REDUCING INTERFACIAL RESISTANCE OF LI-ION BATTERIES THROUGH ATOMIC LAYER DEPOSITION

A Thesis Proposal

by

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1. INTRODUCTION

1.1 Introduction

The attention to solid state batteries are increasing as electrical vehicles start to dominate automobile industry. Solid-state batteries (SSBs) are type of Li-ion batteries that have solid medium. They are regarded as the next-generation energy storage device for electric vehicles because they can potentially solve the problems of conventional Li-ion batteries. In conventional Li-ion batteries, when delivered in high energy densities, they had extremely high possibility for inflammation due to the presence of flammable liquid organic electrolytes [1]. Also, though the use of Li metal anode may significantly increase energy density, likelihood of short circuiting the cell due to the growth of Li dendrites prevents the commercialization of Li-ion batteries with Li anodes. Thus, in order to provide safer and higher energy batteries, SSBs with nonflammable and mechanically robust SSEs which may suppress Li dendrite growth came up as an alternative solution.

However, there are new challenges that need to be overcome for SSBs. Not only are they more expensive than conventional Li-ion batteries, but due to solid-characteristic of the electrolyte, SSBs have critical flaw of high resistance at the SSE-electrode interfaces. The performance of SSBs in high temperature environment may be safer, but the thick SSE membrane and low active loading with the electrodes do not show better performance when compared to the liquid electrolyte cells [2].

To enhance the battery performance, the interfacial resistance in SSBs needs to be reduced. Therefore, the focus of our lab is to come up with a novel coating method that has the least interfacial resistance. This new study will utilize the atomic layer deposition (ALD) technique to coat metal oxides on electrodes and enhance the battery performance, as previous research by many scientists

has already proven that metal oxide coatings are effective at reducing the interfacial resistance in

SSBs [3,4,5,6].

2. BACKGROUND

2.1 Current Problems in the Field of Li-ion Batteries

Li-ion batteries are used in many electrical devices as the energy storage device. They are gaining more attention due to the trend of replacing gasoline powered vehicles with electric vehicles. However, there are still many technical problems and difficulties that scientists and engineers need to solve. First of all, the definition of a "good" battery comes from the performance and safety. When discussing battery performance, one important criterion is the amount of energy the battery can store or deliver. The larger the energy, the longer the battery can power the device or vehicle without the need of charging. The energy of a battery cell is the product of its capacity and its operating voltage, both of which are determined by the electrode materials used in the cell. The optimal battery capacity for Lithium cells is 20~30mAh at 3.5~4.0V [7].

Another important criterion is the cycle life, which is the number of cycles that a battery can be charged and discharged before the capacity decreases to 80% of the initial capacity. The longer the cycle life, the longer the battery can be used without replacement. In addition to the battery cell's ability to store energy, its mass and size also comes in as important control when discussing the performance because they determine the number of battery cells that can be used in a device or vehicle [1]. Therefore, energy density (the amount of energy in a unit mass or unit volume) is a key criterion when evaluating the performance of a battery. One strategy to improve energy is to use Li metal as the anode material to replace the conventional graphite anode. Li has much higher specific and volumetric capacity than graphite, so the use of it can significantly reduce the mass and size of the battery. However, battery cells with Li metal anodes show very short cycle life due to the side reactions between Li and the organic electrolytes. The growth of Li dendrites on Li metal anodes

which may short-circuiting the cell is another problem that prevents the adoption of Li metal anodes. Moreover, the use of flammable liquid electrolytes in Li-ion batteries always causes safety issues. If a battery has a short-circuit or it is subjected to abusive conditions, the increased temperature may trigger a thermal runaway of the battery, which is a series of exothermic reactions that rapidly increase the temperature. In this case the flammable electrolyte may be ignited and result in fire or explosion. Thus, in order to overcome challenges of the conventional li-ion batteries, this study proposes to integrate solid-state electrolyte (SSEs) to Li-ion batteries because SSEs may mechanically prevent Li dendrite growth. In addition, SSEs may solve the safety issues since they are not flammable.

