

LITHIUM DENTRITE GROWTH SUPPRESSION AND IONIC CONDUCTIVITY OF Li_2S -
 P_2S_5 - P_2O_5 GLASS SOLID ELECTROLYTES PREPARED BY MECHANICAL MILLING

by

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Thesis directed by Prof. Sehee Lee

Conductivity of the $77.5\text{Li}_2\text{S}\cdot 22.5\text{P}_2\text{S}_5$ (mol %) and $77.5\text{Li}_2\text{S}\cdot(22.5-x)\cdot\text{P}_2\text{S}_5\cdot x\text{P}_2\text{O}_5$ (mol %) glassy solid state electrolytes (SSEs) and possible correlation among the conductivity, density properties, varying P_2O_5 substitutions, and lithium deposition in symmetric lithium metal batteries were examined. The mechanical milling method was used to prepare the glassy SSEs. The conductivity and density of the $77.5\text{Li}_2\text{S}\cdot 22.5\text{P}_2\text{S}_5$ (mol %) glassy electrolyte could be enhanced by adding a small amount of P_2O_5 . The $\text{Li}/77.5\text{Li}_2\text{S}\cdot(22.5-x)\cdot\text{P}_2\text{S}_5\cdot x\text{P}_2\text{O}_5$ (mol %)/Li metal cells with P_2O_5 substitution of $x < 9$ displayed longer cycling performance compared to $\text{Li}/77.5\text{Li}_2\text{S}\cdot 22.5\text{P}_2\text{S}_5$ (mol %)/Li metal cells. Hence, in the case of this study, the conductivity, density, and small P_2O_5 addition in the $77.5\text{Li}_2\text{S}\cdot 22.5\text{P}_2\text{S}_5$ (mol %) glassy electrolyte would be the main factors of reduced dendrite growth.

Dedication

This thesis is dedicated to family.

To my parents, Abdurrahman and Fatma, who have always supported and trusted me.

To my sister, Xhezal for being a great role model.

To my brother, Selami for being my spiritual guide.

To my girlfriend, Richa who has made my life more meaningful.

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1. Introduction

As rechargeable power sources, lithium ion batteries (LIBs) have attracted remarkable attention because they offer high energy density, flexible and lightweight design, good shelf life, no memory effects and long lifetime¹⁻³. LIBs are essential technologies because of their demanding applications, such as portable electronics, electric vehicles, and grid energy storage. For the safety concerns regarding flammability and toxicity, utilizing the conventional liquid electrolyte system for LIBs has many limitations³⁻⁴. Therefore, replacing organic liquid electrolytes with solid-state electrolytes (SSEs) has great potential to improve the safety properties of next-generation LIBs because of the possible advantages such as high electrochemical, and thermal stability of SSEs^{1,5-10}. Moreover, the solid-state electrolytes are less prone to issues such as electrolyte leaking and pollution unlike organic liquid electrolytes^{5,6}. Among various ceramic and polymeric SSE materials, the sulfide electrolytes, such as $\text{Li}_{10}\text{MP}_2\text{S}_{12}$ crystals, $\text{Li}_2\text{S-SiS}_2$, and $\text{Li}_2\text{S-P}_2\text{S}_5$ glass ceramics, have lithium-ion conductivities of $10^{-4} \text{ S cm}^{-1}$ or even as high as an order of $10^{-3} \text{ S cm}^{-1}$ at room temperature^{5,21,22}. Also, sulfide based glass-ceramic electrolytes are chemically stable at high temperatures and can be easily processed by cold-compacting the powder^{24,25}. This allows the SSEs to be formed into a thin layer with a large area to obtain a low internal resistance and thus provide a high current produced from the battery⁵. Additionally, in order to form a tri-layer pellet, high pressure can be applied to the powder forms of cathode, electrolyte, and anode during the assembly of bulk solid-state cells²³.

Another important advantage that has been predicted of SSEs was the ability to suppress lithium metal dendrite growth^{9,25}. Energy density of the battery system can be improved significantly with lithium metal anodes which have high mass specific capacity (3869 mAh/g) and

low density (0.534 g/cm^3)². However, the growth of lithium dendrites and the subsequent short circuiting phenomenon leading to safety hazards, such as thermal runaway and combustion has been a critical roadblock to the widespread application of lithium metal anode systems².

However, uncontrolled dendritic and mossy lithium growth is still a challenge for solid state batteries and the mechanism is not well understood^{14,26,27,28-33}. There is no confirmed model showing the exact mechanism of dendrite growth through SSEs^{14,26,27,28-33}. Lithium creates heterogeneous depositions during charging of the cells, which causes the growth of lithium dendrites^{23,26,34}. Presenting a buffer layer between the lithium metal and electrolyte, varying electrolyte composition, density or the lithium microstructure, and using self-healing polymers as composite fillers are some of the methods published in literature for improvement of the electrode-electrolyte interface^{23,26,34}. Recently, Porz, L. et al. reported that SSE surface morphology, specifically defect size such as surface cracks, and defect density are important factors for the onset of uncontrolled dendritic lithium growth³⁵. Li-planting in pre-existing flaws creates crack-tip stresses which accelerate crack propagation³⁵.

Tao, Y. et al. reported a glass-ceramic electrolyte based on $\text{Li}_2\text{S-P}_2\text{S}_5\text{-P}_2\text{O}_5$ with high ionic conductivity and chemical stability against lithium metal³⁴. The composition of $75\text{Li}_2\text{S}.24\text{P}_2\text{S}_5.1\text{P}_2\text{O}_5$ was determined to be optimal with the highest conductivity and lowest activation energy among various P_2O_5 compositions and showed stable cycling of Li metal cells without short circuiting³⁴. The addition of small amounts of oxygen to sulfide-based materials had been shown to improve the conductivity and chemical stability previously³⁶⁻⁴².

The Young's modulus was measured⁴³.

The present study reports conductivity properties of the $\text{Li}_2\text{S-P}_2\text{S}_5$ and $\text{Li}_2\text{S-P}_2\text{S}_5\text{-P}_2\text{O}_5$ glassy electrolytes and the possible correlation between the properties of the electrolytes and

lithium metal deposition. The results declare an examination of the glassy electrolytes in the range of $77.5\text{Li}_2\text{S}\cdot(22.5 - x)\text{P}_2\text{S}_5\cdot x\text{P}_2\text{O}_5$ (mol %) for $x=0, 0.25, 0.5, 1, 2, 3, 6, 9$.

2. Experimental

The mechanical milling technique was used for preparation of the $77.5\text{Li}_2\text{S}\cdot 22.5\text{P}_2\text{S}_5$ and $77.5\text{Li}_2\text{S}\cdot(22.5 - x)\text{P}_2\text{S}_5\cdot x\text{P}_2\text{O}_5$ (mol %) glassy electrolytes. As starting materials, Li_2S (Alfa Aesar 99.9%), P_2S_5 (Sigma-Aldrich, 99%), and P_2O_5 (Alfa Aesar 99.9%) crystalline powders were utilized to prepare the glassy SSEs. Proper composition of the starting materials were combined into a stainless ball jar with 3 large stainless steel balls (10mm diameter), and 20 small stainless steel balls (6mm diameter). High energy ball milling was carried out for 20 hours by a planetary ball mill apparatus (SFM-1 Desk-Top Planetary Ball Miller) and rotating speed was 400 rpm. The mass measurements and preparation of the mixture was conducted at $24\text{ }^\circ\text{C}$ in a dry Argon-filled glove box. Symmetric lithium metal cells were created to reveal dendrite initiation and growth in the $77.5\text{Li}_2\text{S}\cdot(22.5 - x)\text{P}_2\text{S}_5\cdot x\text{P}_2\text{O}_5$ (mol %) glasses. Electrolyte pellets were formed by cold pressing under 75 MPa in a polyetheretherketone (PEEK)-lined titanium die for 3 minutes and then the pressure was increased to 375 MPa tons and pressed for 5 minutes. Ionic conductivities were measured by AC impedance spectroscopy with a Solartron 1280C with a frequency from 20 kHz to 0.01 Hz at $60\text{ }^\circ\text{C}$. Thickness of the pellets were range of 0.06096-0.08128 cm which equated to approximately a 0.113 g cm^{-2} mass loading. Figure 1a represents an image of a prepared pellet. For both galvanostatic and polarization experiments, the cell construction was Li foil/ $77.5\text{Li}_2\text{S}\cdot(22.5 - x)\text{P}_2\text{S}_5\cdot x\text{P}_2\text{O}_5$ (mol %) /Li foil. Li metal foil with 0.75 mm thickness (Alfa-Aesar) was attached to the $77.5\text{Li}_2\text{S}\cdot(22.5 - x)\text{P}_2\text{S}_5\cdot x\text{P}_2\text{O}_5$ (mol %) SSE. The cell was pressed by

using a torque wrench at 20 inch pound (corresponding to approximately 20 MPa) for both galvanostatic and polarization tests. Galvanostatic charge and discharge cycling and polarization tests occurred at a current density of 0.1 mA/cm^2 . Schematic diagram for symmetric Li metal cells with the $77.5\text{Li}_2\text{S}\cdot 22.5\text{P}_2\text{S}_5$ and $77.5\text{Li}_2\text{S}\cdot(22.5 - x)\text{P}_2\text{S}_5\cdot x\text{P}_2\text{O}_5$ (mol %) SSEs are illustrated in figure 1b and 1c, respectively. Battery operation was conducted with the cell in an oven at $60 \text{ }^\circ\text{C}$ temperature under Argon. The rest time (the time before cycling was started) was 6 hours for the cell temperature to rise and equilibrate in the oven and cycling took an hour for each charge or discharge cycle. For polarization tests, cells were subjected to a single direction constant current until a sharp drop in voltage was observed which indicates a short circuiting event.

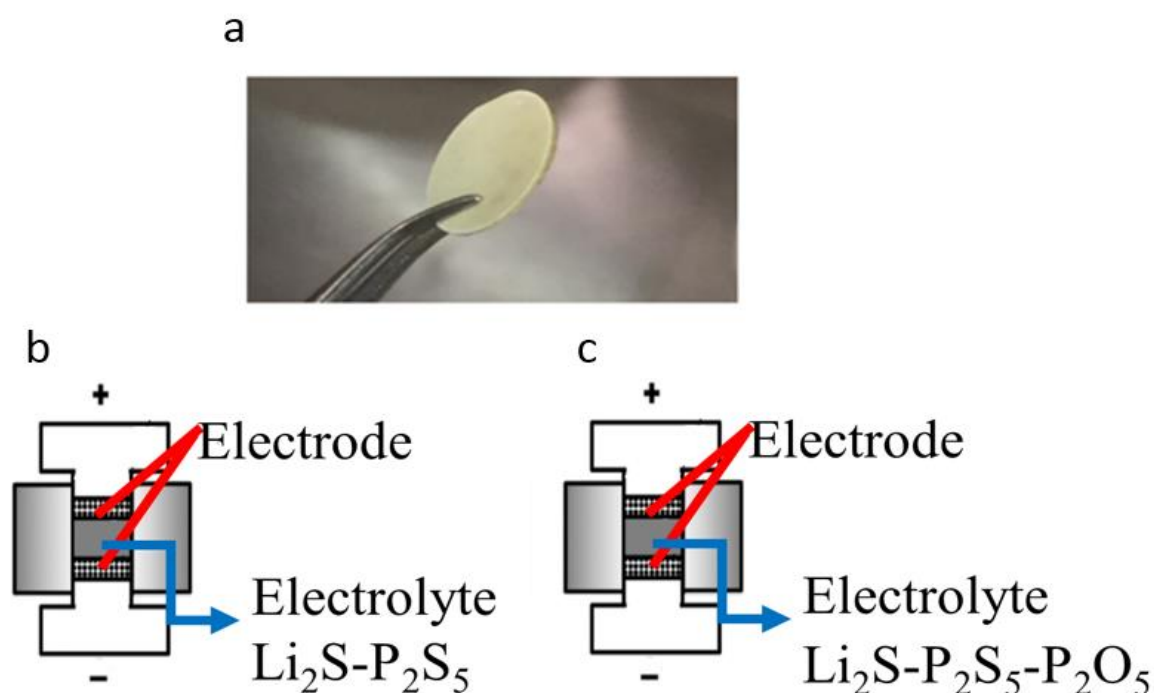
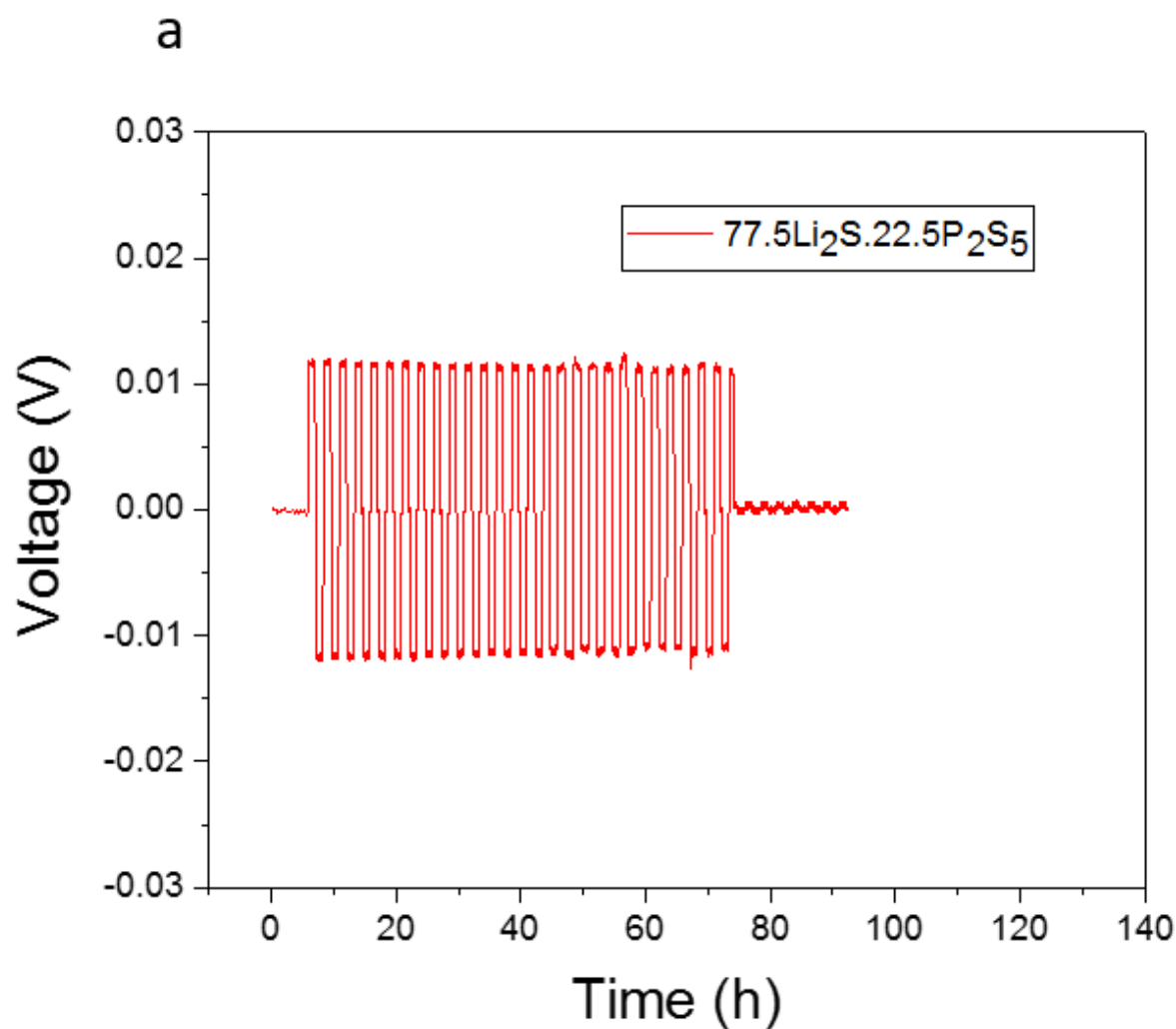


Figure 1. a) The picture of free-standing pellet. b) Schematic diagram of Li/Li lithium metal cells with the $77.5\text{Li}_2\text{S}\cdot 22.5\text{P}_2\text{S}_5$ (mol %) glasses³. c) Schematic diagram of Li/Li cells with the $77.5\text{Li}_2\text{S}\cdot(22.5 - x)\cdot\text{P}_2\text{S}_5\cdot x\text{P}_2\text{O}_5$ glasses³.

