

Li₃N Coated Lithium Anode Utilized in All-Solid-State Lithium Ion Battery with Sulfur Based Solid Electrolyte

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Abstract

Sulfur based solid electrolytes have lithium ion conductivities on the order of 10^{-2} Scm⁻¹ in state-of-art LMPS(M=G,Si,Sn) systems. Utilization of such electrolytes to construct all-solid-state batteries requires constructing compatible anode and cathode pairs. Lithium and Sulfur are the most studied systems to employ in lithium ion batteries as anode and cathode respectively due to their high capacities. Yet highly reactive nature of lithium makes it difficult to combine with solid electrolytes. Similarly sulfur has volume expansion and poor conductivity problems waiting to be solved. This study covers the construction of an all-solid state battery where Li₃N protected Li metal, Li₇P₃S₁₁ and quaternary sulfur composite utilized as anode, electrolyte and cathode respectively. By protecting the lithium anode from corrosion through Li₃N coating and utilizing sulfur based cathode composite we assembled an all-solid state battery with 780 mAh/g capacity.

1. Introduction

Constructing all-solid state batteries are now the most promising alternatives to replace Li-ion batteries with liquid electrolytes. With the synthesis of sulfur based solid electrolytes having ionic conductivity on the order of liquid electrolytes it is now more concrete to get rid of the flammability risks of liquid electrolytes by assembling all solid state batteries[1]. Besides, such batteries yield more energy density through better stackability of solids.

Although solid electrolytes are promising alternatives to replace liquid electrolytes several issues has to be eliminated before assembling a complete cell. The main challenge to construct an all-solid-state batteries is to construct compatible anode and cathode pairs with electrolyte especially if one wants to use lithium as anode. Due to the reactive nature of lithium, it spontaneously forms solid-electrolyte interface(SEI) layer in contact with solid electrolyte. Depending on the ionic and electronic conductivity characteristics of the SEI, the thickness of the layer increases through reducing electrolyte leads to the corrosion of anode metal[2].

One plausible way of preventing the corrosion of the anode metal is to coat it with structures that are ionically (electronically) conductive (insulator).Li₃N is one of the important structure that can be utilized as coating layer due to its high ionic conductivity[3–5]. Besides, its facile synthesis technique makes it more attractive due to economical concerns comparing with expensive thin film coating techniques.

As cathode material, sulfur is one of the most studied materials with its theoretical energy density of 2600 Wh kg⁻¹ with its well known problems of volume expansion and insulating nature. In order to overcome such problems it is mostly composited with graphene to host its volume expansion and impart electronic conductivity into cathode[6].

In this study we utilized Li₇P₃S₁₁ solid electrolyte to assemble an all solid state battery where Li₃N protected lithium and quaternary sulfur composite utilized as anode and cathode respectively.

2. Experimental Procedure

2.1 Synthesis of Li₇P₃S₁₁ solid electrolyte

Li₇P₃S₁₁ solid electrolyte synthesized by mechanical activation of Li₂S (99.98%, Sigma Aldrich) and P₂S₅ (99%, Merck) powders and subsequent heat treatment. Appropriate amount of precursors were ball milled at 400 rpm for 20hrs to convert ingredients into glassy form that will be converted into glass-ceramic with heat treatment. The glassy powders were heat treated at 250 °C for 3hrs to crystallize Li₇P₃S₁₁ phase. Due to the air sensitive nature of powders all processes were carried out in glovebox having trace amount of humidity and oxygen.

Synthesized powders were than characterized by XRD with air sensitive sample holder. DSC analysis were carried out to determine the crystallization temperature from the glassy phase.

2.2 Li₃N coated Li anode synthesis

Li_3N coated Lithium were synthesized through flowing N_2 gas in a sealed reaction chamber having lithium chip inside. Through controlling the gas flow rate and temperature black colored Li_3N phase formed on the Li chip and characterized by XRD analysis.