Proposing the solid-state batteries (SSBs) as an alternative to the conventional batteries is, surprisingly, not the newest idea. Considering the fact that the first idea of SSBs came out in the late 20th CE, there has been some efforts made and continuation of studies of SSBs [8]. One major problem of SSB is the large resistance at the SSE-electrode interface. Many SSEs are not electrochemically stable in the operating voltage range of Li-ion batteries, so they decompose and form solid-state interphase (SEI) which may be highly resistive. In addition, the large impedance can be a result of the poor interfacial contact due to the high mechanical strength of some SSE materials. Moreover, the active materials in electrodes experience volume changes during lithiation and delithiation, which can cause interfacial delamination from the SSE. Generally, many scientists work on finding the best coating material on the anode or the cathode to improve the performance of SSBs. For example, in an article from Ceder's group, they conducted multiple screenings and calculations for different cathode coating materials, such as LiH_2PO_4, $LiTi_2(PO_4)_3$, and $LiPO_3$[9]. The figures and graphs in the article display how the phase stability of the cells differ depending on the morphology of the electrodes. This suggests that infusing different particles and materials in the electrode impacts the electrochemistry of the cell. Moreover, charts in the article illustrates thickness

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and theoretical capacity for each electrode coating material, which gives a clear guidance that specific electrode coating material is more efficient for SSEs and that utilizing certain electrode coating materials can bring out the best battery performance. Experimentally, Li2O-ZrO2[10] and Li4Ti5O12[11] coatings on NCA cathodes, and LiNbO3[12, 13] coatings and LiCO3[14] on LCO cathodes, have been utilized by researchers to improve cycling performance of SSBs. In these works, coatings were applied on cathode particles with rather complicated chemical reaction processes.

Alternatively, in order to improve the interfacial contact at the SSE-electrode interface and reduce the interfacial resistance, deposition techniques can be used to coat SSEs or electrodes. For instance, Fu et al. deposited a thin layer Al on garnet SSE to improve the wetting of molten Li on the SSE. Fu asserts that reducing interfacial resistance might be a better solution for creating better SSBs than selecting electrode materials [15]. Similarly, Han used ALD to coat Al2O3 on garnet SSE to reduce the resistance at the SSE-Li interface [6]. Likewise, in order to best bring out the battery performance, this study chose ALD because this method is proven to be a viable method to wet the electrolyte. Coating by ALD was also done on electrode materials, as Woo's studies claim that the addition of ALD coated Al2O3 layers increases capacities and prevents degradation of SSBs [4, 5]. Therefore, incorporating ALD coated Al2O3 in the SSB construction will reduce the resistance in the SSBs and bring out better performance.

Another problem in SSBs is the reduced energy density due to the thick SSE membrane and large fractions of SSE in electrodes. In Yushin's group, we developed a novel method of melt infiltrating molten SSE into electrodes for fabrication of SSBs. This method is aimed to increase the energy density of SSBs by using densely packed electrodes and decreasing the thickness of SSE between electrodes. In this work, ALD coated Al2O3 was applied on electrodes to improve the wetting of molten SSE on the electrodes and to assist the melt-infiltration process. However, the

thickness of the Al2O3 coating was not optimized as the effect of coating thickness on the resistance at the SSE electrode interface and its impact on cell cycling performance were not examined. In addition, other metal oxides such as ZrO2 or TiO2 which may improve cell performance can also be coated on electrodes by ALD. For example, Machida coated ZrO2 on NCM electrodes for SSBs [7].

In order to overcome the major problem of larger interfacial resistance in SSBs, one of the most probable solutions is reducing interfacial resistance by artificial coatings. There is additional unique approach, such as inventing bio-based polymer electrolytes due to environmental concerns [16]. Nevertheless, there is still room for improvement to come up with SSEs with higher conductivity and better compatibility with electrode materials, which will enable the replacement of conventional Li-ion batteries with SSBs.

3. METHODS AND MATERIALS

In order to create a battery cell, three main steps are needed: electrode preparation, electrolyte synthesis, and cell assembly. They need to be in chorological order and for each step, chemicals and the procedures will be explained so the experiment can be duplicated easily.

3.1 Electrode Preparation

The cathode material for the cell will be lithium iron phosphate (LFP). The slurry material for making LFP cathode includes five materials in total:

- lithium iron(II) phosphate(LFP)(Sigma-Aldrich)

- carbon black (CB) (C-NERGY Super C45, TIMCAL)

- polyvinylidene fluoride (PVDF) (Alfa Aesar)

- polyamideimide (PAI) (Torlon 4000TF, Solvay)

- 1-methyl-2-pyrrolidone (NMP) (anhydrous, 99.5%, Sigma-Aldrich)

The slurry was mixed in LFP: CB: PVDF: T = 95:1:2:2 ratio, and graphite foils were used as current collector. After being casted onto current collectors with a Dr. Blade No.10, all electrodes were tried at 80C for 12 hours. Then, to improve the wettability of the electrodes, atomic layer deposition (Fiji F202, Cambridge Nanotech) was performed at $200°C$ for 50 to 200 cycles to deposit Al_2O_3 coating. Thus, 200nm to 400nm thickness of the surface oxide coating was produced.

