Influence of Atomic Deposition Surface Modification Technology on the Cycle Efficiency and Capacity of Lithium Ferrous Silicate Cathodes for Lithium-ion Batteries

Wang Qingsheng[1, 2], Povel Nivokov[1, 2], Anadoli Popovich[2], Yu Yao[1], Yang Zhelong[1]

[1]Technical Department, Zhejiang Changxing Sino-Russian New Energy Material and Technology Research Institute, Changxing, China

[2]Material Institute, Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

Email address:
tse-battery@mail.ru (Wang Qingsheng), novikov.p.a@gmail.com (P. Nivokov)

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Abstract: This article explored the use of atomic layer deposition to deposit cathode material LF(M)S coated with nano-scale Al_2O_3(C) film by growth coating, and successfully obtained the composite LF(M)S coated with Al_2O_3 (C) cathode material. The test results of various electrochemical performance parameters show that the surface modification treatment method can effectively improve the various electrochemical properties of the cathode material. The synthesized LF(M)S was analyzed by a Time of Flight Secondary Ion Mass Spectrometer, and a clear topography and three-dimensional topography of the surface coated with Al_2O_3 and C were obtained; the surface morphology and uniformity of the deposited layer were studied by Atomic Force Microscope and the crystal structure of the material was analyzed by XRD. The electrochemical performance of the battery assembled with the positive electrode material was characterized by an electrochemical workstation and a charge-discharge tester. The results showed that the surface coating can effectively prevent the side reaction between the material and the electrolyte at high voltage, and reduce the irreversible capacity loss in the first charge and discharge process, because the chemical properties of the coating are not active. At the same time, due to the stable structure and good conductivity of the coating material, the stability of the structure during charging and discharging of the material is maintained, thereby reducing the loss of battery capacity, maintaining good conductivity between the material particles, and improving the cycle performance of the material.

Keywords: Atomic Layer Deposition (ALD), Material Coating Modification, Electrode Passivation, Growth Coating

1. Preface

Atomic Layer Deposition (ALD) is one of the commonly used surface modification treatment methods in recent years. Based on the lithium ion battery cathode material Lithium Ferrous Silicate [LF(M)S] has a lot of eye-catching advantages, but its structural stability and conductivity is not satisfactory, so ALD method was used to modify the material surface in this study.

The deposition coating modification is carried out on the Picosun R-150 atomic deposition equipment (Figure 1). The MH Picosun R-150 equipment is equipped with an automated system that can independently provide 6 kinds of precursors (liquid and solid reagents with high vapor pressure), which makes it possible to grow multilayer coatings of a given thickness. In this system, it is possible to use gases: argon, nitrogen, oxygen. In addition, the device is equipped with an ozone generator and a plasma generator, which can reduce the synthesis temperature caused by the formation of high-energy particles, free radicals, molecules, atoms, etc. One of the distinguishing features of this machine is the replaceable module, which allows growth coating of various powder materials (Figure 2).
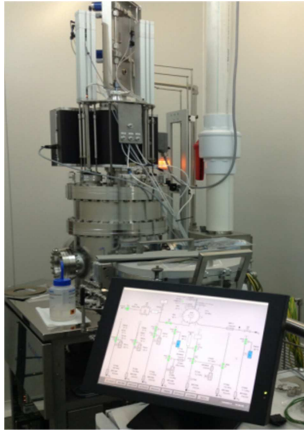
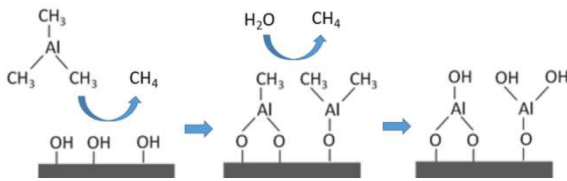**Figure 1.** *Picosun R-150 ALD atomic deposition device.*