2.3 rGO/S/CB/ $\text{Li}_7\text{P}_3\text{S}_{11}$ Composite cathode synthesis

Composite sulfur based material synthesized to be utilized as cathode. Elemental sulfur first composited with rGO through melt diffusion method. rGO/S composite were then combined with carbon black to impart electronic conductivity into cathode. The ternary rGO/S/CB composite were then combined with $\text{Li}_7\text{P}_3\text{S}_{11}$ solid electrolyte to make the cathode ionically conductive.

Synthesized composite structure were analyzed by Field Emission Scanning Electron microscope (FESEM) characterize the morphology and distribution of sulfur particulates inside the cathode composite.

2.4 Electrochemical tests

Electrochemical tests were performed with a custom-made PEEK insulated cell. $\text{Li}_7\text{P}_3\text{S}_{11}$ powders were spread into cell and 350 MPa pressure applied to pelletize the powder that will be utilized as solid electrolyte. Then cathode powders were carefully spread on to electrolyte and pressed at 200 MPa. At last Li (or Li_3N coated Li) were put into opposite side and pressed at 150 MPa to obtain three layered cell.

Galvanostatic charge-discharge tests were performed at 0.8 - 3.6V (vs Li/Li+) with a current density of 160 mA/g. Capacity of the cell calculated according to the amount of sulfur active material in the cathode.

3. Results and Discussion

Figure 1 displays the DSC analysis of the $\text{Li}_7\text{P}_3\text{S}_{11}$ amorphous powders where crystallization of $\text{Li}_7\text{P}_3\text{S}_{11}$ and impurity phase $\text{Li}_4\text{P}_2\text{S}_6$ was observed at around 260 and 310 °C respectively.

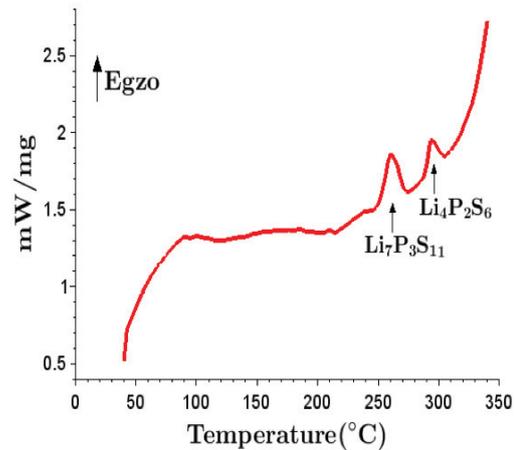


Figure 1. DSC analysis of $\text{Li}_7\text{P}_3\text{S}_{11}$ amorphous powders.

Precursor powders that are initially in amorphous phase were converted into crystalline $\text{Li}_7\text{P}_3\text{S}_{11}$ phase upon heating in a sealed quartz tube. Figure 2 shows the XRD analysis of crystalline $\text{Li}_7\text{P}_3\text{S}_{11}$ phase. The obtained structure has triclinic symmetry with P1 space group.

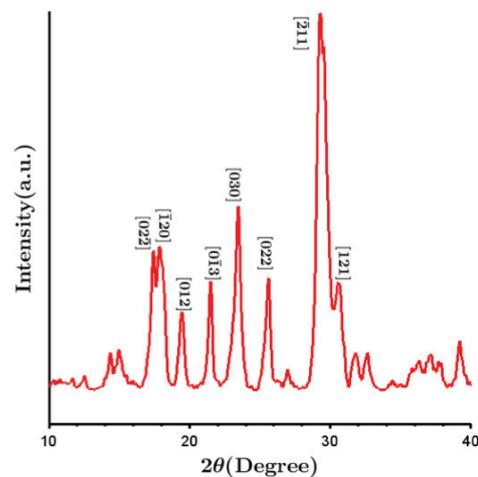


Figure 2. XRD analysis of synthesized $\text{Li}_7\text{P}_3\text{S}_{11}$ solid electrolyte.

rGO/S cathode composite structure synthesized through melt diffusion method. Figure 3 shows the morphology of the composite where tiny sulfur particles with about 10 nm size were homogeneously distributed within the rGO.