3.2 Solid-state Electrolyte Synthesis

All procedures were done inside an Argon-filled glove box. Two types of the electrolytes were used to test the efficacy of ALD: Li_2OHCl and polymer glycolic acid LiTFSi. For the first electrolyte,

LiOH (anhydrous, 98% alfa aesar) and LiCl (anhydrous, 99%, alfa aesar) were mixed to make the electrolyte. Before the synthesis, the two materials were dried at 120°C for 24 hours, and they were mixed in the molar ratio of LiOH:LiCl = 10:9. As for the latter electrolyte, glycolic acid and LiTFSi were mixed by 10:1 by weight. Then, for the both electrolytes, they were grinded and was heated inside a graphite crucible via an induction heater (MD-700 Mini Ductor II, Induction Innovations) until 650°C at a rate of $400°C \, min^{-1}$. After the molten electrolyte was first naturally cooled until 550°C, it was poured onto a graphite plate so it solidifies faster. The final solid-state electrolyte was ground so it was ready to be used for further characterization and pellet making process.

3.3 Cell Assembly

All procedures were performed inside an Argon filled glovebox. Before cell assembly, punched out electrodes, solid state electrolyte (SSE), cell case, and stainless spacers were assembled to make Li half cells. Li was used as anode and LFP was used for the cathode. Inside a CR2032 coin cell, the following sandwiches were sealed and pressed with 0.8ton pressure: LFP/SSE/Li/spacer.

3.4 Cell Data Analysis

3.4.1 EIS Measurement

In order to measure the ionic conductivity of the SSE in symmetric cells, electrochemcial impedance spectroscopy (EIS) was performed. For each assembled CR2032 coin cells, charge-discharge tests of the cells were conducted under Arbin battery tester (Arbin Instruments, USA). In a stepwise matter, the EIS measurement was done in following temperatures: 25, 30, 40, 50 ,60 , 70, 80, 90, 100, and 110°C . In addition, the frequency ranged from 1 MHz to 1Hz, and for each of these conditions, the current and voltage were recorded.

3.4.2 SEM Images

The scanning electron microscopy(SEM) images do not necessarily give quantitive values, but the photos provide good representations of the cell material's microstructure. For this study, SEM images of the cathode material were taken in the range of 5μm to 40μm to closely examine the microstructures of LFP material.

4. RESULTS

4.1 Electrochemical Performance

In order to compare the efficacy of atomic layer deposition, three sets of cell cycles were tested. The first one, which is shown in Figure 1, is a cell cycle without ALD.
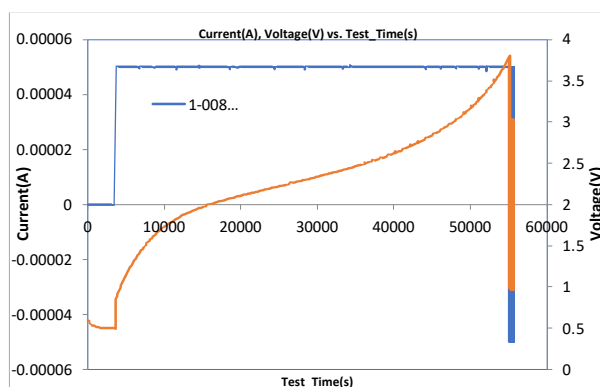

Figure 1. Electrochemical Performance of a cell without Atomic Layer Deposition

The latter two experiments are cell cycles of batteries with ALD. Figure 2 shows the EIS data of the cells with Li_2OHCl electrolytes, that has been layered with ALD. Figure 3 is the same set of data, but for the cells that used LiTFSi as electrolytes.
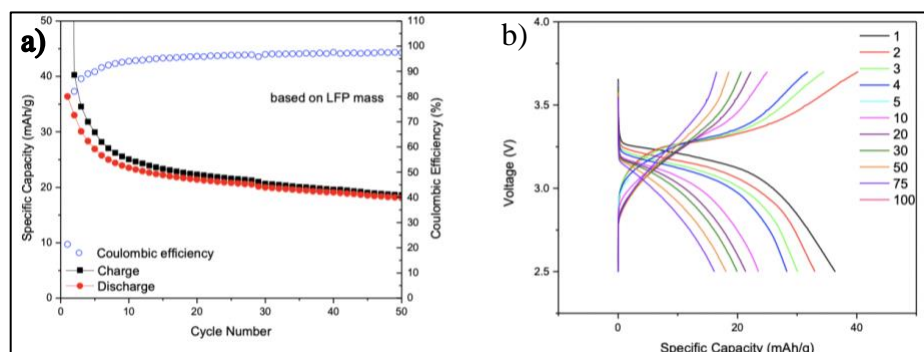

