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ELECTROCHEMICAL UTILIZATION OF AN EXCESS LITHIUM SULFIDE IN SOLID LITHIUM-ION ELECTRODES

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1. Abstract

Solid state lithium-ion batteries with most commonly available electrodes suffer from poor ionic conductivity of the active material and its poor inter particle contact with the solid glass-ceramic electrolyte. While this can be addressed by interlacing the active material like $n\text{-LiTiS}_2$ with glass-ceramic binary solid-state electrolyte like $\text{Li}_2\text{S-P}_2\text{S}_5$, this often reduces the loading of active material in the composite electrode, and thus a reduction in specific capacity of the cell. This article explores the concept of electrochemical utilization of excess Li_2S in the electrode by cycling the cell at high temperatures, and thus activating the Li_2S and creation of parallel $\text{S/Li}_2\text{S}$ conversion chemistry along with $\text{TiS}_2/\text{LiTiS}_2$ chemistry and thus increasing the specific energy density of the solid-state batteries without changing the active material loading in the composite electrode.

Keywords: Solid state batteries, Lithium-ion batteries, electrochemical utilization, composite electrodes, $n\text{-LiTiS}_2$

2. INTRODUCTION

Solid state lithium-ion batteries have growing body of scientific evidence that confirms their inherent safety compared to their conventional counterparts- liquid lithium-ion batteries. Adding to their several other list of advantages is their ability to reversibly convert a variety of high-capacity active materials for their use as electrodes[1]–[4]. However, due to poor interparticle contact between a solid electrolyte and the positive electrode's active material the solid-state batteries may suffer from a poor ionic support[5]. To address this issue of low conductivity, the electrodes are often constructed with a composite mixture of materials including a component of glass-ceramic electrolyte. The active material part of the composite electrode is commonly 40% by weight or less depending on its ionic and electronic transport properties[5]–[7]. For comparison, conventional electrodes have 90%wt or more active material before liquid electrolyte impregnation. Although the theoretical capacity of Li_2S - a component of well-known $x \text{Li}_2\text{S} - (100-x) \text{P}_2\text{S}_5$ binary electrode- is 116 mAhg^{-1} , it is not optimal material for its use as an active electrode material due to its poor ionic and electronic transport properties[8], [9]. However, it is demonstrated that excess Li_2S can be electrochemically utilized from the glass-ceramic solid-state electrolyte (SSE) $80 \text{Li}_2\text{S} - 20 \text{P}_2\text{S}_5$ at room temperature when mixed with elemental Copper (Cu^0). It was found that Cu^0 functions as a catalyst for oxidation of Li_2S during charge, which allowed the cell to function with $\text{Li}_x\text{Cu}_x\text{S}$ conversion chemistry after the first cycle. Therefore, Hayashi et al.'s study demonstrated that otherwise inert excess Li_2S can be electrochemically utilized to increase the overall specific energy density of the battery without changing the electrode composition and sacrifice of the required ionic transport.

In this article, a different process through which the same results of above-described Hayashi et al.'s studies are discussed. It has already been demonstrated how n- TiS_2 and n- LiTiS_2 can be used as active material of positive composite electrode composition[6], [10]. Post optimization process, an electrode composition with a weight ratio of 10:20:1 for n- LiTiS_2 : SSE: Acetal Black (AB) was chosen for this study. This weight composition translates to 73 mAhg^{-1} specific capacity for the electrode based on theoretical capacity of 226 mAhg^{-1} for LiTiS_2 . When the cells were initially charged at 60°C , the specific capacity of the electrodes was determined to increase threefold. It is being reported that this is due to electrochemical utilization of excess Li_2S in the glass-ceramic solid electrolyte $85 \text{Li}_2\text{S}: 15 \text{P}_2\text{S}_5$ and creation of parallel S/ Li_2S and $\text{TiS}_2/\text{LiTiS}_2$ conversion chemistry.

