the LTO-RT-600 is only a half of the LTO-600, which could protect circuit.

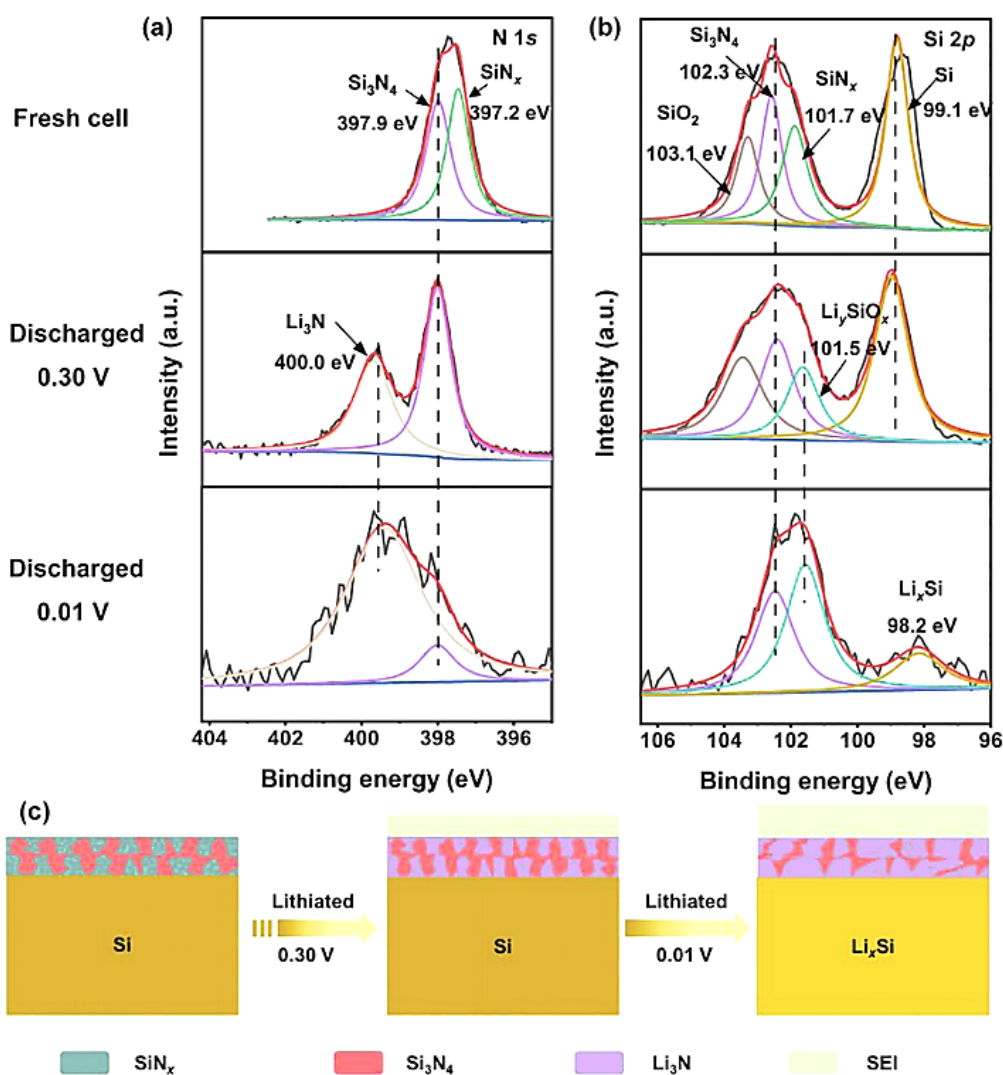


Fig. 1 XPS analysis and Li^+ storage mechanism [16]. XPS spectra for N 1s (a) and Si 2p (b) fresh cells. (c) Phase evolution for p-Si@SiN composite.

2.4. Silicon nitride nanocoatings

High theoretical specific capacity of silicon makes it as a potential anode material. However, there would be volume expansion when the process of charging or discharging [16]. Si-based anodes in LIBs are restricted by poor performance on capacity and rate. This is because poor conductivity and unable solid electrolyte inter-face. To address these problems, a new method has been developed that can be used to enhance the stability and electrical conductivity of structures, thereby enhancing their storage properties. By hot nitriding Mg_2Si powder to obtain porous silicon, the prepared porous silicon was etched in 2 wt% diluted hydrofluoric acid. The surface treated porous silicon is annealed in ammonia (NH_3) atmosphere to produce SiN composite nanocoatings. As part of the coating, Si_3N_4 provides high mechanical strength, helping to make structure of the silicon more integrally anode, preventing breakage and pulverization due to silicon volume expansion. SiN_x in the coating is able to generate Li_3N with fast ionic conductivity during the lithium process, which promotes the transport of lithium ions. The presence of Si_3N_4 inhibits the formation of unnecessary solid electrolyte interfaces (SEI), reducing further reaction of the electrolyte with fresh silicon (Fig. 1). In long-term cycle tests, SiN-coated batteries showed excellent cycle stability and a small capacity decay rate,

indicating that the coating helps to improve battery life. SiN-coated batteries perform well in fast-charging tests, being able to complete a charge in minutes while maintaining a high discharge capacity, which is critical for fast charging needs in real-world applications. The coating's protective effect slows down the capacity attenuation of the silicon anode during the cycle, enhancing the long-term cycle stability of the battery.