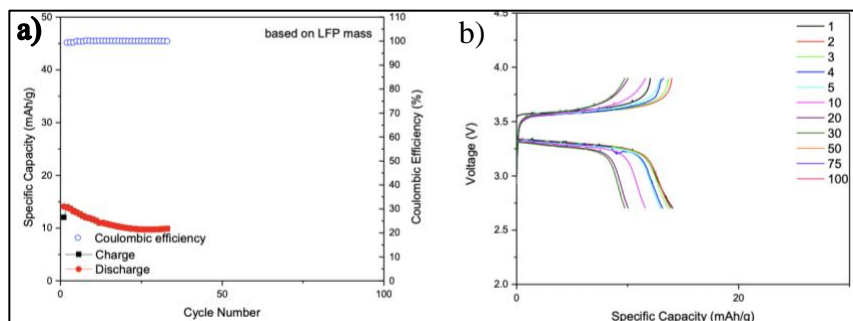Figure 2. Electrochemical performance of Li_2OHCl cell. (a) Cell capacity at C/10. (b)Voltage profile at C/10.

Figure 3. Electrochemical performance of LiTFSi cell. (a) Cell capacity at C/10. (b)Voltage profile at C/10.

The comparison of electrochemical performance of cells with and without the ALD emphasizes the importance of coating on the interface.

4.2 Scanning Electron Microscopy

The SEM images well present the microstructure of LFP cathode and the interfacial boundary between the cathode and the electrolyte. The efficiency of ALD deposition can be closely observed and determined. In Figure 4, the SEM images show homogenous surface of the LFP cathodes.
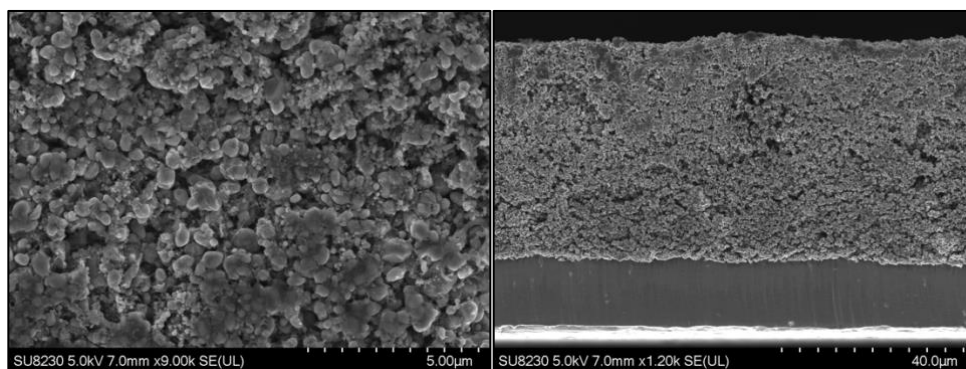

Figure 4. SEM imges of LFP cathodes. (a) In a scale of 5μm (b) In a scale of 40μm.

5. DISCUSSION

5.1 Influence of Atomic Layer Deposition

In total, three sets of cells were cycled and tested to figure out the influence of Atomic Layer Deposition. As a control, the first set was not added with Al_2O_3. Thus, as shown in Figure 1, a cell cycle failure is illustrated. It is crucial to have a lower interfacial resistance between the electrodes and electrolytes to produce an efficient cell, yet the lack of ALD coating results in uneven surface area, producing way too much interfacial resistance that the cell does not run. The cell voltage, shown in orange, increases as cell charges, but as it reaches its peak before discharge, high interfacial resistance results in cell cycle failure.

On the other hand, the two cells with Li_2OHCl and LiTFSi electrolyte, showed a successful cell cycle when ALD coating was applied. In Figure 2, the electrochemical analysis of Li_2OHCl is illustrated. Figure 2a) illustrates the cell specific capacity of the cell over the number of cycles. Due to formation of solid electrolyte interface (SEI) layer, the charge/discharge specific capacity drops in the first few cycles. However, as the cell reaction proceeds, the charge/discharge decreases slowly and reaches the plateau near the end of cell cycles, which is a natural trend for batteries. Likewise, Figure 2b) demonstrates the specific capacity change under the voltage change. It also shows how as the graph shifts left, which represents the cell cycle continuation, the specific capacity decreases in the same voltage range. Moreover, the similar trend is shown in LiTFSi cell. Both Figure 3a) and 3b) illustrate the exact same trend as charts in Figure 2, where the specific capacity decreases as the cycle number increases; yet, the two cells with ALD coating has minimized interfacial resistance that the cell does not fail.