3. Results and discussion

The 77.5Li₂S-22.5P₂S₅ (mol %) glassy electrolyte shows a conductivity of 4.92×10^{-4} S cm⁻¹ (J. M. Whiteley et al⁷) and the symmetric lithium metal cell using this electrolyte showed a good cyclability of over 30 cycles without short circuiting. Figure 2a and 2b demonstrate the cycling performance of the Li/77.5Li₂S-22.5P₂S₅ (mol %)/Li cells. The short circuit capacity of the 77.5Li₂S-22.5P₂S₅ (mol %) glassy electrolyte is 3.2 mAh/cm². Also, the results of the deposition tests with the 77.5Li₂S-22.5P₂S₅ (mol %) glassy electrolyte are displayed in figure 3.



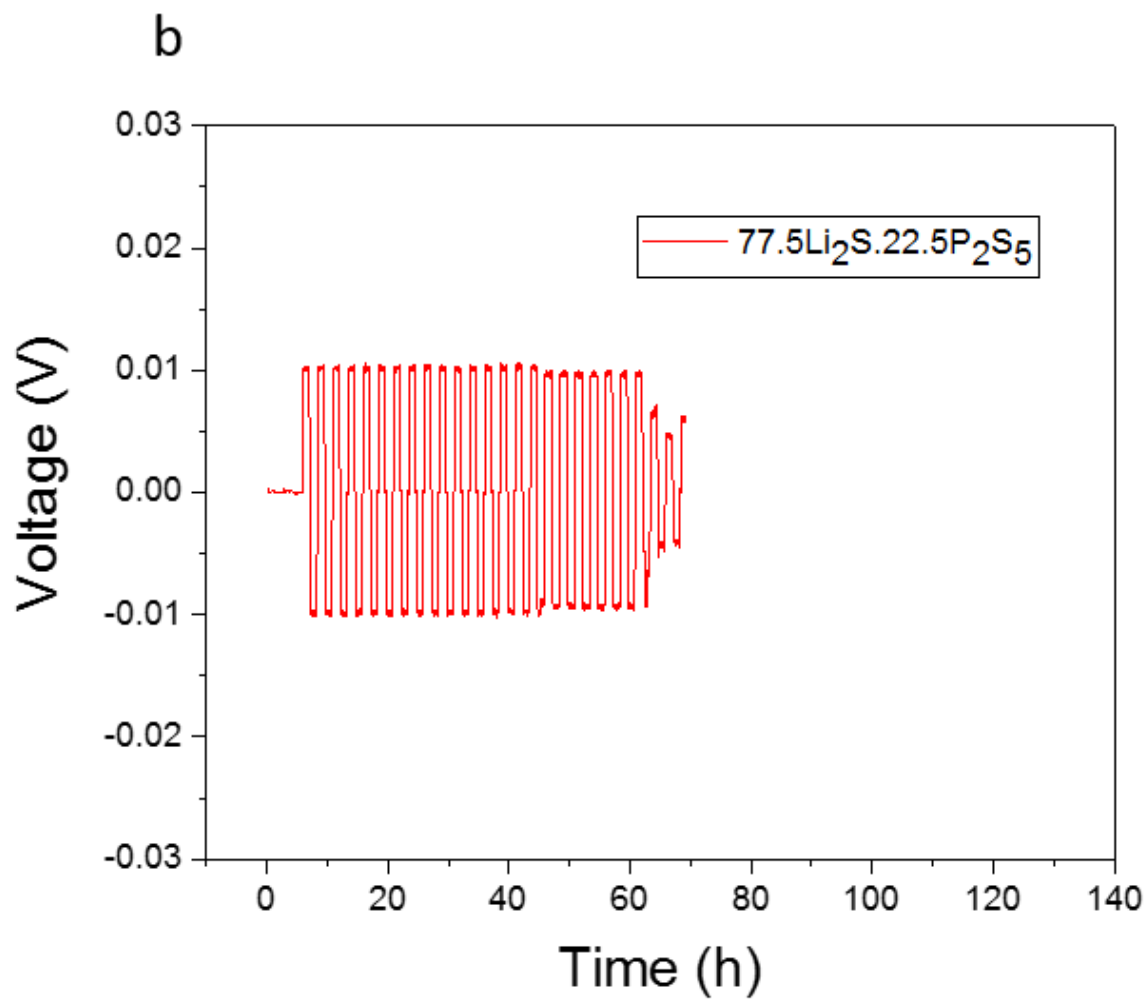


Figure 2. a) and b) show the cycling performance of the Li/77.5Li₂S.22.5P₂S₅ (mol %) /Li metal cells.

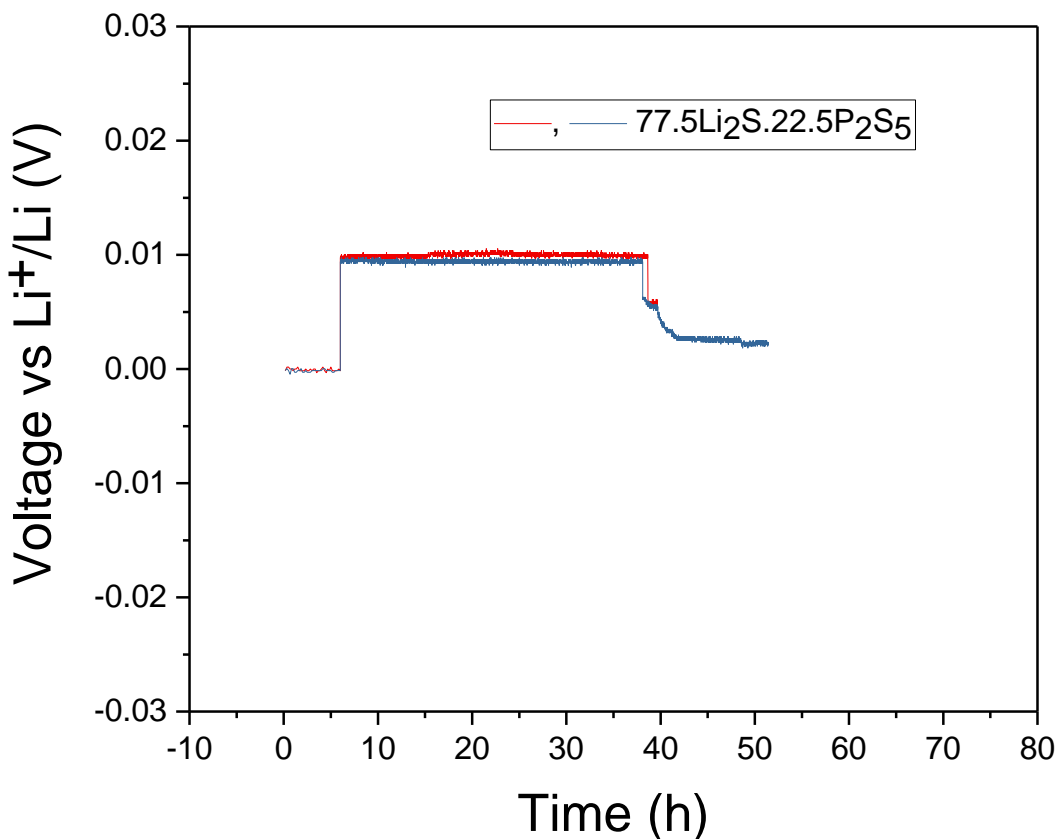


Figure 3. Galvanostatic plating of lithium metal cells with using the $77.5\text{Li}_2\text{S}.22.5\text{P}_2\text{S}_5$ (mol %) SSE.

Figure 4 demonstrates a comparison of the conductivity of the $77.5\text{Li}_2\text{S}.(22.5-x)\text{P}_2\text{S}_5.x\text{P}_2\text{O}_5$ (mol %) glassy electrolytes. Also, impedance data of the $\text{Li}/77.5\text{Li}_2\text{S}.22.5.\text{P}_2\text{S}_5$ (mol %) /Li and $\text{Li}/77.5\text{Li}_2\text{S}.(22.5-x)\text{P}_2\text{S}_5.x\text{P}_2\text{O}_5$ (mol %)/Li metal cells are illustrated in figure 5a and 5b. An increasing conductivity can be seen from adding a small amount of P_2O_5 . The $77.5\text{Li}_2\text{S}.(22.5-x)\text{P}_2\text{S}_5.x\text{P}_2\text{O}_5$ (mol %) SSE with 0.25 mol% P_2O_5 substitution displays the highest conductivity of $6.5 \times 10^{-4} \text{ S cm}^{-1}$. Tao, Y. et al. indicates that a reduction of the activation energy of Li diffusion happens when a non-bridging sulfur atom is substituted with a bridging oxygen atom³⁴. This formation works as a weaker trap for Li ions³⁴. Therefore, a conductivity increase in

the glassy electrolyte occurs³⁴. In the case of this study, 0.25 P₂O₅ substitution could create the bridging oxygen atoms so the conductivity would be increased. However, further P₂O₅ substitution decreases the conductivity. For instance, the conductivity of 0.5 mol P₂O₅ % substitution is $5.74 \times 10^{-4} \text{ Scm}^{-1}$. Moreover, the conductivity of the 77.5Li₂S. (22.5 - x)P₂S₅ .xP₂O₅ (mol %) solid state electrolyte with 1, 2, 3, 6 and 9 mol% P₂O₅ substitution are smaller than the conductivity of the pure 77.5Li₂S. 22.5P₂S₅ (mol %) glassy electrolyte. A large P₂O₅ substitution causes of formation of the P₂S₆⁴⁻ ions with P-P bond and the PO₄³⁻ ions with non-bridging oxygen^{34,39}. These formations create a stronger trap for Li diffusion so the conductivity of the electrolyte decreases³⁴. In the case of this study, 1 mol % and more P₂O₅ substitution could create P₂S₆⁴⁻ and PO₄³⁻ ions. Thus, the conductivity of glassy SSEs would be decreased by the formation of these ions.

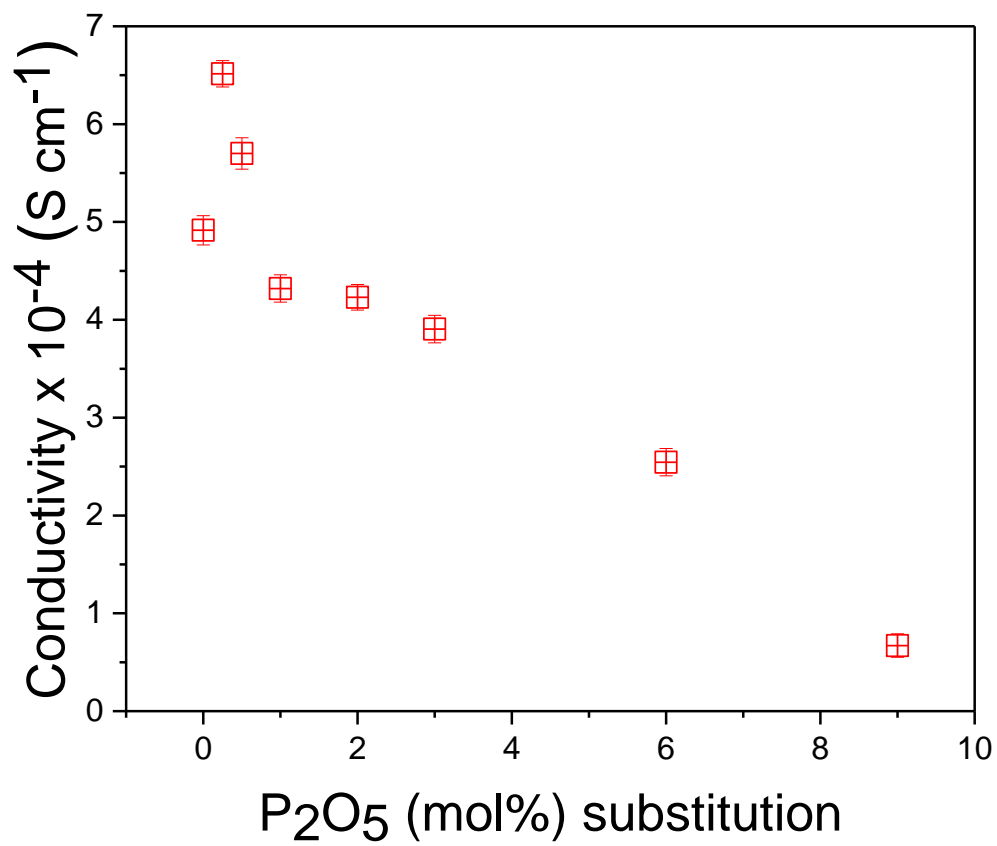
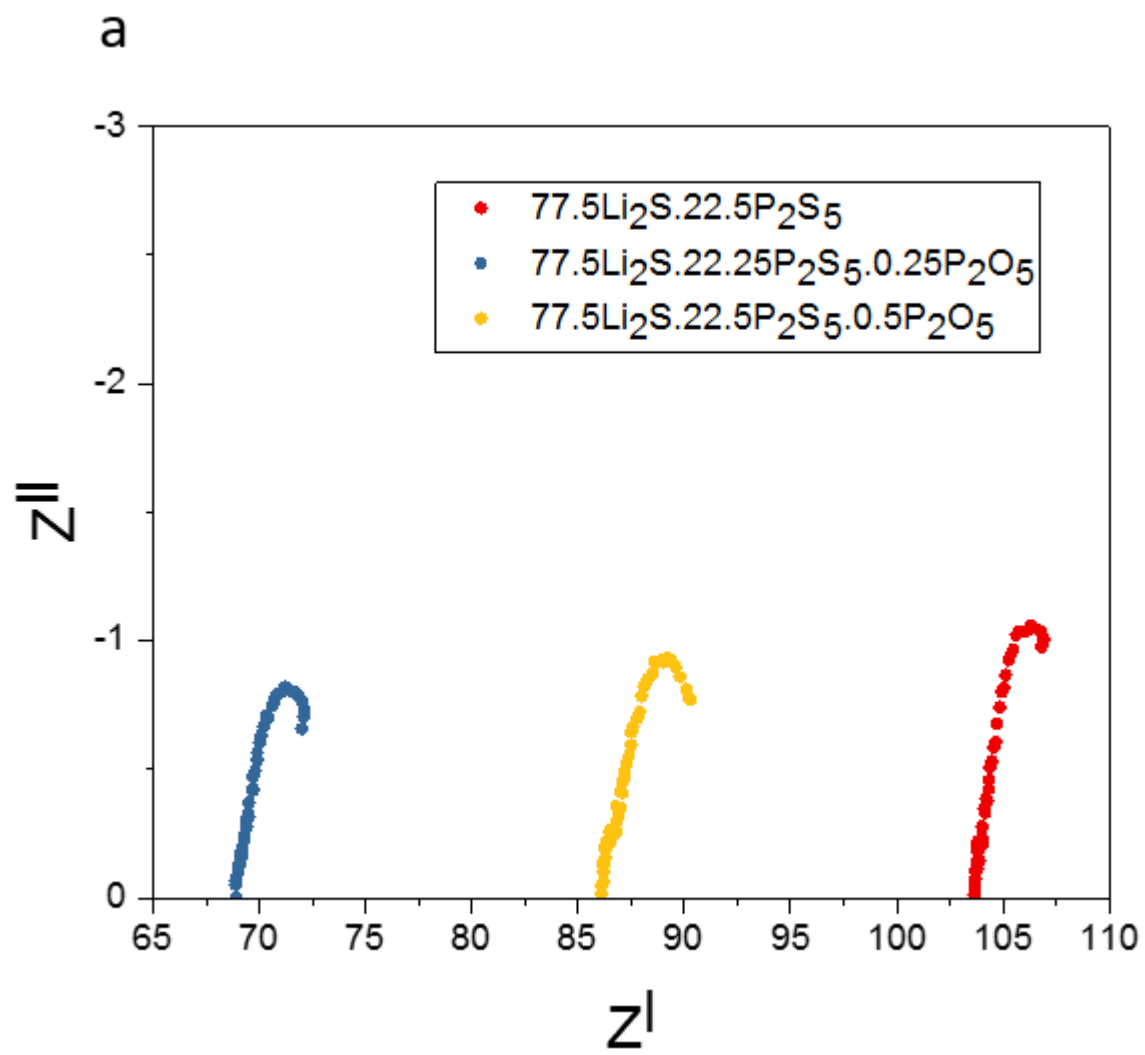