2.5. TiO₂ nanocoatings

Ni-rich transition metal layered oxides have higher working potential, higher practical capacity and the lower cost [17]. This is the reason why it is widely used in current commercial cathodes. However, there are some side reactions. Because of the structural stability and chemical inertness, TiO₂ is seen as one of the most ideal material. To form a uniform TiO₂ nanocoating on the LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM) surface, the morphology of the TiO₂ nanocoating is controlled by precise controlling of the hydrolysis kinetics of tetrabutyltitanate (TBOT). This nanocoating has showed various excellent performance. TiO₂ nanocoatings, due to their chemical inertness to the electrolyte at high voltage, effectively safeguard the positive electrode material during high voltage charge and discharge. TiO₂ nanocoatings facilitate both phase transition directions during the charging and discharging cycle of the device. Additionally, TiO₂ nanocoatings can reduce the side reactions by providing a stable interface, thus reducing the polarization of the battery during charging and discharging. It could not only improve thermal stability and magnification performance, but it also suppresses structure attenuation and enhance ion diffusion.

2.6. Integrated layered-spinel structures with nanocoatings

Due to a high specific capacity, Li-rich solid solution is the most promising cathode material. However, there are issues like poor cycle stability and low rate performance [18]. The integration of artificial protective layer and induced laminar-spinel structure is formed by introducing AlF₃ on the surface to improve cyclic stability and high rate performance. AlF₃ is generated a chemical process called "coating induction strategy". This nanocoating have various functions. AlF₃ nanocoating effectively minimizes irreversible capacity loss during the initial charge and discharge process by minimizing side reactions between the cathode material and electrolyte. It could improve cycling stability and high magnification performance. It could reduce voltage decay, which is essential to make the long-term cycle more stable and energy retention rate of it. The reduction of the battery's charge transfer resistance enhances its charging and discharging efficiency and power density.

2.7. AlPO₄ nanocoatings

The research has been conducted on new cathode materials of LIBs with high specific capacities. LiNi_{0.80}Co_{0.15}Al_{0.05}O₂ (NCA) is a highly desirable cathode material because it shows high specific capacity [19]. Poor cycle performance and thermal stability are one of the most common issues. AlPO₄ is gaining attention for its scalable and simple industrialization feature, which is uniformly coated on NCA surfaces using a wet chemical method. This nanocoating have various functions. The cycle stability and thermal stability are significantly improved. The capacity retention rate of coated NCA was significantly higher than uncoated NCA, reaching 86.9%. the AlPO₄ coating helps to reduce side reactions between electrode and electrolyte, thereby reducing the charge transfer impedance. NCA materials coated with AlPO₄ show significant improvement in thermal stability. The initial decomposition temperature of the coated NCA material was increased from 191.4 °C to 263.2 °C. AlPO₄ coating forms a uniform protective layer on the NCA surface, effectively inhibits the corrosion of the electrolyte to NCA, and reduces the side reaction in the charging and discharging process.

2.8. Carbon-Al₂O₃ double coatings

To develop high energy LIBs, one class of materials is of interest because of their accumulated cationic and anionic reversible REDOX activity, which can significantly increase the energy density and capacity. Nickel-based cationic disordered oxides exhibit high theoretical capacity. However,

cycle performance is restricted by nickel's low REDOX capacity and unstable oxygen REDOX reactions. This is because electron on nickel 3d and oxygen 2p orbitals overlap each other severely [20]. The carbon/alumina double coating and partial aluminum ion substitution have enhanced the capacity and cycling performance of nickel-based cationic disordered oxides, providing various functionalities. The carbon coating enhances the capacity of the positive electrode material by enhancing oxygen redox activity, generating peroxy-like species. It also helps to improve electronic conductivity, making the material more efficient in electron transport during charging and discharging. The aluminum oxide coating and aluminum ion doping improve the cyclic stability of the positive electrode material, thanks to their shielding effect on side reactions and a more stable oxygen lattice. The combined use of carbon and alumina double-layer coatings not only improves cycle performance but also increases capacity, providing a new method to prepare disordered cationic oxide cathode materials with high energy density.