Figure 2. *ALD reaction mechanism.*

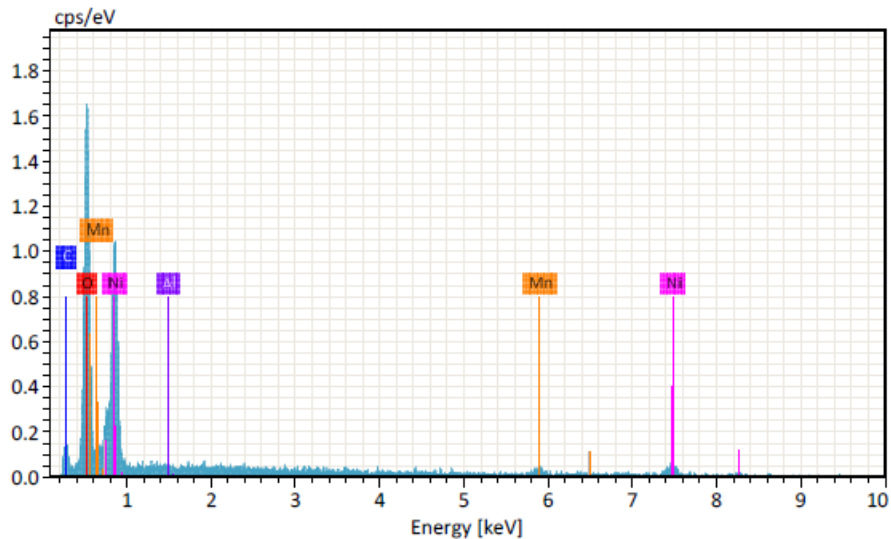# 2. Experimental Process and Result Characterization

2.1. Preparation of Materials

LiAc·2H$_2$O   (appropriate   amount),   Fe(NO$_3$)$_3$·9H$_2$O

(appropriate amount), TEOS (appropriate amount) and glucose (appropriate amount) were stirred and mixed in ethanol solution (AR grade), solidify and sinter at 650°C for 7h under N$_2$/Ar$_2$ protective gas; the generated products were ground and screened to obtain Li$_2$FeSiO$_4$ basic material [1].

Preparation method of Al$_2$O$_3$ film: According to the characteristics of the equipment MH Picosun R-150, the following deposition procedures were drawn up and tested (according to the deposition parameters of different materials provided by the manufacturer, see Figure 3).

1. Respectively select trimethylaluminum [Al(CH$_3$)$_3$, TMA] (99.9999%) with carrier gas flow rates of 100 sccm and 150 sccm and deionized water as the precursor of Al$_2$O$_3$, and the temperature is 20°C.
2. The intermediate space pressure is about 7hPa, and there is a constant flow of 300sccm nitrogen (purity is 99.99%) in the reactant pipeline.
3. Pump the vacuum to 1kPa and place the powder in the vacuum chamber. The synthesis temperature of the growth in the chamber is 330°C.
4. The beginning of the deposition process: Start the continuous supply of TMA, C and H$_2$O, and purge with nitrogen for 1 second between filling the reagents.
5. After finishing the specified number of cycles of deposition, stop the process and cool to room temperature.
6. The pressure is delivered to standard atmospheric pressure, and samples are taken for research.

Element	At. No.	Line s.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	abs. error [%] (2 sigma)	abs. error [%] (3 sigma)
Nickel	28	L-Serie	5112	44.34	44.34	18.66	6.94	13.88	20.82
Oxygen	8	K-Serie	6167	42.05	42.05	64.92	6.37	12.74	19.12
Manganese	25	K-Serie	160	7.00	7.00	3.15	0.73	1.47	2.20
Carbon	6	K-Serie	470	6.32	6.32	13.01	1.82	3.65	5.47
Aluminium	13	K-Serie	28	0.29	0.29	0.26	0.09	0.17	0.26
		Sum	100.00		100.00	100.00			

Figure 3. *ALD-(10 deposition cycles) 250eV Cs spray gun energy parameters for different materials deposition.*

After atomic deposition, LF(M)S material coated with Al_2O_3(C) was obtained.

2.2. Characterization of Structure and Morphology

The XRD test uses the D8 Advance tester. After grinding, the sample is laid flat on the sample holder. The Cu target is used as the radiation source of the device. The scanning angle range is 5°-90°, and the scanning speed is 10°/Min. The surface morphology analysis equipment is Tescan Maia3, which observes the uniformity of the surface morphology of the sample [2].