Figure 4. Composition dependence on conductivities at 60°C temperature for the Li/77.5Li₂S. (22.5 x)P₂S₅.xP₂O₅/Li metal cells.



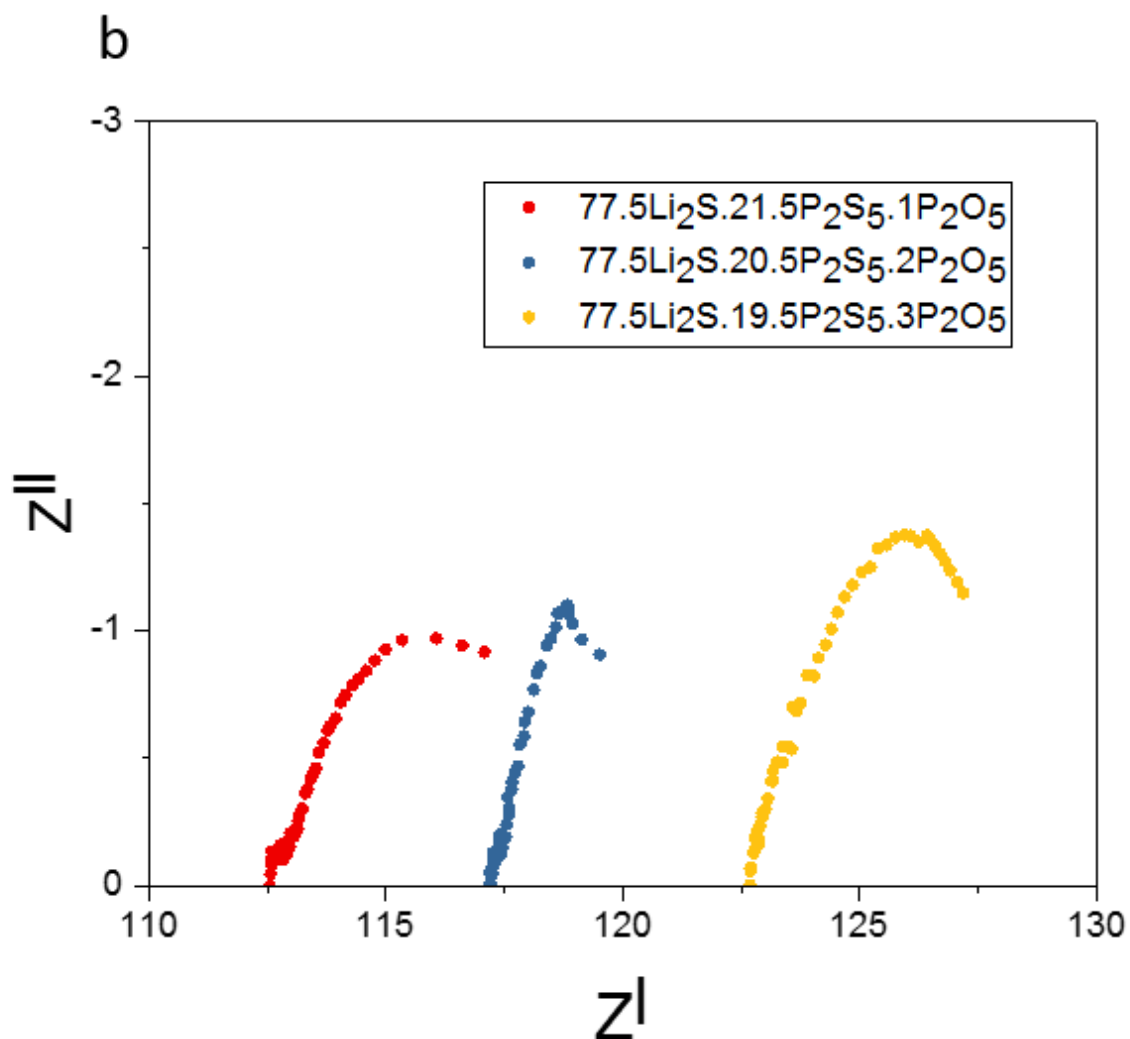


Figure 5. a) Impedance for Li/77.5Li₂S.22.5P₂S₅/Li, Li/77.5Li₂S₅.(22.25)P₂S₅.0.25P₂O₅/Li, and Li/77.5Li₂S₅.(22)P₂S₅.0.5P₂O₅/Li cells. b) Impedance for Li/77.5Li₂S₅.(21.5)P₂S₅.1P₂O₅/Li, Li/77.5Li₂S₅.(20.5)P₂S₅.2P₂O₅/Li, and Li/77.5Li₂S₅.(19.5)P₂S₅.3P₂O₅/Li cells.

Figure 6 demonstrates a correlation between composition of P₂O₅ and density of the 77.5Li₂S-22.5P₂S₅, and 77.5Li₂S₅.(22.5-x)P₂S₅.xP₂O₅ glassy electrolytes. The 77.5Li₂S₅.(22.5-x).P₂S₅.xP₂O₅ (mol %) glassy electrolyte with P₂O₅ substitution of x=0.25 was better compressed into a thin layer than 77.5Li₂S-22.5P₂S₅ glassy electrolyte. The increase in density might be due to change in mechanical properties of the glassy electrolyte. However, thickness of the pellets were

increased by further P_2O_5 substitution (>0.25 mol %). Moreover, the thickness of pure $77.5Li_2S \cdot 22.5P_2S_5$ (mol %) glassy electrolyte pellet was higher than thickness of $77.5Li_2S \cdot (22.5 - x) \cdot P_2S_5 \cdot xP_2O_5$ (mol %) with P_2O_5 substitution of $x < 6$ pellets. Thus, a small P_2O_5 addition allows the glassy electrolyte to be better compressed into a thin layer. Kato, A. et al. reported that P_2O_5 substitution will increase the bond dissociation energy because the P-O bonds are stronger than the P-S bonds⁴³. Therefore, the density will increase by P_2O_5 substitution⁴³. In the case of this study, 6 mol % and more P_2O_5 substitution could increase the bond dissociation energy and decrease the thickness of the pellets.

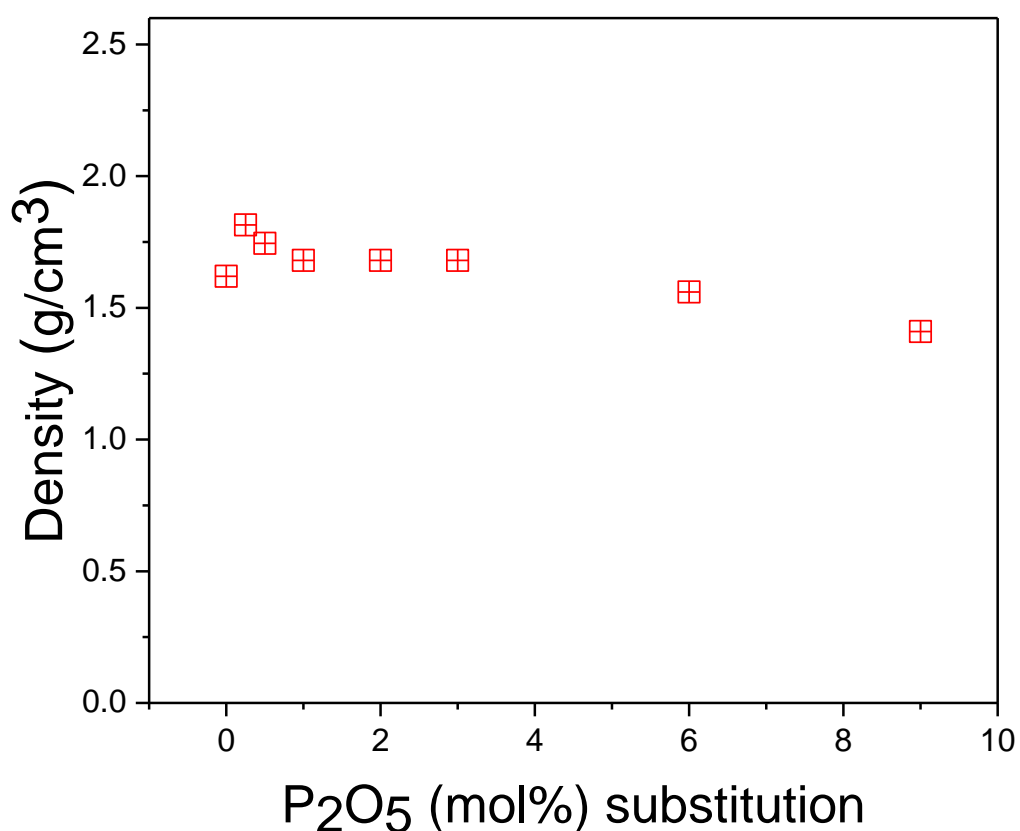


Figure 6. Density of the $77.5Li_2S \cdot 22.5P_2S_5$ (mol %) SSE, and $77.5Li_2S \cdot (22.5 - x) \cdot P_2S_5 \cdot xP_2O_5$ (mol%) glassy electrolyte with varying composition of P_2O_5 .

Introducing oxide species into a sulfide based electrolyte increased the cycle stability. Figure 7 shows a comparison of the cycling numbers of Li/Li metal cells with the 77.5Li₂S.22.5P₂S₅ (mol %) glassy SSE, and 77.5Li₂S.(22.5-x)P₂S₅.xP₂O₅ (mol %) glassy electrolytes having varying substitution of P₂O₅.

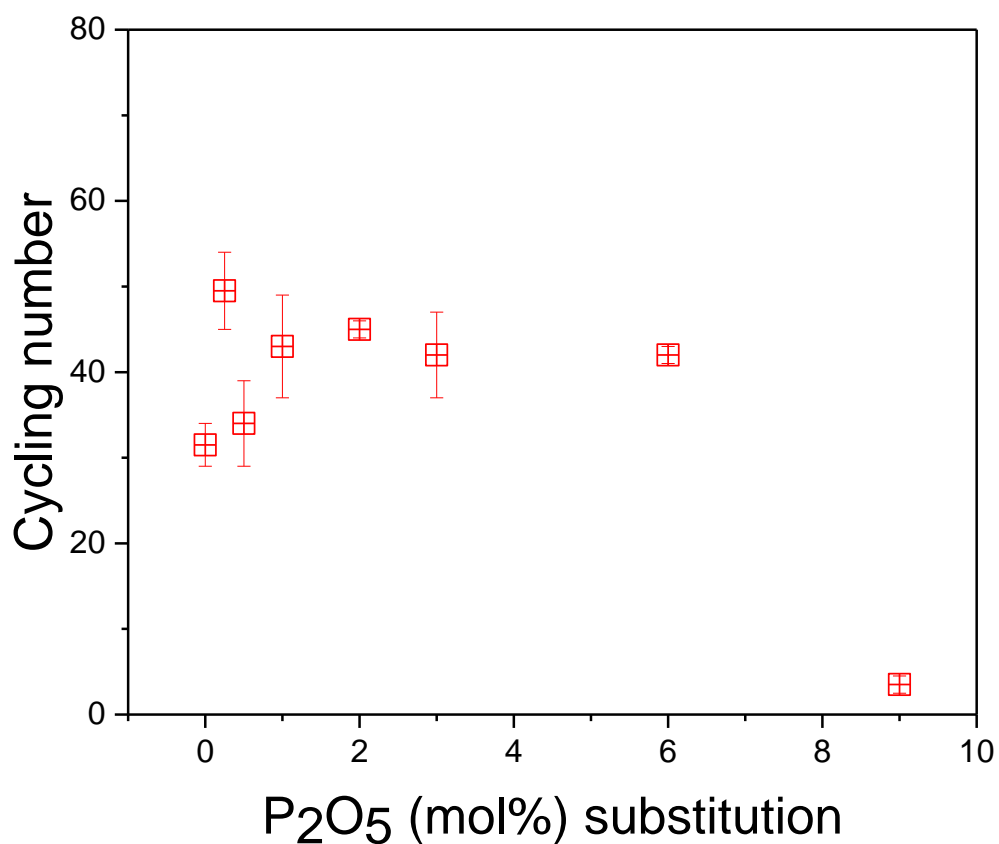
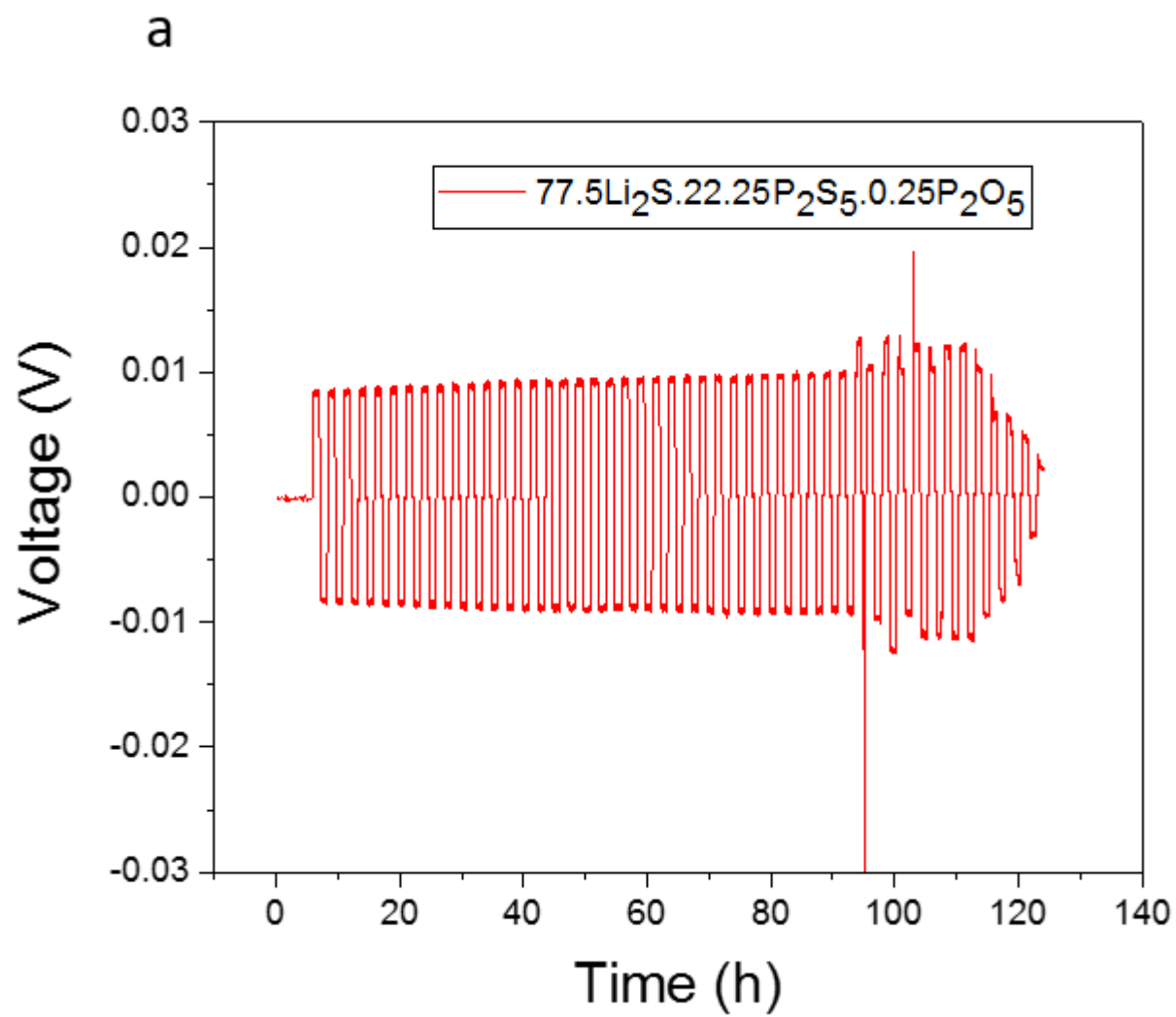