In addition to the electrochemical cell measurement, the efficacy of ALD coating can be observed through SEM images, shown in Figure 4. By applying ALD coating, the LFP cathode and the electrolyte surface show homogenous surface, with spherical microstructure. The well mixture of the active material and the solid state electrolyte impacts the interfacial resistance of the cell, as well as its charge/discharge state.

6. CONCLUSION

6.1 Conclusion

The objective of this study was to determine the positive effect of the metal oxide coatings on electrodes in solid state batteries. Examining the electrochemical performance of both Li_2OHCl and LiTFSi cells, the atomic layer deposition (ALD) reduced the interfacial resistance of the electrodes and improved the battery performance. However, the extent of improvement is still not sufficient compared to the conventional lithium cells. The battery performance of the solid state cells with ALD is evidently better than those without ALD coating, which failed after a few cell cycles, and approach method of reducing interfacial resistance seems rational, yet more research is needed to create a perfect solid state batteries with lower interfacial resistance.

REFERENCES

[1] Niu, C.J., et al., High-energy lithium metal pouch cells with limited anode swelling and long stable cycles. Nature Energy, 2019. 4 (7): p. 551-559.

[2] Kerman, Kian., et al., Review-Practical Challenges Hindering the Development of Solid State Li Ion Batteries. Journal of the Electrochemical Society, 2017. 164 (7): p. 1731-1744.

[3] Woo, J. H., et al., Nanoscale Interface Modification of LiCoO2 by Al2O3 Atomic Layer Deposition for Solid-State Li Batteries. Journal of The Electrochemical Society, 2012. 159 (7): p. 1120-1124.

[4] Woo, J. H., et al., Utilization of Al2O3 Atomic Layer Deposition for Li Ion Pathways in Solid State Li Batteries. Journal of The Electrochemical Society, 2015. 162 (3): p. 344-349.

[5] Han, X., Gong, Y., Fu, K., et al., Negating Interfacial Impedance in Garnet-Based Solid-State Li Metal Batteries. Nature Material, 2016. 16: p. 572-579.

[6] Machida, Nobuya., et al., Electrochemical Properties of All-Solid-State Batteries with ZrO2-coated LiN1/3Mn1/3Co1/3O2 as Cathode Materials. Solid State Ionics, 2012. 225: p. 354-358.

[7]

[8] Wright, Peter V. (September 1975). "Electrical conductivity in ionic complexes of poly(ethylene oxide)". British Polymer Journal. 7 (5): 319–327.

[9] Ceder, Gerbrand., et al., Computational Screening of Cathode Coatings for Solid-State Batteries. Joule, 2019. 3(5): p. 1252-1275.

[10] Ito, Seitaro., et al., A Rocking Chair Type All-Solid-State Lithium Ion Battery Adopting Li2OeZrO2 coated LiNi0.8Co0.15Al0.05O2 and a Sulfide Based Electrolyte. Journal of Power Sources, 2014. 248: p. 943-950.

[11] Seino, Yoshikatsu., et al., High Rate Capabilities of All-Solid-State Lithium Secondary Batteries Using Li4Ti5O12-coated LiNi0.8Co0.15Al0.05O2 and a Sulfide-based Solid Electrolyte. Journal of Power Sources, 2011. 196 (15): p. 6488-6492.

[12] Ohta, Narumi., et al., LiNbO3-coated LiCoO2 as Cathode Material for All Solid-state Lithium Secondary Batteries. Electrochemistry Communications, 2007. 9 (7): p. 1486-1490.

[13] Ohtomo Takamasa., et al., All-solid-state Lithium Secondary Batteries Using the 75Li2S·25P2S5 Glass-ceramic as Solid Electrolytes. Journal of Power Sources, 2013. 248: p. 943-950.

[14] Kim, Junghoon., et al., Enhanced Electrochemical Performance of Surface Modified LiCoO2 for All-Solid-State Lithium Batteries. Ceramics International, 2016. 42 (2): p. 2140-2146.

[15] Fu, K., et al., Toward Garnet Electrolyte-based Li Metal Batteries: An Ultrathin, Highly Effective, Artificial Solid-state Electrolyte/Metallic Li Interface. Science Advances, 2017. 3(4).

[16] Rayoung, M., et al., Bio-Based Polymer Electrolytes for Electrochemical Devices: Insight into the Ionic Conductivity Performance. Materials, 2020. 13(4).