3. Experimental Results and Discussion

3.1. XRD Result Analysis

Figure 4 is a pure phase Li_2FeSiO_4 basic material. From the XRD spectrum, it can be seen that the crystallinity is not very good and the peak shape is not sharp enough. Figure 5 is the Li_2FeSiO_4 material coated with Al_2O_3 after atomic deposition. It can be seen from the XRD spectrum that the original structural characteristics of the material are not found after the coating modification, but the peak shape becomes sharper and the surface crystallinity is better.
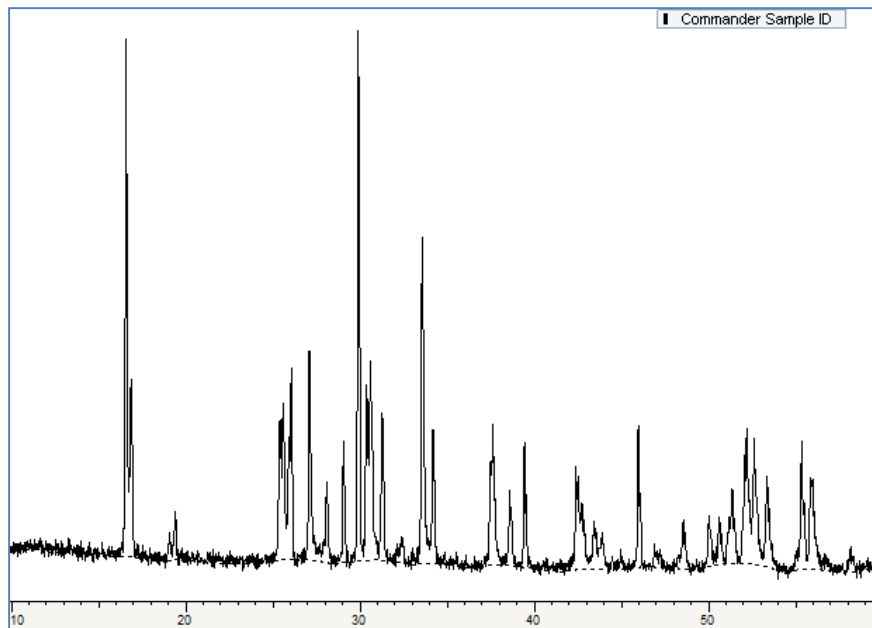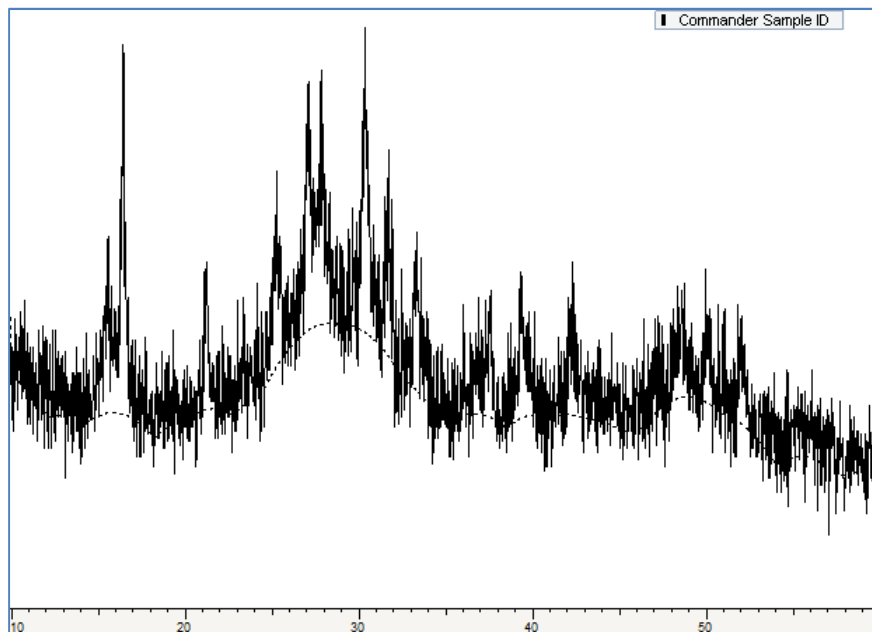

Figure 4. Li_2FeSiO_4 basic material.

Figure 5. Li_2FeSiO_4 coated with Al_2O_3.