Figure 7. The cycling numbers of Li/77.5Li₂S₅.(22.5-x)P₂S₅.xP₂O₅/Li cells with varying composition of P₂O₅.

As it can be seen from cycling performance of Li/77.5Li₂S₅.(22.5 - x)P₂S₅.xP₂O₅ (mol %) /Li cells, the growth of lithium dendrites could be suppressed by adding a small amount of P₂O₅. While the cycling number of a symmetric lithium metal cell with 77.5Li₂S₅.22.5P₂S₅ (mol %) glassy electrolyte is 34, the cycling number of Li/77.5Li₂S₅.(22.5 - x) P₂S₅.xP₂O₅ (mol %) /Li cells having

0.25% content of P_2O_5 is 54. This could be from enhanced conductivity in the electrolyte, and increased density of the pellet. However, further substitution of P_2O_5 could increase the dendrite growth effects of the $Li/77.5Li_2S \cdot (22.5 - x) \cdot xP_2O_5$ (mol %)/Li metal cells since the conductivity was decreased by further P_2O_5 addition. The cycling numbers 0.5, 1, 2, 3, 6, and 9 mol % P_2O_5 are 39, 49, 46, 47, 43, and 4, respectively. Thus, $Li/77.5Li_2S \cdot (22.5 - x) \cdot P_2S_5 \cdot xP_2O_5$ (mol %)/Li cells with P_2O_5 substitution of $x < 9$ displayed longer cycling performance without short circuiting compared to cells with pure $77.5Li_2S \cdot 22.5P_2S_5$ (mol %) glassy SSE. The cycling performances of $Li/77.5Li_2S \cdot (22.5 - x)P_2S_5 \cdot xP_2O_5$ (mol %)/Li cells with varying composition of P_2O_5 are illustrated in figures 8a, and b (0.25 mol % P_2O_5), 9a and b (0.5 mol % P_2O_5), 10a and b (1 mol % P_2O_5), 11a and b (2 mol % P_2O_5), 12a and b (3 mol % P_2O_5), 13a and b (6 mol % P_2O_5), and 14a and b (9 mol % P_2O_5) in the next pages. Two cycling performance of each composition were displayed to support the accuracy of figure 7. Some of the figures have voltage increases in specific cycles due to temperature change in the oven.



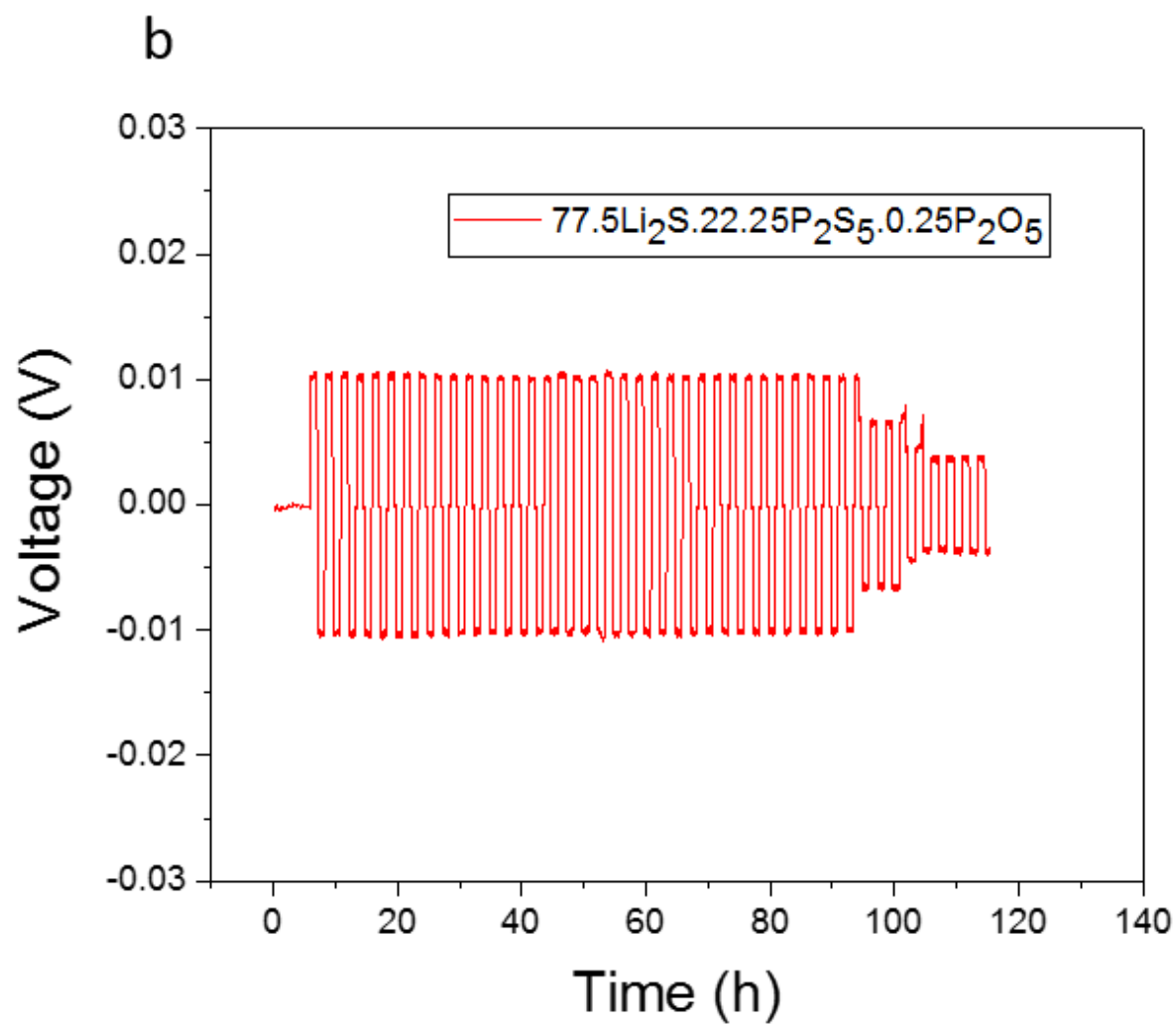
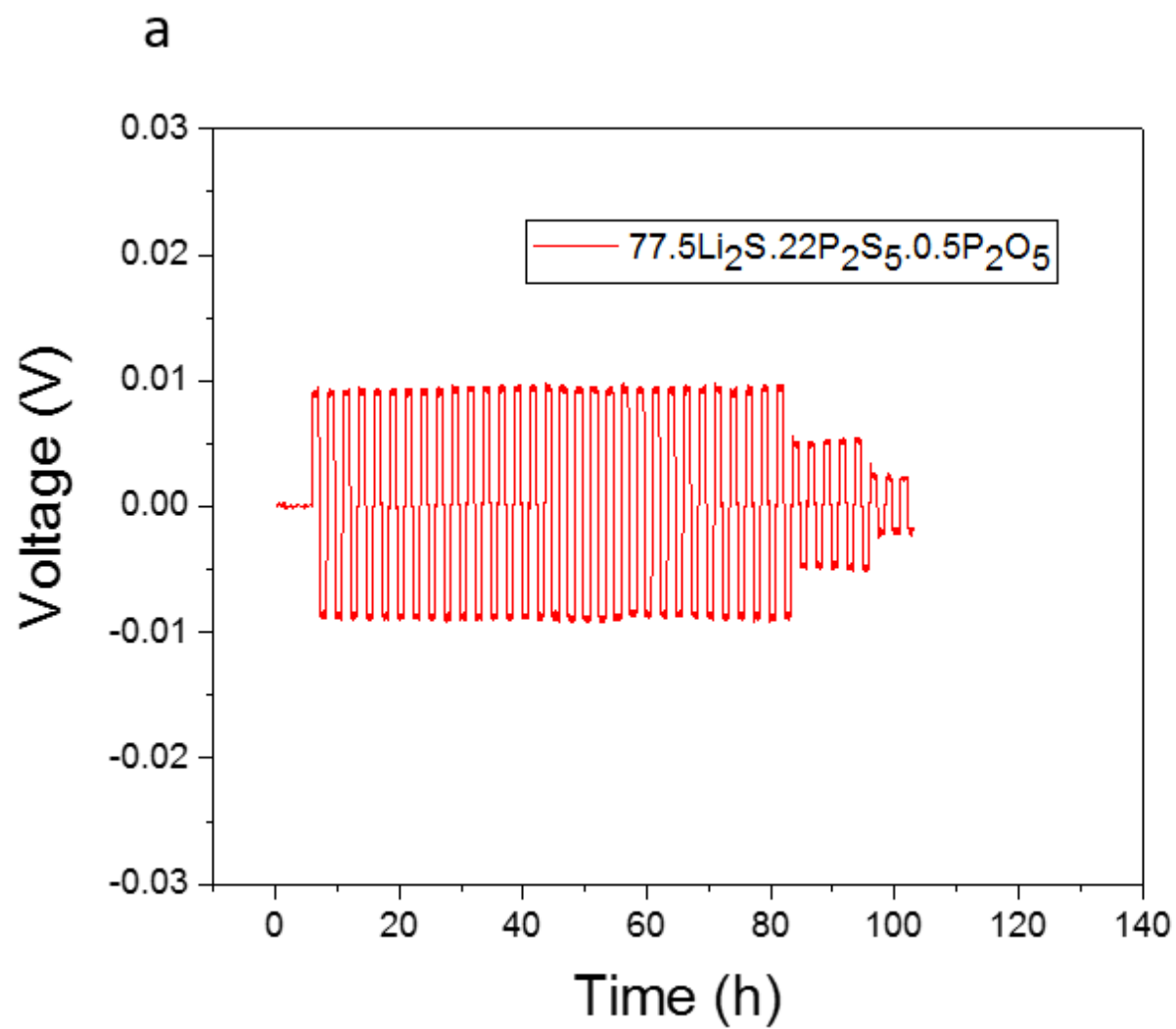


Figure 8. a) and b) show the cycling performance of the Li/77.5Li₂S.22.25P₂S₅.0.25P₂O₅ (mol %)/Li metal cells.