3. Materials and Methods

The material synthesis, cell fabrication and cell testing were carried out in a dry argon gas environment with n- LiTiS_2 synthesized via mechanochemical milling of stoichiometric mixture of TiS_2 and Li_3N as previously demonstrated[10]. The glass electrolytes $x \text{Li}_2\text{S} - (100-x) \text{P}_2\text{S}_5$ (molar, $x=70, 75, 80, 85$) are prepared using Li_2S and P_2S_5 also as detailed previously by Trevey et al[11]. The working electrode is a 10mg of n- LiTiS_2 , SSE ($x=70, 75, 80$ and 85) and acetylene black (AB) composite electrode in 10:20:1 weight ratio respectively. Each cell is fabricated with 200mg of $77.5 \text{Li}_2\text{S} - 22.5 \text{P}_2\text{S}_5$ glass electrolyte pressed at 1 metric ton inside a PEEK die, with Indium metal foil as counter electrode for the n- LiTiS_2 composite electrode. The composite electrode is pressed into PEEK cell over one side of SSE at 5 metric ton, while the indium metal foil is pressed at 0.5 metric ton on the other side of SSE. The cells were cycled under constant current constant voltage(CCCV) conditions using Arbin battery tester at 30°C or 60°C temperatures. Based on n LiTiS_2 theoretical specific capacity of 226 mAhg^{-1} the cells are cycled at C-rates of C/10 for first cycle, and C/5 for subsequent cycles.

4. Results and Discussion

To quantitatively assess the amount of Li_2S available for electrochemical utilization, the glass-electrolyte composition is analyzed using Cu-K α x-ray measurement. Figure 1(a) represents $x \text{Li}_2\text{S} - (100x) \text{P}_2\text{S}_5$ indexed reflections of Li_2S (vertical red lines) for different electrolyte compositions, with $x=80, 85$ compositions showing clear indications of presence of excess Li_2S for electrochemical utilization. Therefore, these two electrolyte compositions were selected for this study, considering they have good ionic conductivity based on other tests not reported in this article.

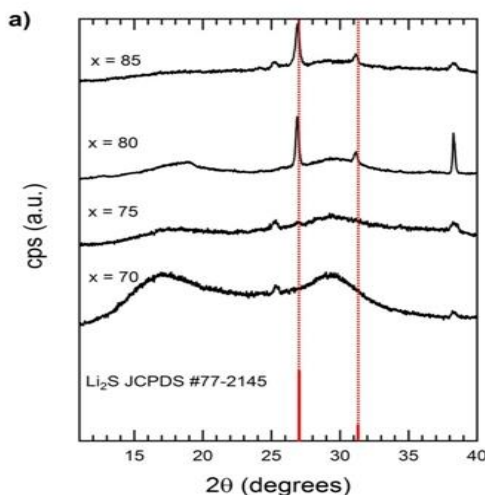


Figure 1 (a) Powder X-ray measurement of the $x\text{Li}_2\text{S}-(100-x) \text{P}_2\text{S}_5$ (molar) glass electrolyte with compositions $x = 70, 75, 80$ and 85

When the cells with Li_2S rich electrolytes in composite electrodes were cycled continuously at 60°C , specific capacities that exceeded theoretical values for LiTiS_2 were observed. Specific charge capacities as high as 945 mAhg^{-1} were observed for initial cycles of $x=85$ electrolyte composition. A high difference between $x=80$ and 85 was observed due to the amount of excess Li_2S available for electrochemical utilization. This additional high capacity of $x=85$ electrolyte translates to approximately 21.6 weight % of Li_2S being reversibly utilized.