3.2. SEM Structure Morphology Analysis

Figure 6 shows the basic material (a), multiple element coated with C (b), Li_2FeSiO_4 material coated with Al_2O_3 (c) electron microscope image and element deposition material, the figure C shows the coating effect and distribution of the material surface, it is beneficial to improve the diffusion rate of lithium ions [3].
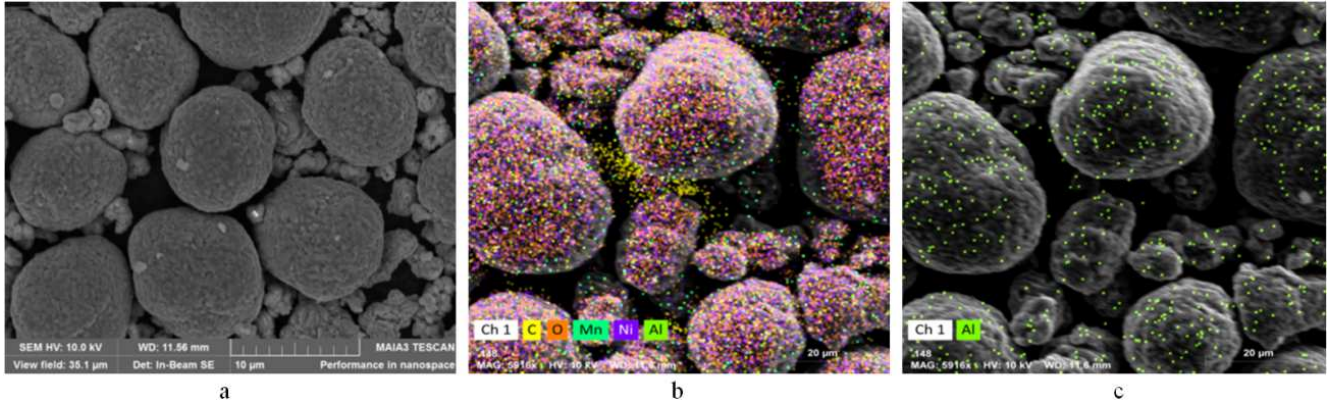

Figure 6. *Li_2FeSiO_4 basic material (a) coated with different element materials (b) coated with Al_2O_3 (C).*

3.3. TOFSIMS Structure Analysis

The TOF-SIMS mass spectrum of the sample is shown in Figure 7. Al element and other hydroxide groups are found on the surface, which indicates that there is an alumina passivation layer [4], and a certain content of -OH groups is also found, which indicates that the material insufficient passivation (Figure 8).