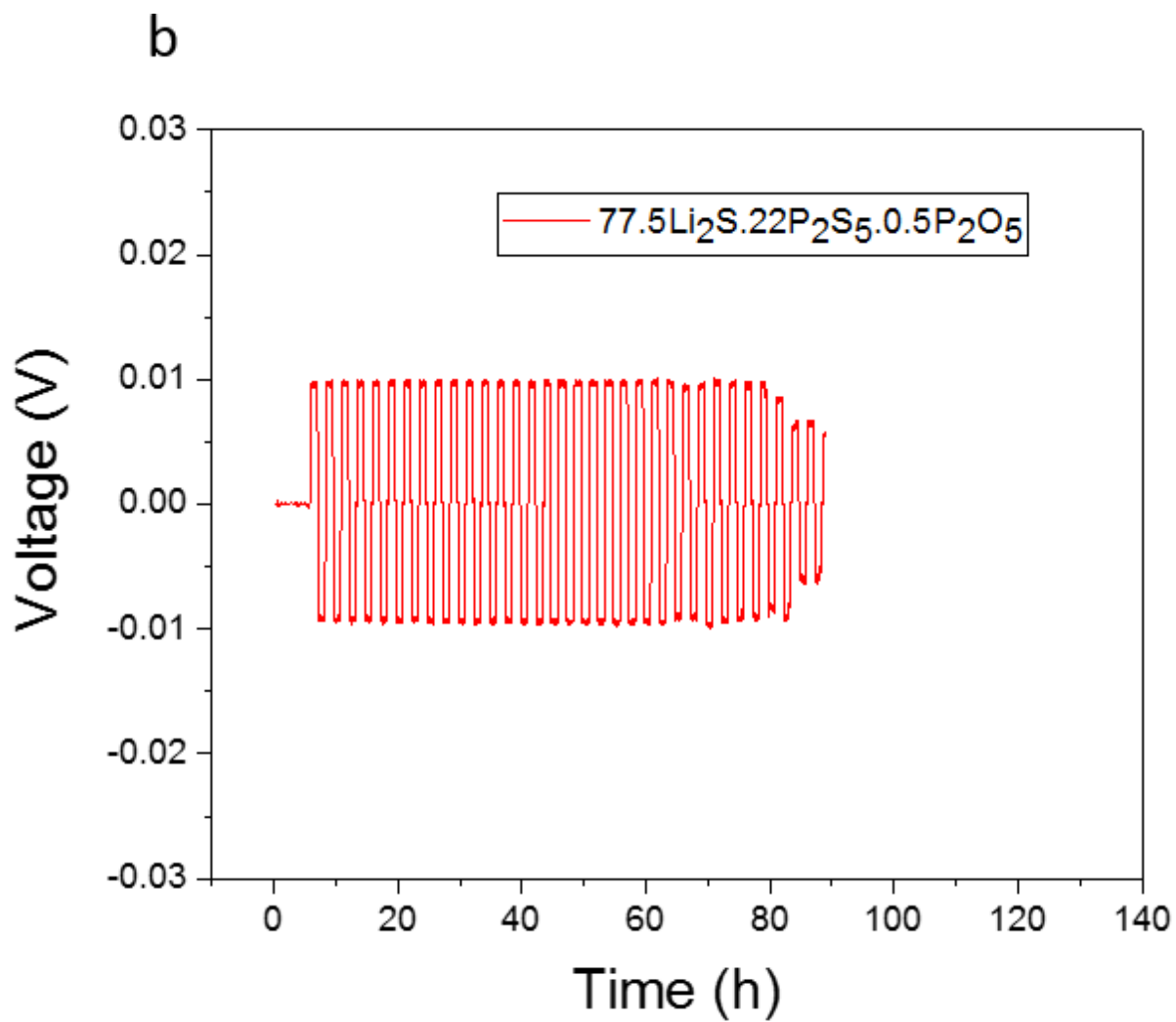
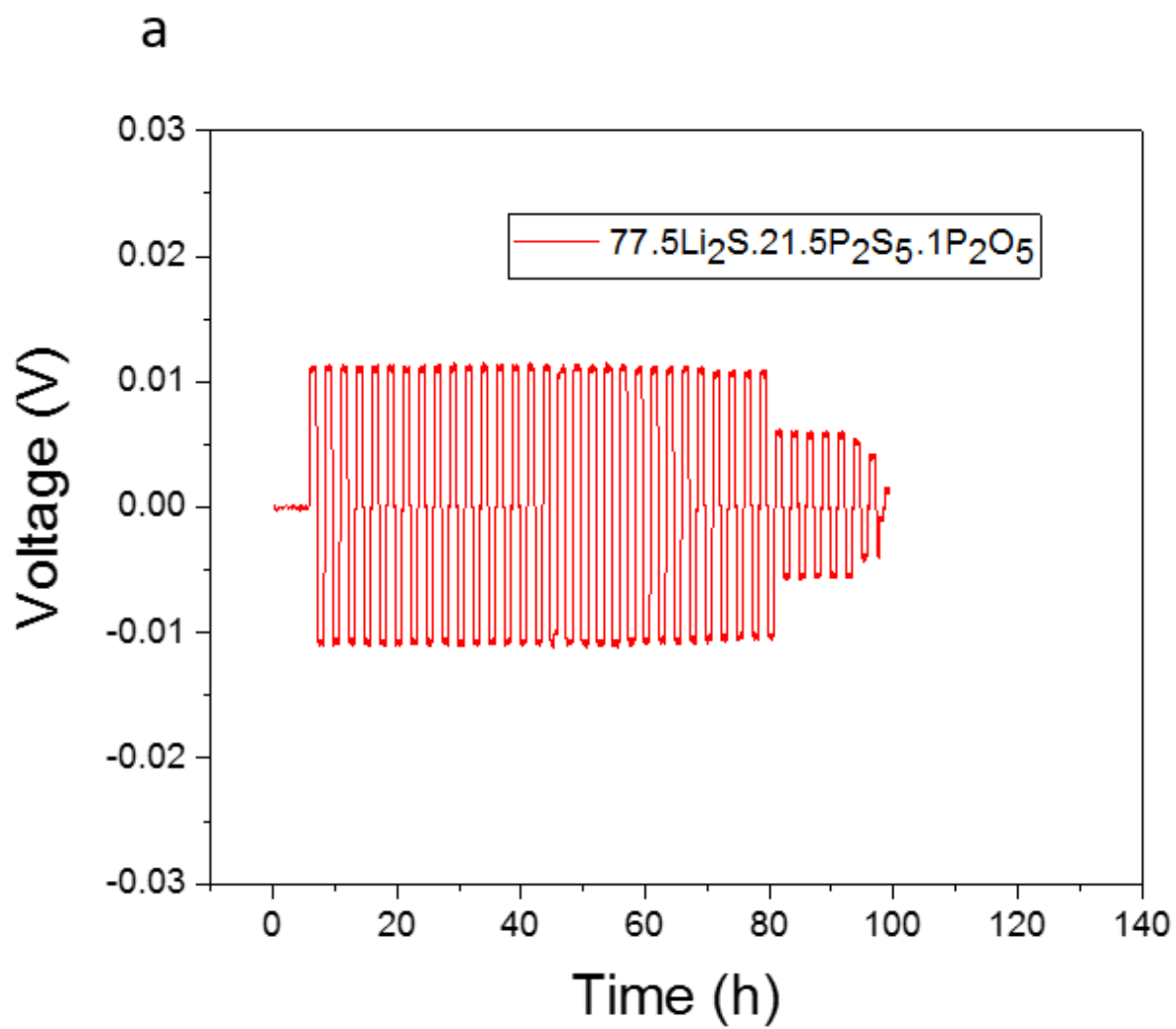


Figure 9. a) and b) show the cycling performance of the Li/77.5Li₂S.22P₂S₅.0.5P₂O₅ (mol %)/Li metal cells.



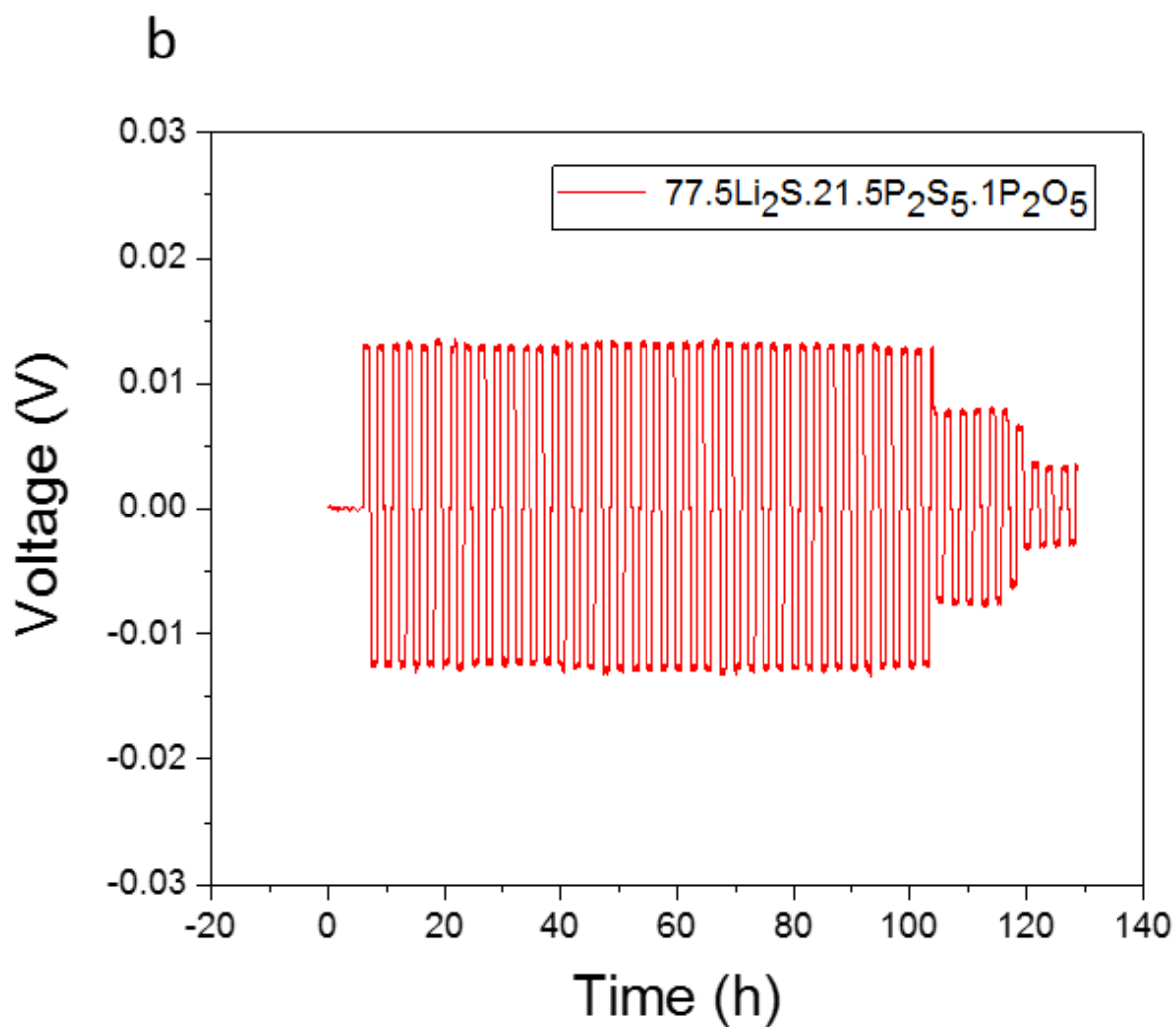
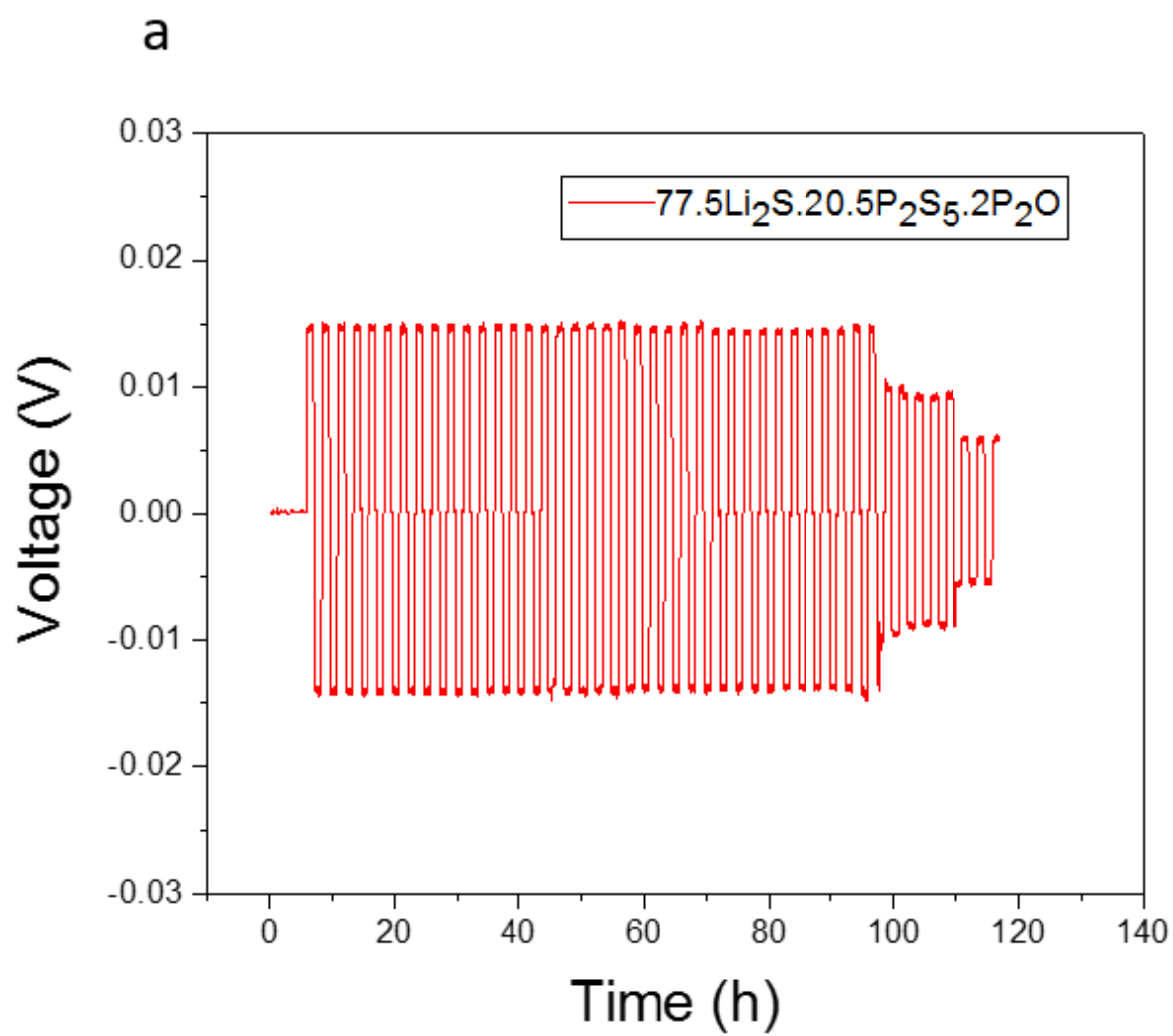


Figure 10. a) and b) show the cycling performance of the Li/77.5Li₂S.21.5P₂S₅.1P₂O₅ (mol %)/Li metal cells.