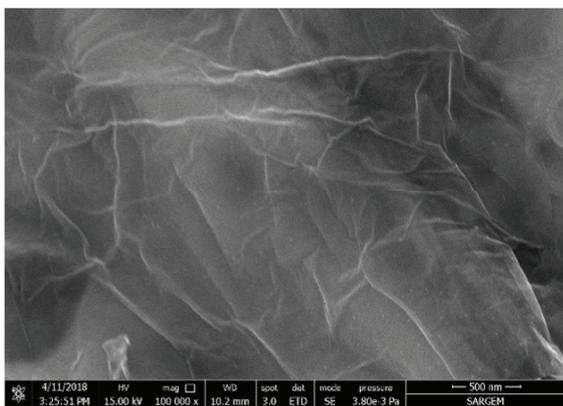


Figure 3. Synthesized rGO/S composite with tiny sulfur particulates distributed throughout the graphene matrix.

Li_3N coated Lithium metal was synthesized inside a sealed reaction chamber under N_2 gas flow at temperatures below 100°C . Figure 4 shows the reaction process where black colored Li_3N phase is forming on the surface of Li chip



Figure 4. Li_3N coated Li chips.

Figure 5 displays the XRD analysis result of Li_3N coated Li metal where pure Li_3N phase compatible with JCPDF 30-0759 card observed.

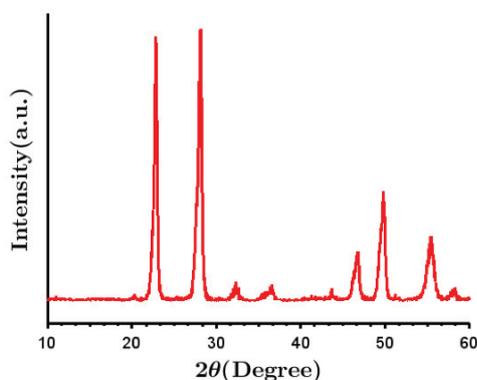


Figure 5. XRD analysis of synthesized Li_3N coating.

Figure 6 display the charge-discharge analysis of all-solid-state battery where 780 mAh/g and 710 mAh/g capacities were obtained in assembled cell with Li and Li_3N coated Li used as anode respectively. Our result indicates that Li_3N coating does not deteriorate charge transfer in the system possibly due to the high ionic conductivity of Li_3N phase.

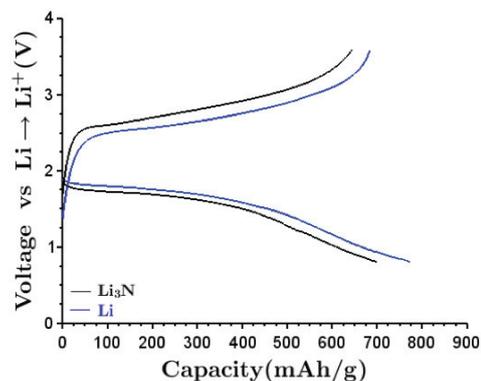


Figure 6. Charge-discharge curve of Li and Li_3N coated Li with $\text{Li}_7\text{P}_3\text{S}_{11}$ electrolyte and sulfur based composite cathode.

4. Conclusion

Sulfur based $\text{Li}_7\text{P}_3\text{S}_{11}$ solid electrolyte were successfully synthesized and characterized. Synthesized solid electrolyte were used to construct an all-solid-state lithium ion battery where Li_3N coated Li utilized as anode. On cathode side rGO/CB/S/ $\text{Li}_7\text{P}_3\text{S}_{11}$ used as cathode. Our results indicate that pure phase Li_3N were successfully coated onto lithium metal. Besides sulfur active material were homogeneously distributed in rGO matrix and composited with Carbon Black and $\text{Li}_7\text{P}_3\text{S}_{11}$. Electrochemical tests of assembled all-solid-state battery results revealed that Li_3N coating does not substantially deteriorate charge transfer on LIBs. Moreover it is expected that Li_3N coating will elongate the cycle life of the battery through protecting the lithium anode in contact with solid electrolyte.

5. Acknowledgment

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