3. Conclusion

In conclusion, this research introduces eight application of nanocoating in LIBs. Almost all nanocoatings increase the reversible capacity and enhance the cyclic stability. Additionally, as for protecting the electrode material, carbon nanocoating, TiO₂ nanocoating and AlPO₄ nanocoating also show these properties. TiO₂ nanocoating could reduce the side reaction by provide a stable interface. Integrated layered-spinel structures combined with nanocoating and rutile-TiO₂ nanocoating could decrease the residence. AlPO₄ nanocoating and TiO₂ nanocoating could increase the heat stability of LIBs. Silicon nitride nanocoating offers high mechanical strength, maintaining the structural integrity of the silicon anode during charge and discharge, and excels in fast-charging tests.

References

- [1] Lindquist E, Mosher-Howe K N, Liu X. Nanotechnology... What is it good for?(Absolutely everything): A problem definition approach. *Review of Policy Research*, 2010, 27(3): 255-271.
- [2] Nasrollahzadeh M, Sajadi S M, Sajjadi M, et al. Applications of nanotechnology in daily life. *Interface science and technology*, 2019, 28: 113-143.
- [3] Malik S, Muhammad K, Waheed Y. Nanotechnology: A revolution in modern industry. *Molecules*, 2023, 28(2): 661.
- [4] Chinglenthoba C, Ramkumar K, Shanmugaraja T, et al. Study on nanotechnology, nanocoating and nanomaterial. *The Economist*, 2005.
- [5] Gu Y, Xia K, Wu D, et al. Technical characteristics and wear-resistant mechanism of nano coatings: a review. *Coatings*, 2020, 10(3): 233.
- [6] Rovera C, Ghaani M, Farris S. Nano-inspired oxygen barrier coatings for food packaging applications: An overview. *Trends in Food Science & Technology*, 2020, 97: 210-220.
- [7] Mohammad Z H, Ahmad F. Nanocoating and its application as antimicrobials in the food industry: A review. *International Journal of Biological Macromolecules*, 2024, 254: 127906.
- [8] Itani K, De Bernardinis A. Review on new-generation batteries technologies: trends and future directions. *Energies*, 2023, 16(22): 7530.
- [9] Dominko R, Gabersček M, Drogenik J, et al. A novel coating technology for preparation of cathodes in Li-ion batteries. *Electrochemical and Solid-State Letters*, 2001, 4(11): A187.
- [10] Gaberscek M, Dominko R, Bele M, et al. Binding and wiring in electrodes for Li ion batteries. *New Trends in Intercalation Compounds for Energy Storage and Conversion. Proceedings of the International Symposium (Proceedings, 2003–20)*. 2003: 309-315.
- [11] Dominko R, Gaberscek M, Bele M, et al. Carbon nanocoatings on active materials for Li-ion batteries. *Journal of the European Ceramic Society*, 2007, 27(2-3): 909-913.
- [12] Dominko R, Arčon D, Mrzel A, et al. Dichalcogenide nanotube electrodes for Li-ion batteries. *Advanced Materials*, 2002, 14(21): 1531-1534.

- [13] Dominko R, Gaberscek M, Arcon D, et al. Electrochemical preparation and characterisation of Li_2MoS_2 -x nanotubes. *Electrochimica acta*, 2003, 48(20-22): 3079-3084.
- [14] Campbell B, Ionescu R, Tolchin M, et al. Carbon-coated, diatomite-derived nanosilicon as a high rate capable Li-ion battery anode. *Scientific reports*, 2016, 6(1): 33050.
- [15] Wang Y Q, Gu L, Guo Y G, et al. Rutile- TiO_2 nanocoating for a high-rate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode of a lithium-ion battery. *Journal of the American Chemical Society*, 2012, 134(18): 7874-7879.
- [16] Mei S, Guo S, Xiang B, et al. Enhanced ion conductivity and electrode–electrolyte interphase stability of porous Si anodes enabled by silicon nitride nanocoating for high-performance Li-ion batteries. *Journal of Energy Chemistry*, 2022, 69: 616-625.
- [17] Fan Q, Lin K, Yang S, et al. Constructing effective TiO_2 nano-coating for high-voltage Ni-rich cathode materials for lithium ion batteries by precise kinetic control. *Journal of Power Sources*, 2020, 477: 228745.
- [18] Zhao T, Chen S, Chen R, et al. The positive roles of integrated layered-spinel structures combined with nanocoating in low-cost Li-rich cathode $\text{Li}[\text{Li}_{0.2}\text{Fe}_{0.1}\text{Ni}_{0.15}\text{Mn}_{0.55}]\text{O}_2$ for lithium-ion batteries. *ACS applied materials & interfaces*, 2014, 6(23): 21711-21720.
- [19] Qi R, Shi J L, Zhang X D, et al. Improving the stability of $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ by AlPO_4 nanocoating for lithium-ion batteries. *Science China Chemistry*, 2017, 60: 1230-1235.
- [20] Yu Z, Huang H, Liu Y, et al. Design and tailoring of carbon- Al_2O_3 double coated nickel-based cation-disordered cathodes towards high-performance Li-ion batteries. *Nano Energy*, 2022, 96: 107071.