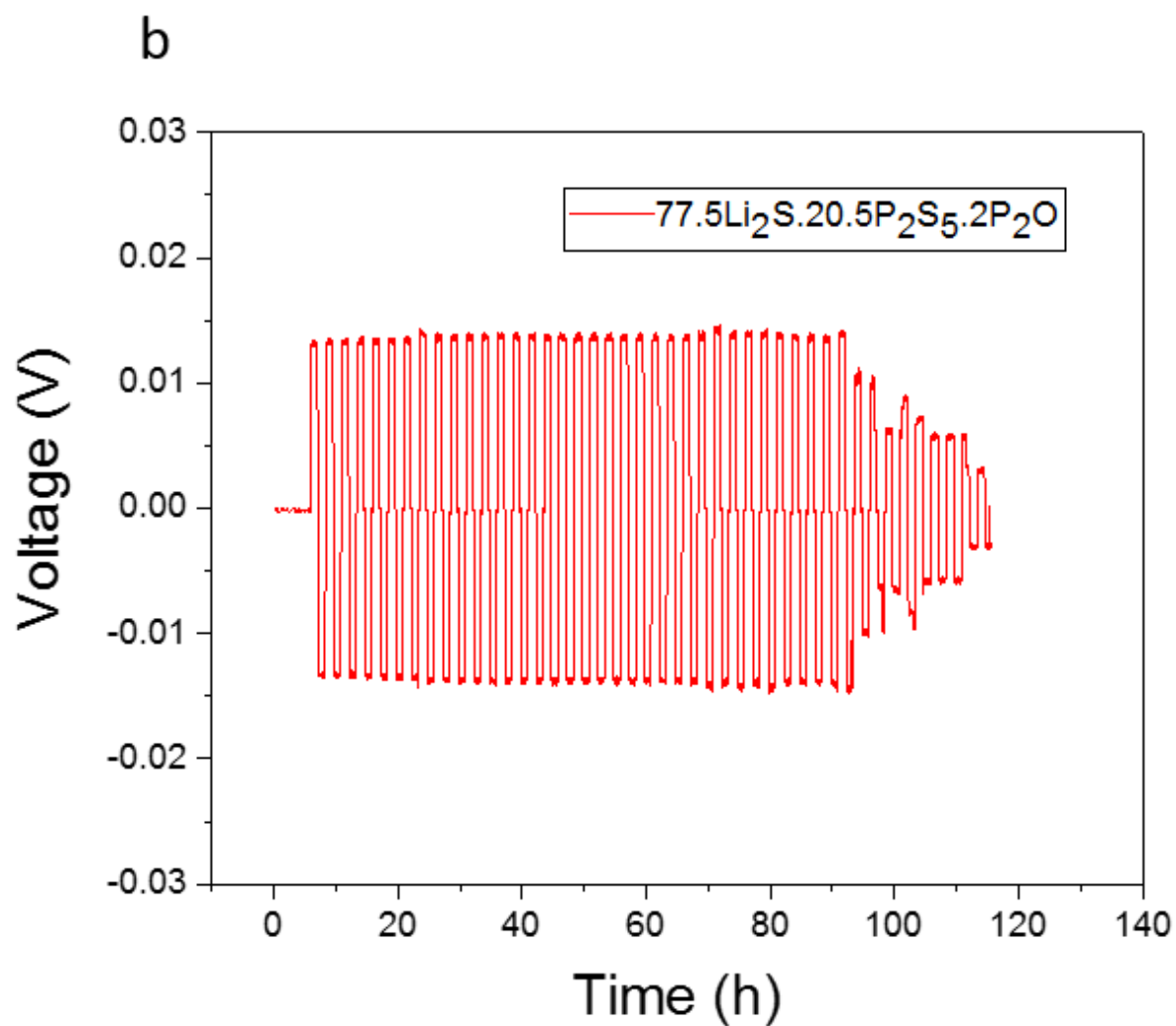
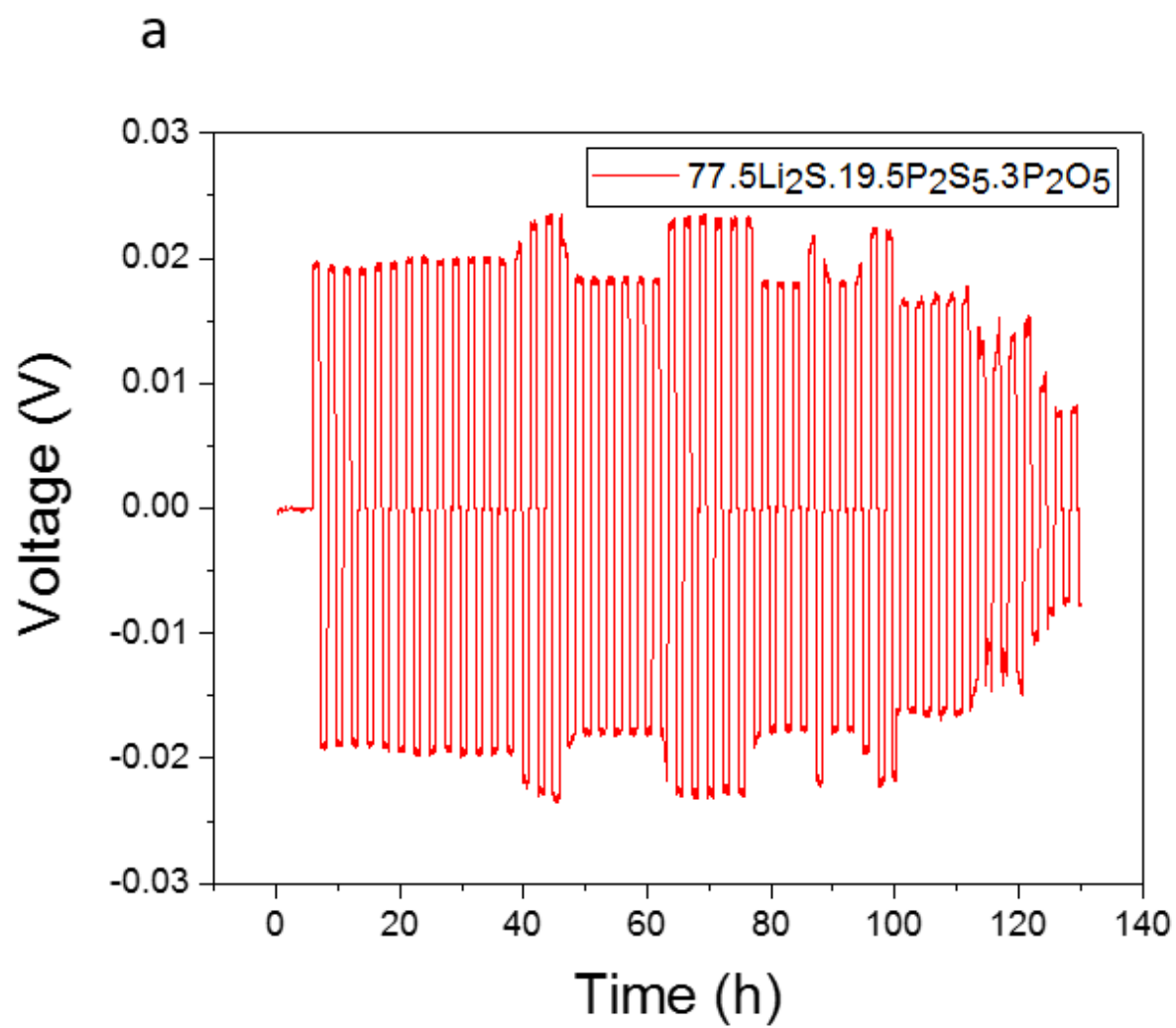


Figure 11. a) and b) show the cycling performance of Li/77.5Li₂S.20.5P₂S₅.2P₂O₅ (mol %)/Li metal cells.



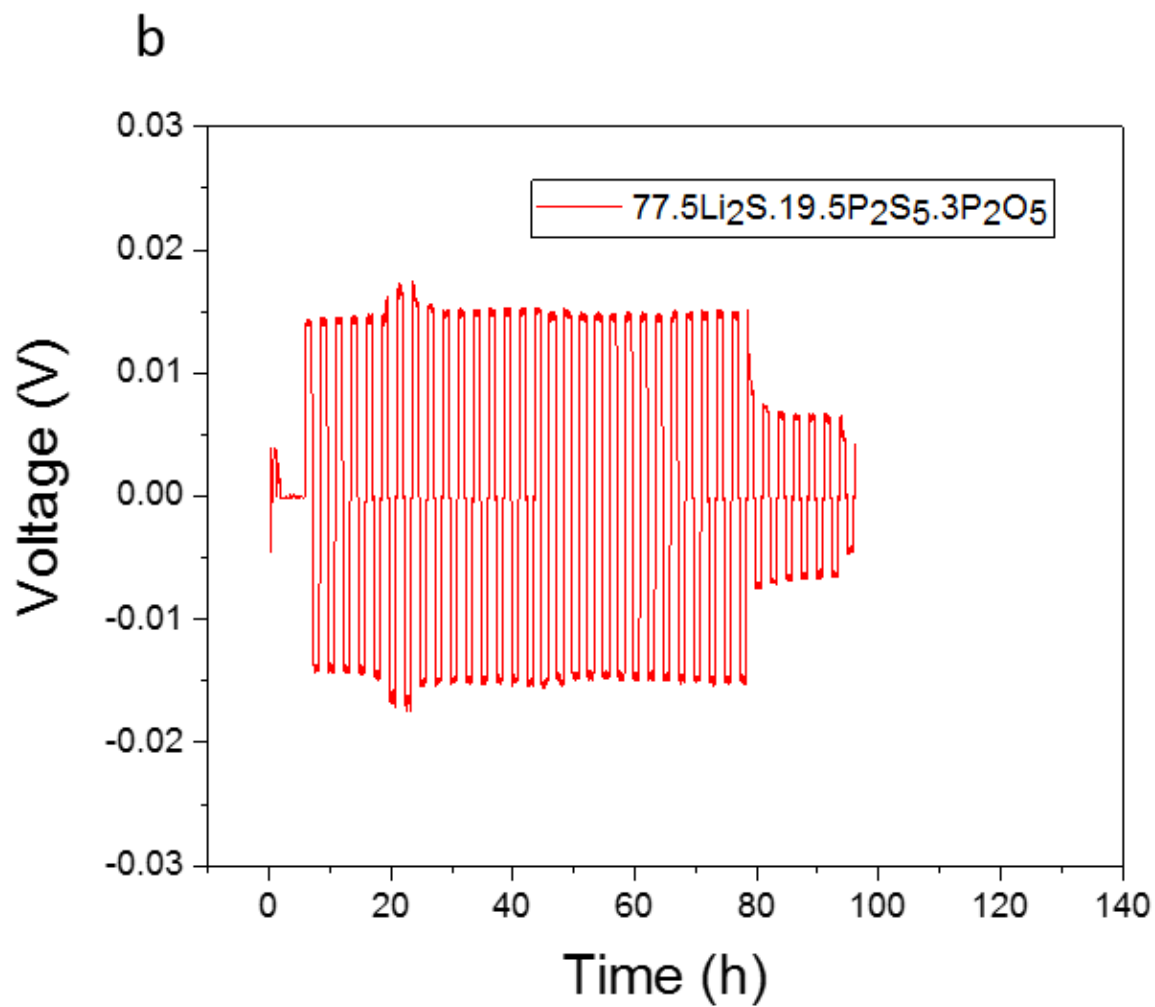
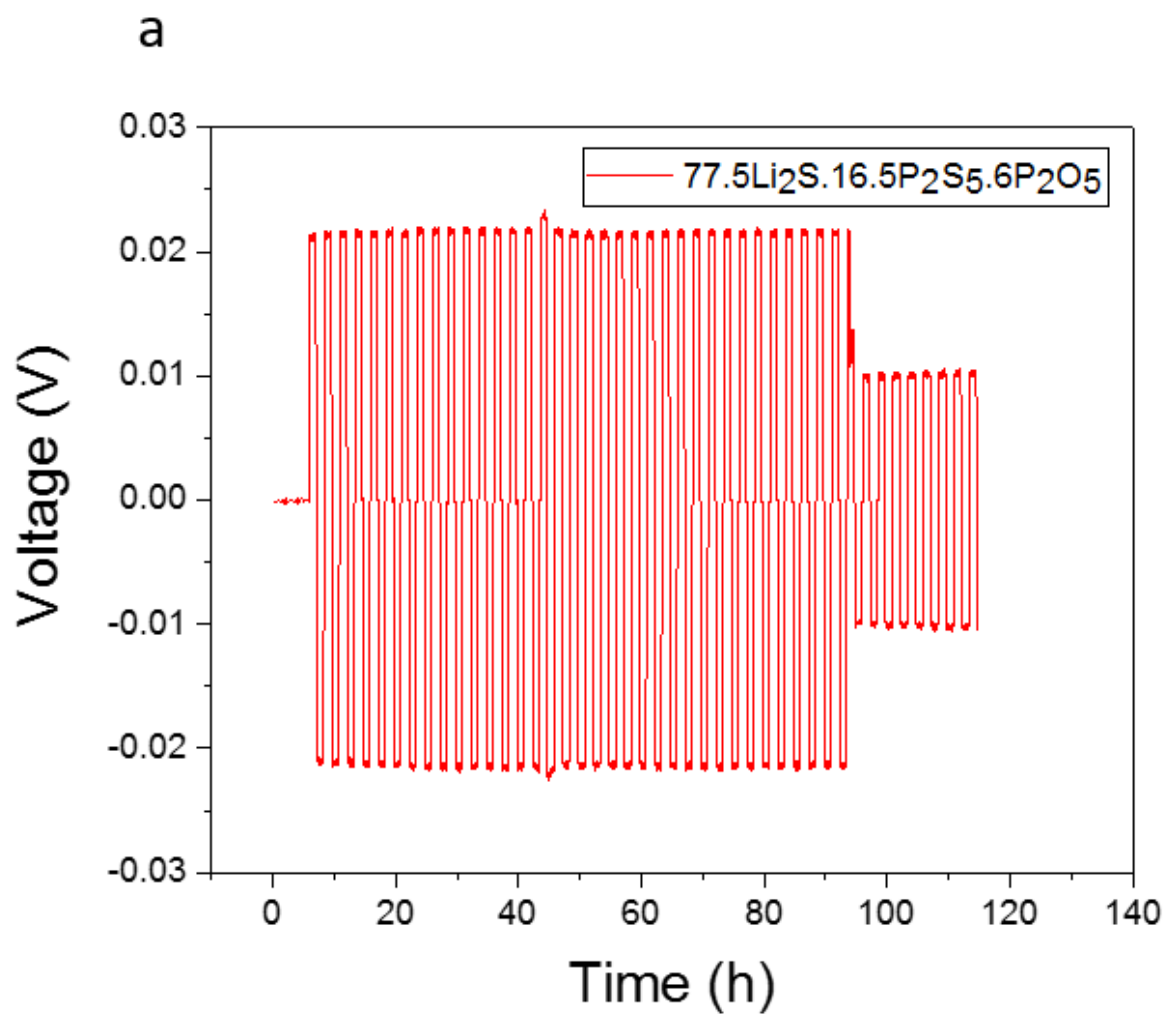


Figure 12. a) and b) show the cycling performance of the Li/77.5Li₂S.19.5P₂S₅.3P₂O₅ (mol %)/Li cells.