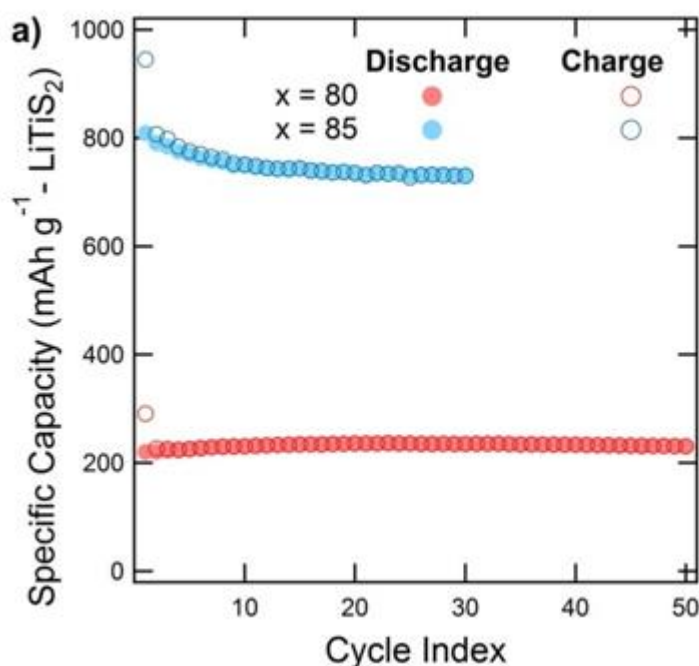


Figure 2 Cycling performance of cells cycled continuously at 60°C

Alternatively, the cells cycled at 60°C only for initial cycle were brought back to 30°C to check if the additional activated capacity was reversible. The results indicate that the cell with $x=85$ composition for SSE showed initial specific charge capacity of 897 mAhg^{-1} and a specific discharge capacity of 478 mAhg^{-1} by its 43rd cycle. While the cells with $x=80$ SSE electrolyte had specific capacity near theoretical values for LiTiS_2 .

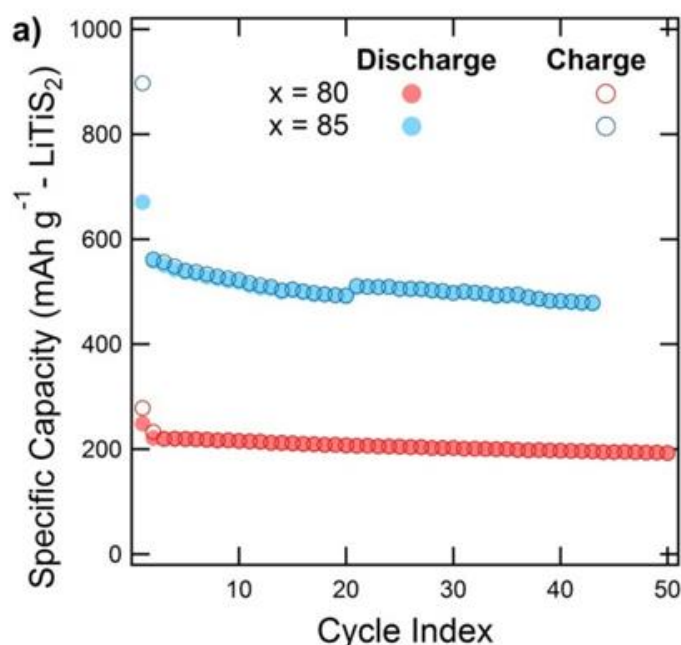


Figure 3 Cycling performance of cells cycled initially at 60°C and at 30°C for subsequent cycles

5. Conclusion

The extra Li_2S not embedded in the glassy network of SSE in nano LiTiS_2 composite electrode can be electrochemically activated when the cell is operated at 60°C by thermo-electrochemical activation mechanism. Qualitative analysis of the XRD patterns of cycled electrodes indicate that the reversible capacity is due to the electro-chemical activation of excess Li_2S component of the $\text{Li}_2\text{S} : \text{P}_2\text{S}_5$ electrolyte system. The utilization of solid electrolyte material in the composite electrode

improves the interfacial contact area with the active material to a great extent providing extra pathways for Li⁺ ion transport. The low active material mass loading of all-solid state composite electrodes is addressed to a reasonable extent with this activation phenomenon. The result is a high capacity and high energy density all-solid-state electrode.

6. References

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