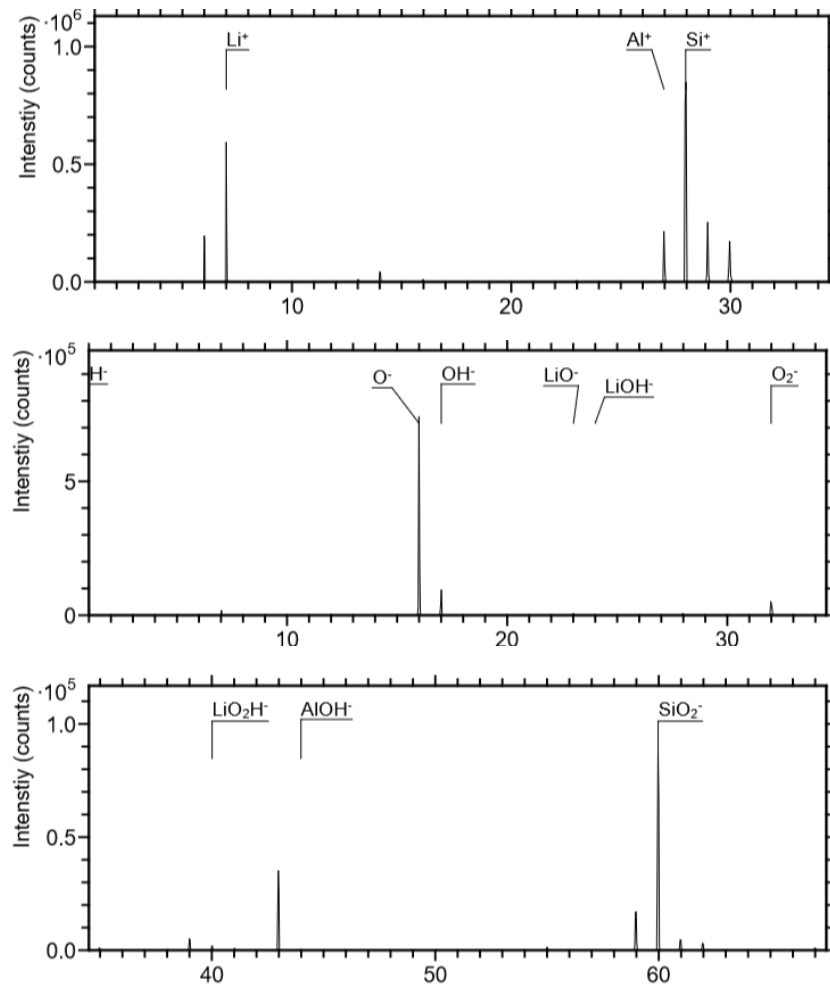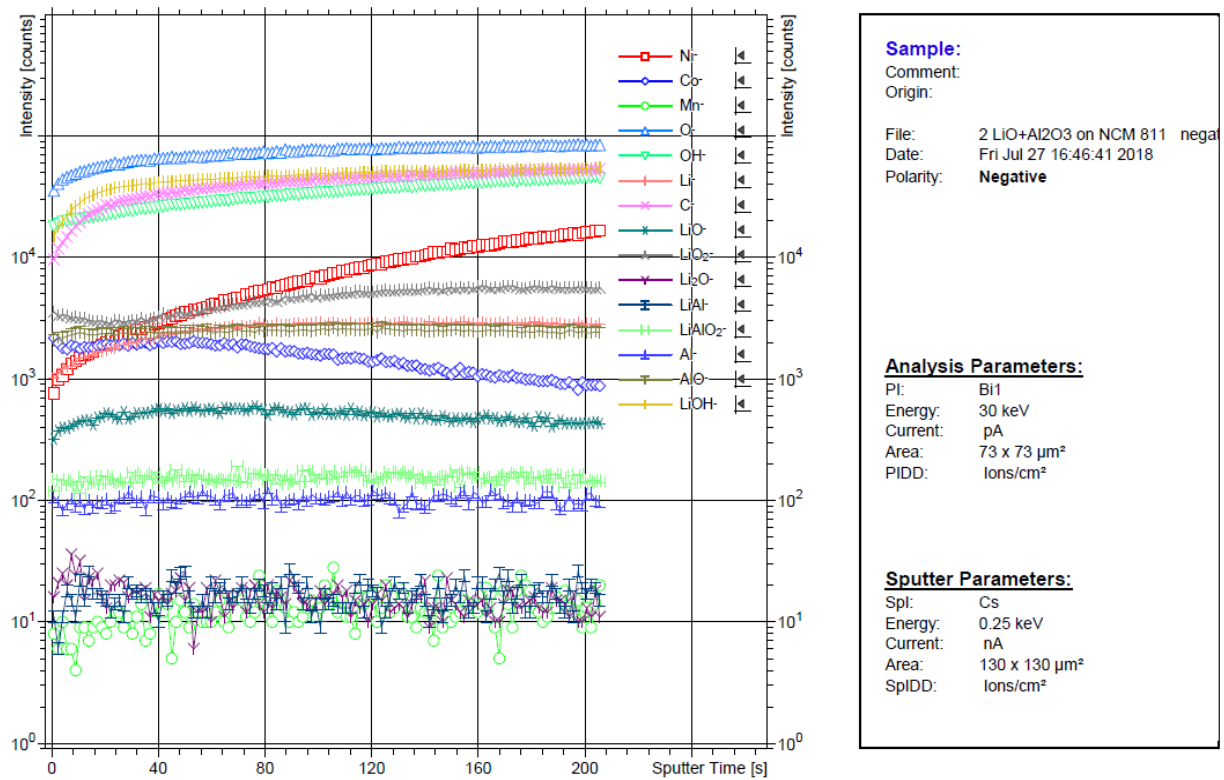**Figure 7.** *Mass spectrum of Li_2FeSiO_4 coated with Al_2O_3.*

Figure 8. *TOF SIMS analysis results (10 deposition cycles).*

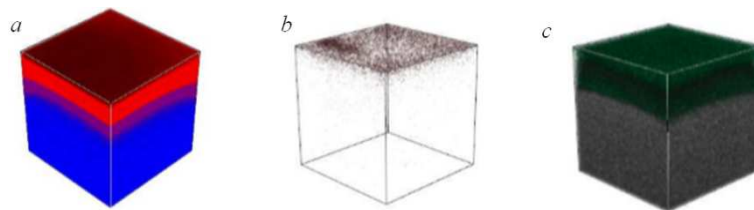Analysis in positive mode using 250eV of O_2 spray gun energy found high lithium and aluminum oxides.