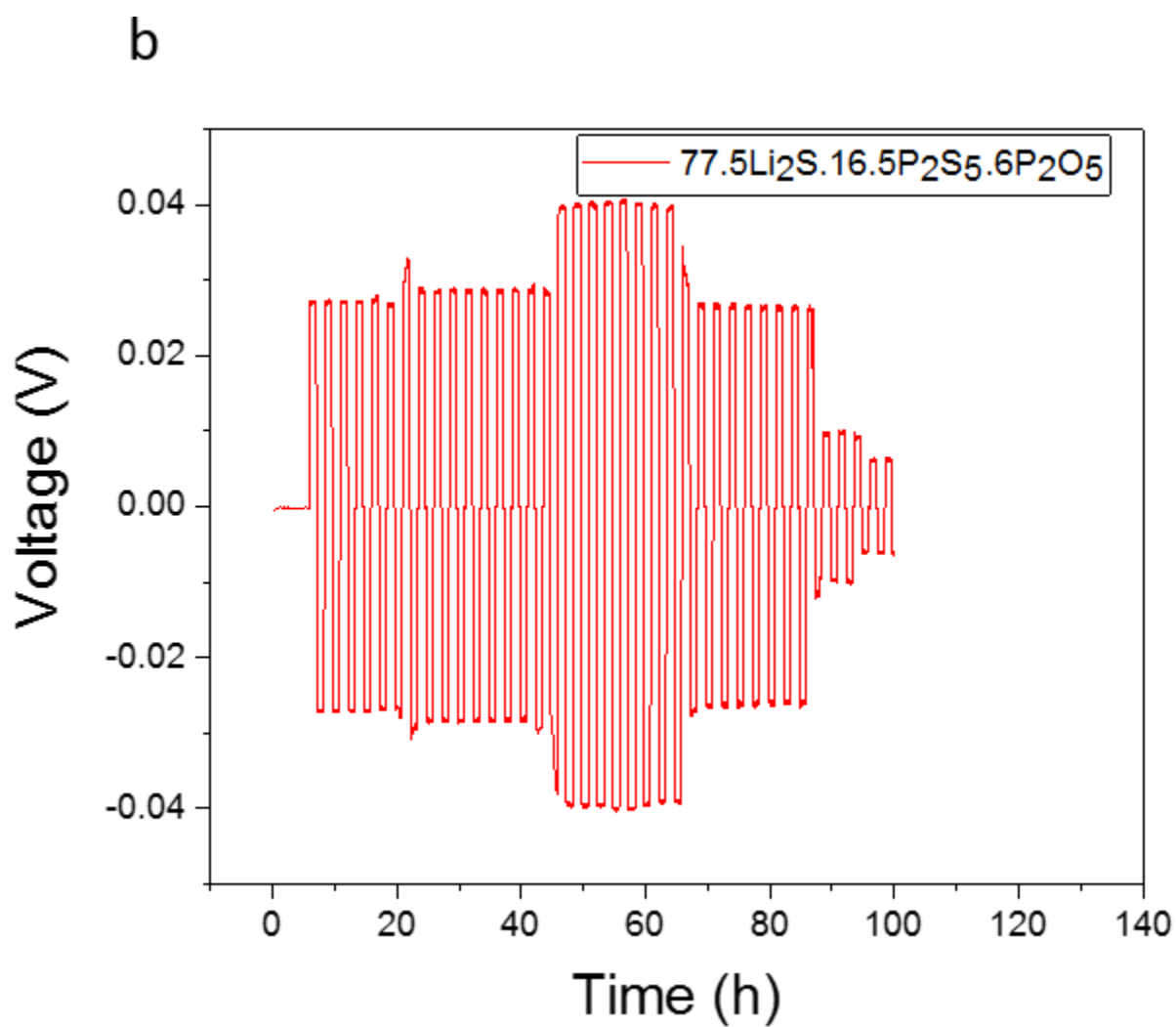
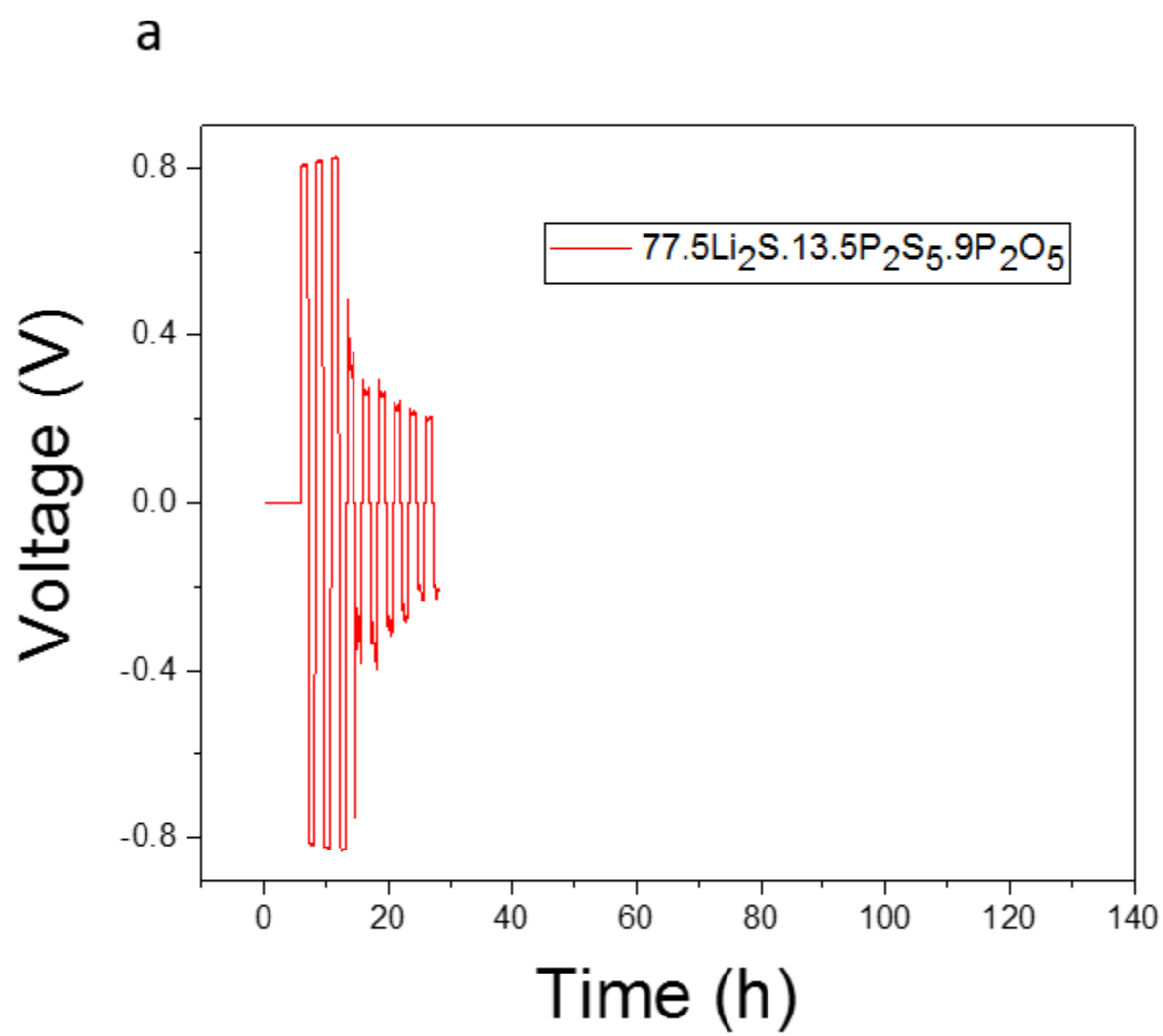


Figure 13. a) and b) show the cycling performance of the $\text{Li}/77.5\text{Li}_2\text{S}.16.5\text{P}_2\text{S}_5.6\text{P}_2\text{O}_5$ (mol %)/Li metal cells.



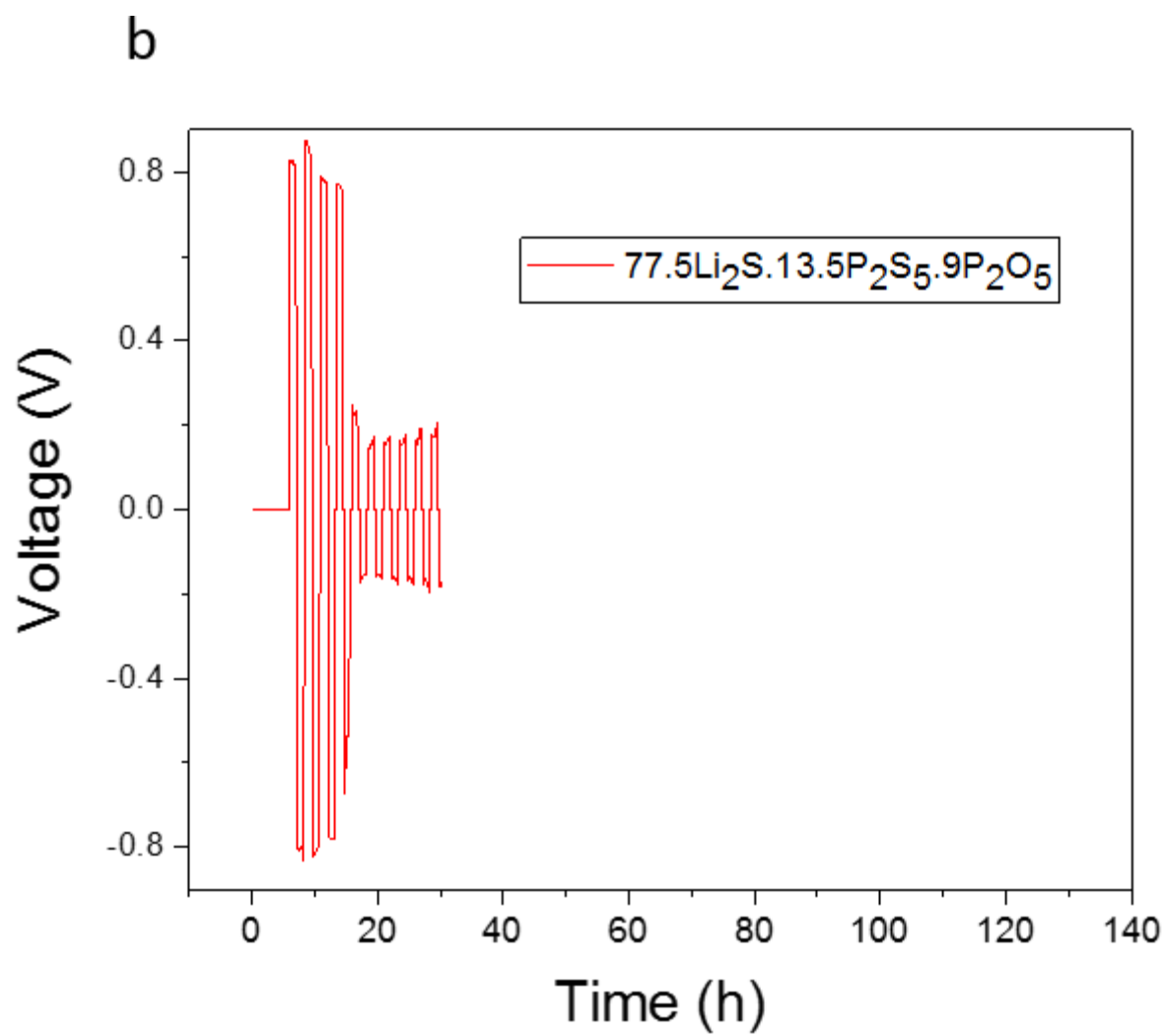


Figure 14. a) and b) show the cycling performance of the Li/77.5Li₂S.13.5P₂S₅.9P₂O₅ (mol %)/Li metal cells.

Figure 15 is short circuit capacity as function of P_2O_5 substitutions at the fixed current of 0.1 mA/cm^2 . Also, the results of the deposition tests with varies P_2O_5 compositions are shown in figure 16, 17, 18, 19, 20, 21, and 22 below. Two deposition tests of each P_2O_5 substitutions were demonstrated to support the accuracy of the figure 15. The $77.5Li_2S.(22.5 - x)P_2S_5.xP_2O_5$ (mol %) glassy SSE with 0.5 mol% P_2O_5 displayed the highest short circuit capacity of 4.5 mAh/cm^2 . This could be from enhanced conductivity in the electrolyte and increased density of the pellet. Moreover, the short circuit capacity of $Li/77.5Li_2S.(22.5 - x)P_2S_5.xP_2O_5$ (mol %)/Li metal cells with 0.25, 1,2 and 3 mol% P_2O_5 substitutions were similar to short circuit capacity of $Li/77.5Li_2S.22.5P_2S_5$ (mol %)/Li cells. Additionally, 9 mol% P_2O_5 substitution had the lowest short circuit capacity of 0.2 mAh/cm^2 . This could be from diminished conductivity in the electrolyte and decreased density of the pellet.

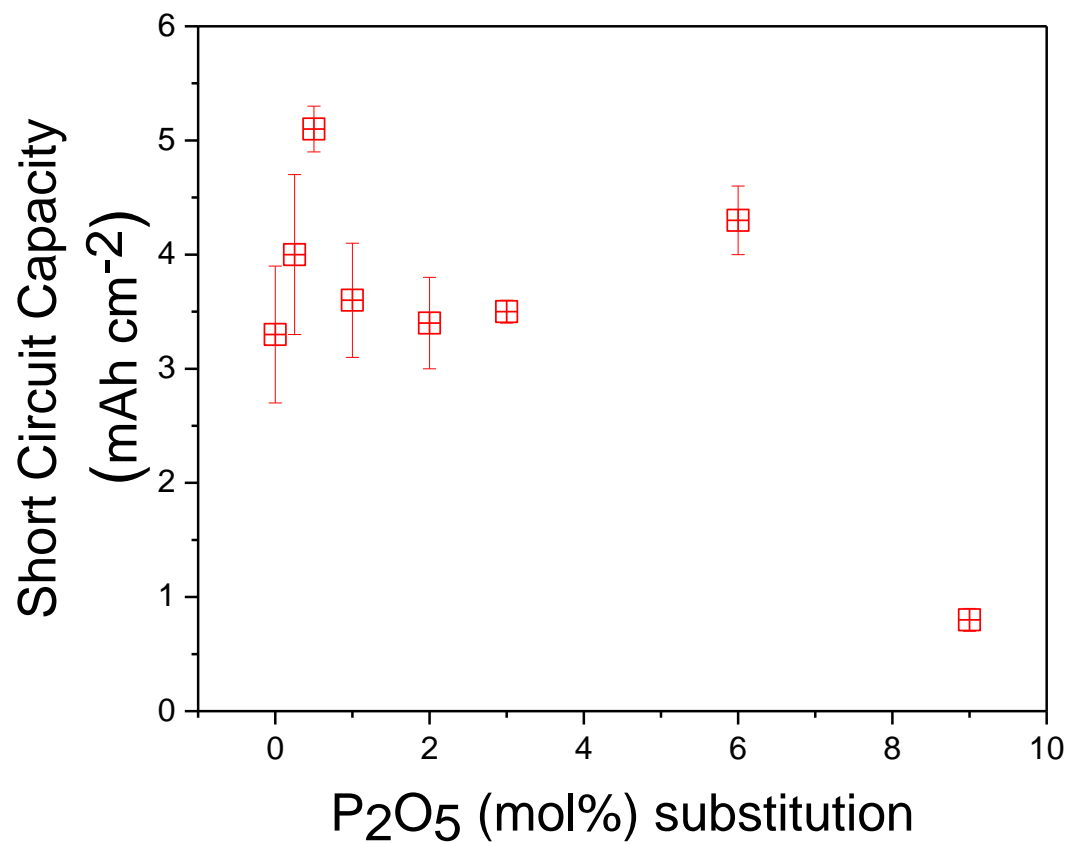


Figure 15. Short circuit capacity of symmetric cell with using the $77.5\text{Li}_2\text{S} \cdot (22.5 - x) \cdot \text{P}_2\text{S}_5 \cdot x\text{P}_2\text{O}_5$ (mol %) solid electrolyte at 0.1 mA/cm^2 with different variants of P_2O_5 .