Figure 9. *TOF-SIMS-3D reconstruction of Al_2O_3 deposited on Li_2FeSiO_4.*

Figure 9 shows the TOF-SIMS 3D reconstruction of the surface deposition layer of the fitting material, shows the effect of surface deposition and the uniformity of the deposition layer thickness and distribution.

3.4. Use AFM to Observe Surface Topography

The prepared material was observed under an atomic force microscope (Figure 10), and it was found that the surface coating was uniform, the particles were not significantly agglomerated, and the 2D image surface particle dispersion performance was good. There is no obvious stress between the particles on the surface of the 3D image.
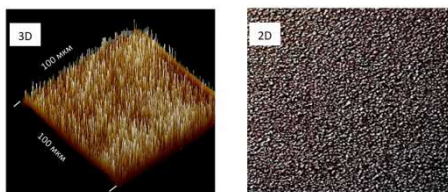

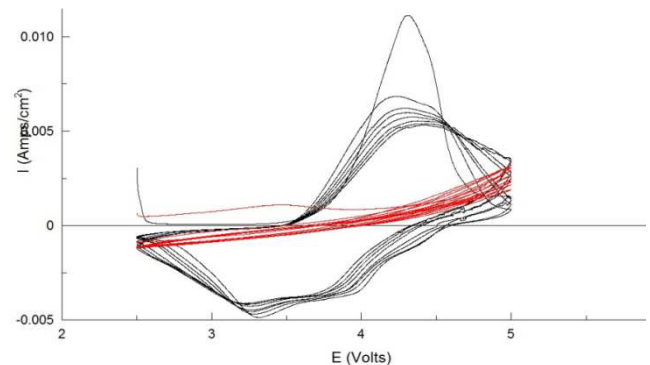**Figure 10.** *AFM surface analysis.*

Figure 11. *Cyclic voltammetry curve of Li_2FeSiO_4 coated with Al_2O_3.*

3.5. Cyclic Voltammetry Analysis

The cyclic voltammetry curve (Figure 11) shows good consistency, indicating that the material has great cyclic performance. The impedance is small during the recycling process, and the loss of capacity is small, indicating that the coated material has excellent dynamic performance [5],

Which reduces the polarization of the electrode material during charging and discharging. In the process of electrochemical reaction, electrode passivation reduces solvent erosion, reduces the potential of the micro-area, and improves the stability of materials and electrodes. The coated material may penetrate into the lattice of the material to maintain the stability of the structure when the material is charged and discharging, thus reducing the loss of capacity and improving the circulation performance of the material [6].

4. Electrochemical Performance Test

First, weigh the required materials according to the mass ratio of cathode material: conductive carbon black: PVDF of 8:1:1, and then put them in a ceramic mortar for dispersion and grinding. After fully grinding and dispersing, add an appropriate amount of NMP and continue grinding for some time, after the slurry becomes a certain viscosity, it is evenly coated on the current collector, and then the coated current collector is placed in a vacuum oven and placed at 80°C for 12 hours. The button battery CR2032 has a cathode electrode. The thickness of the porous polyethylene membrane is 25μm. The metal lithium sheet is assembled in the argon-filled glove box as the negative electrode. The $H_2O<1ppm$ and $O_2<50ppm$ in the argon-filled glove box. Use electrolyte $1 M$ $LiPF_6$ solution, dissolved in a ternary solvent with a volume ratio of ethylene carbonate, dimethyl carbonate and methyl ethyl carbonate of 1:1:1. Before starting electrochemical measurement, all batteries keep it at open circuit voltage for 6 hours.

Using BTS-NEWARE-CT-3008-5V10mA (NEWARE, China) battery test system, in the voltage range of 1.5-4.8V (VS-Li/Li+), the battery is charged and discharged with a current of 0.05C [8].
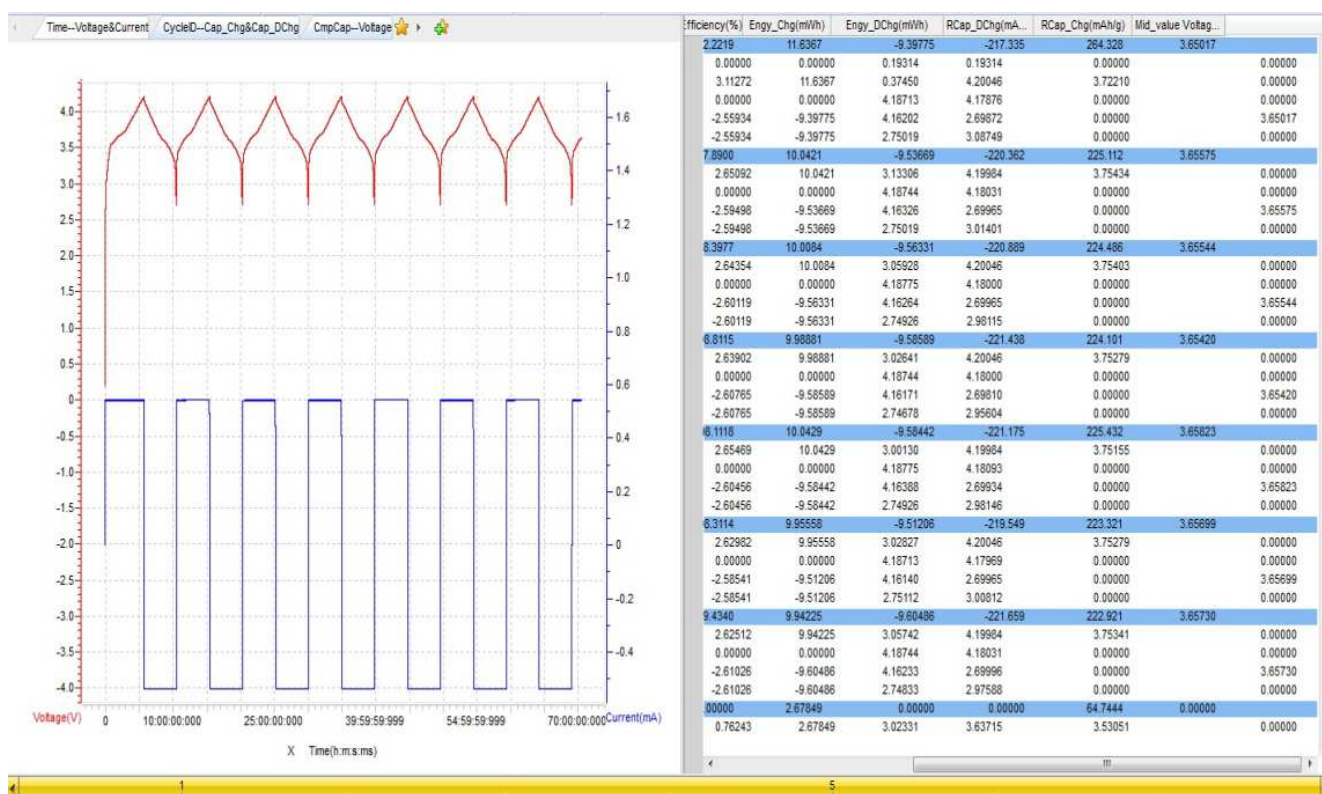

Figure 12. Charge and discharge curve of Li₂FeSiO₄ coated with Al₂O₃.

Charge and discharge performance analysis:

Using the above battery test system, the battery is charged and discharged at a current of 0.05C in the 1.5-4.8V (VS-Li/Li+) voltage range. After multiple cycles, the capacity remains unchanged until the specified number of cycles (Efficiency 98-99%), the measured specific capacity of the battery is 220 mAh/g, as shown in Figure 12, the surface material has excellent stability [7].

5. Conclusion

The structure of the coated LF(M)S cathode material did not change. The dispersibility of the material is good, the distribution is relatively uniform, the particles are massive, and the average particle size is 100-200nm, which is beneficial to increase the diffusion rate of lithium ions.

The electrochemical properties of materials coated by $Al_2O_3(C)$ were characterized by electrochemical workstations and charge and discharge test instruments. Due to the inactive chemical properties of the surface coating, the formation of electrode passivation layer in the process of electrochemical reaction can effectively prevent the side reactions between the material and the electrolyte solvent under high voltage and reduce the irreversible capacity loss during the first charge and

discharge [9]. It can be speculated that in the process of material growth coating, the coated material and the carbon generated by organic decomposition enter the cathode material lattice together, forming a composite cathode material with stable structure and good electrical conductivity, maintaining the structural stability of the material when charging and discharging, thus reducing the loss of capacity and improving the circulation performance of the material [10]. The coated cathode material maintains good ion conductivity between the particles, thus improving electrochemical characteristics.

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