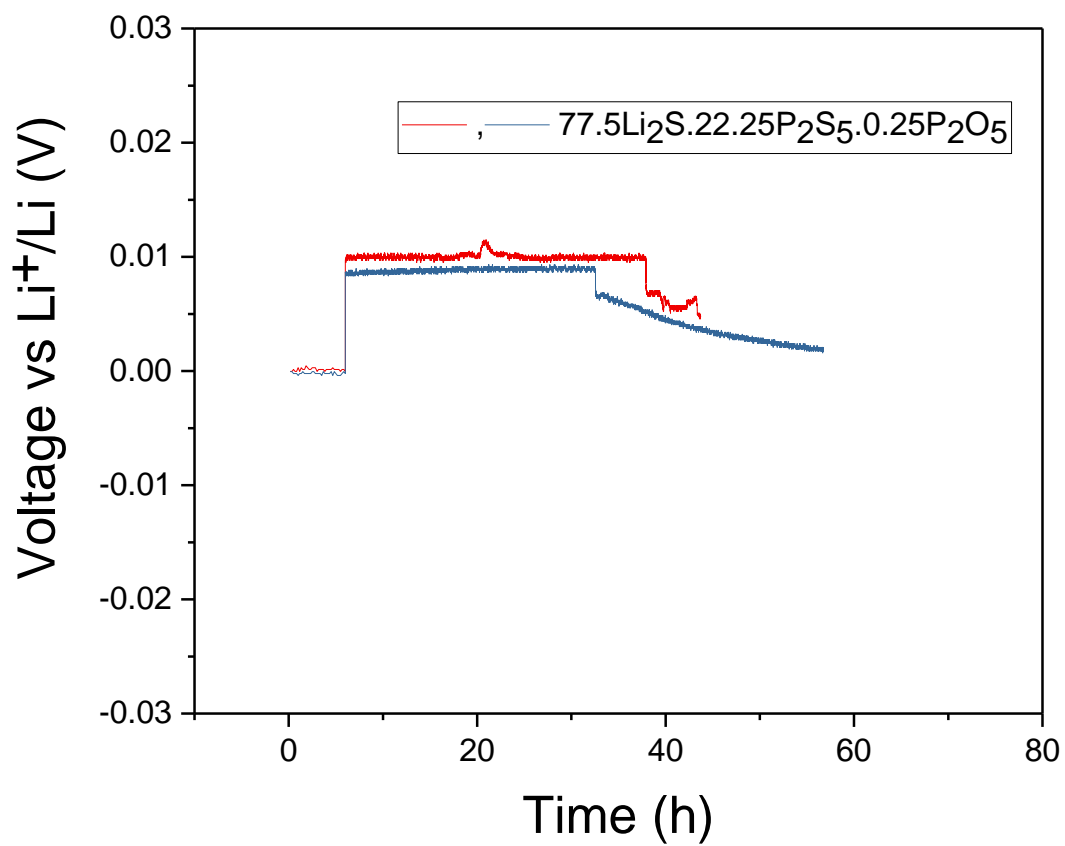


Figure 16. Galvanostatic plating of lithium in a metal cell using the $77.5\text{Li}_2\text{S}.(22.5 - x).\text{P}_2\text{S}_5.x\text{P}_2\text{O}_5$ (mol %) SSE with 0.25 mol% P_2O_5 substitution.

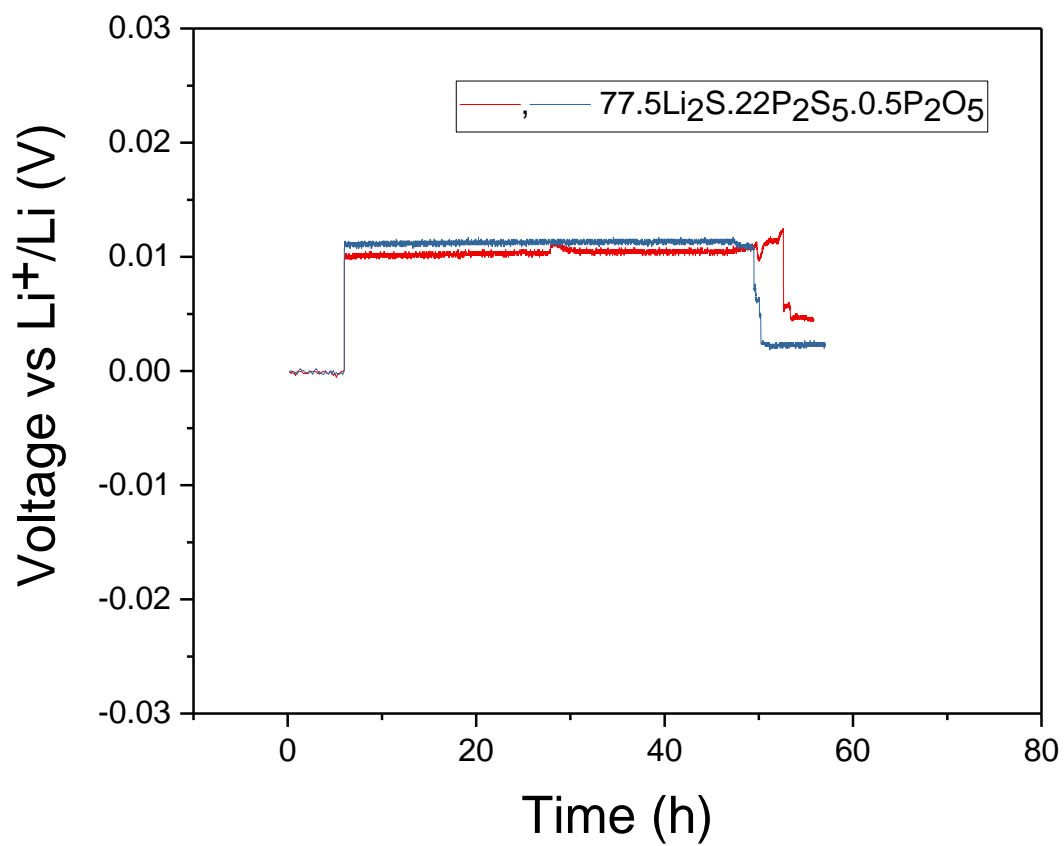


Figure 17. Galvanostatic plating of lithium in a metal cell using the $77.5\text{Li}_2\text{S} \cdot (22.5 - x) \cdot \text{P}_2\text{S}_5 \cdot x\text{P}_2\text{O}_5$ (mol %) SSE with 0.5 mol% P_2O_5 substitution.

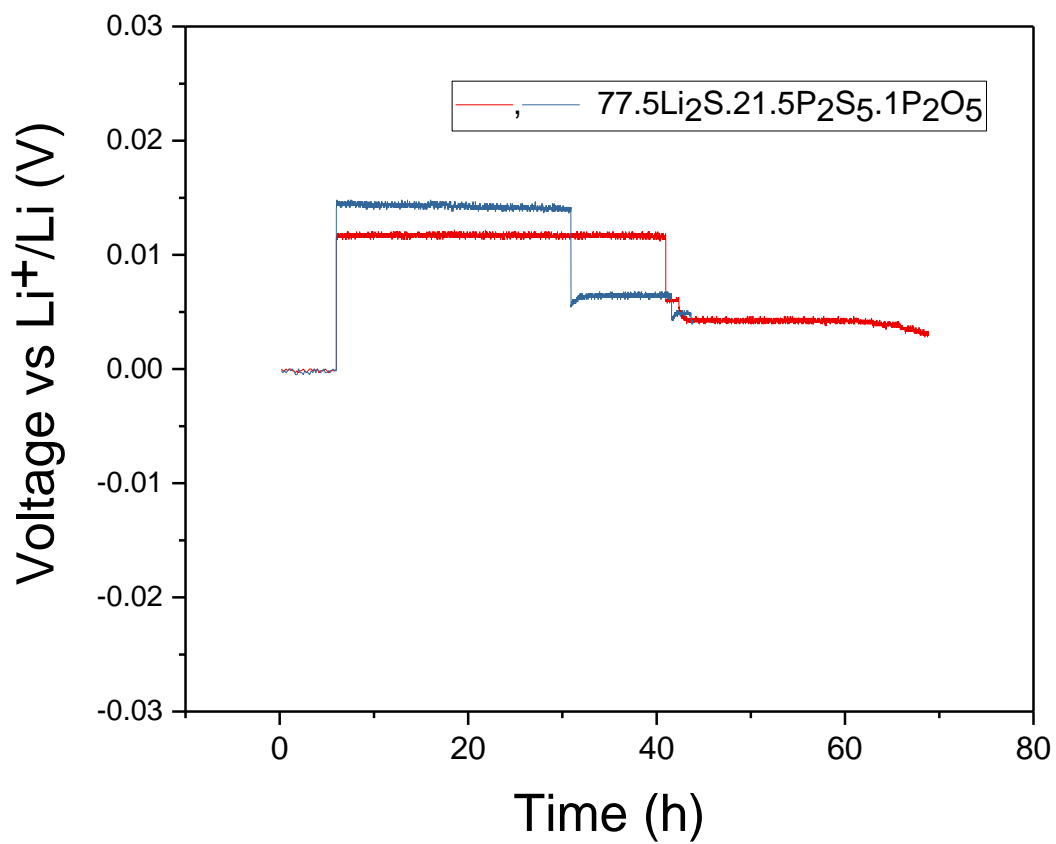


Figure 18. Galvanostatic plating of lithium in a metal cell the $77.5\text{Li}_2\text{S}.(22.5 - x).\text{P}_2\text{S}_5.x\text{P}_2\text{O}_5$ (mol %) SSE with 1 mol% P_2O_5 substitution.

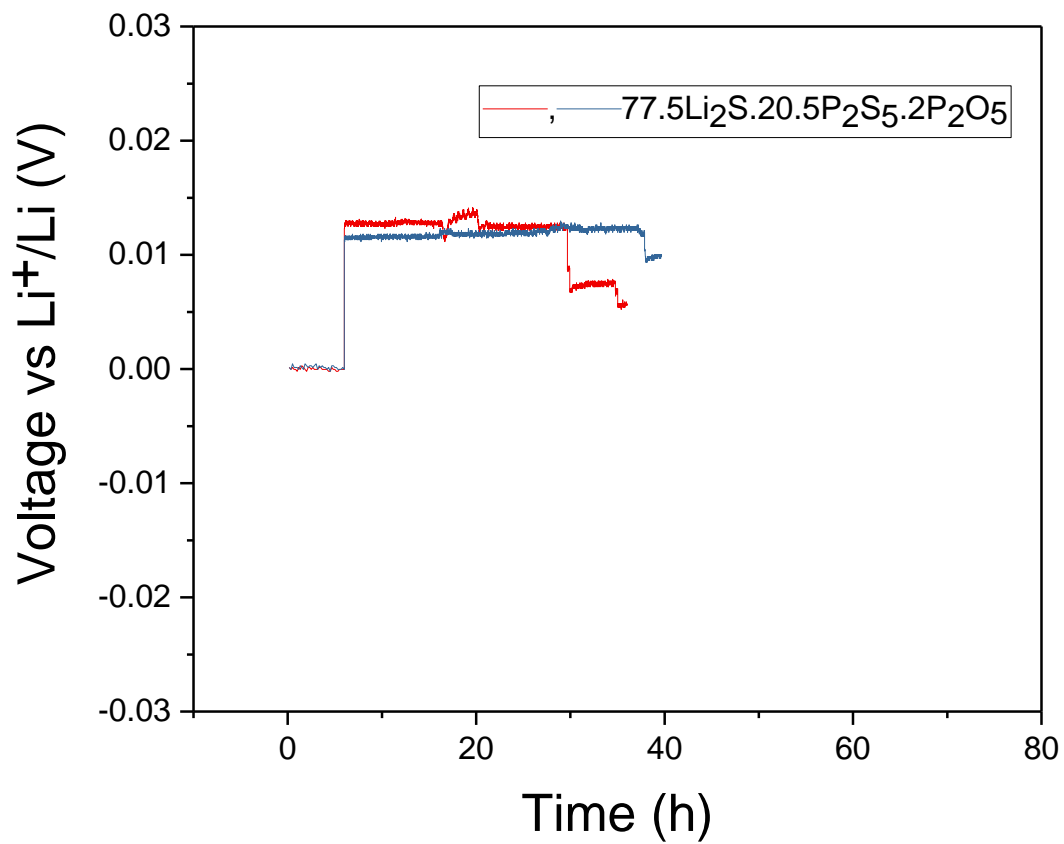


Figure 19. Galvanostatic plating of lithium in a metal cell using the $77.5\text{Li}_2\text{S} \cdot (22.5 - x) \cdot \text{P}_2\text{S}_5 \cdot x\text{P}_2\text{O}_5$ (mol %) SSE with 2 mol% P_2O_5 substitution.

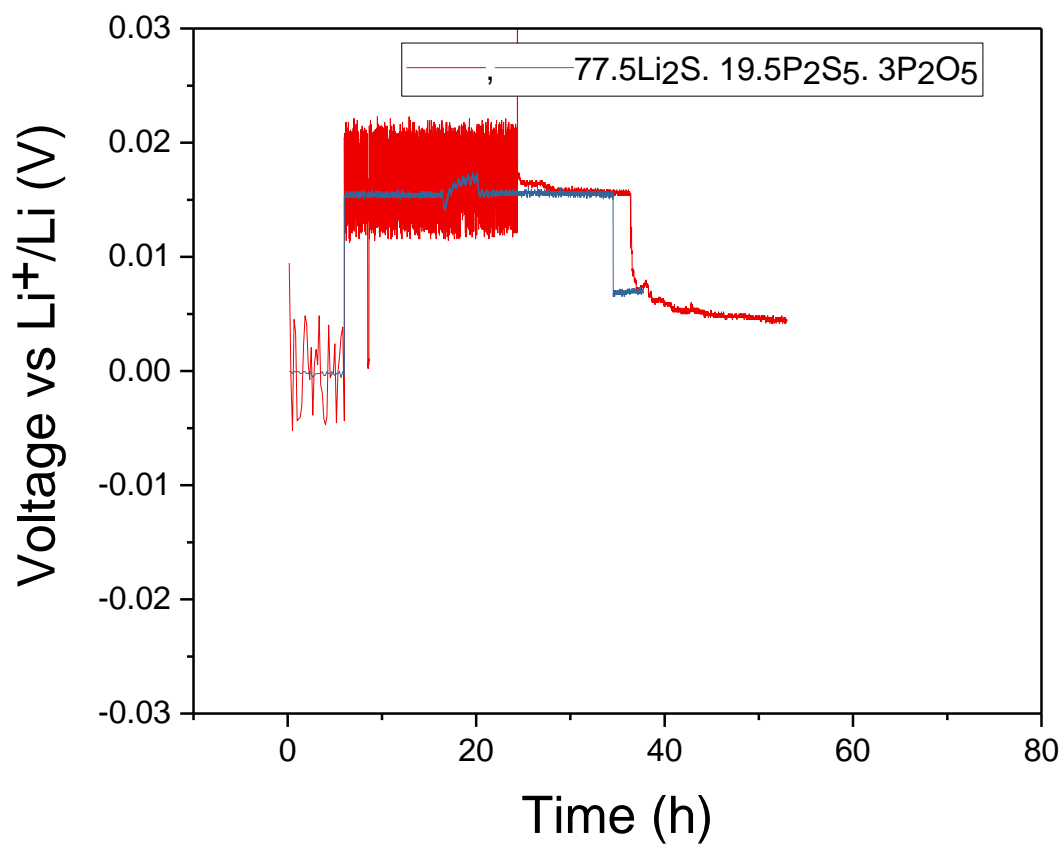


Figure 20. Galvanostatic plating of lithium in a metal cell using the $77.5\text{Li}_2\text{S} \cdot (22.5 - x) \cdot \text{P}_2\text{S}_5 \cdot x\text{P}_2\text{O}_5$ (mol %) SSE with 3 mol% P_2O_5 substitution.

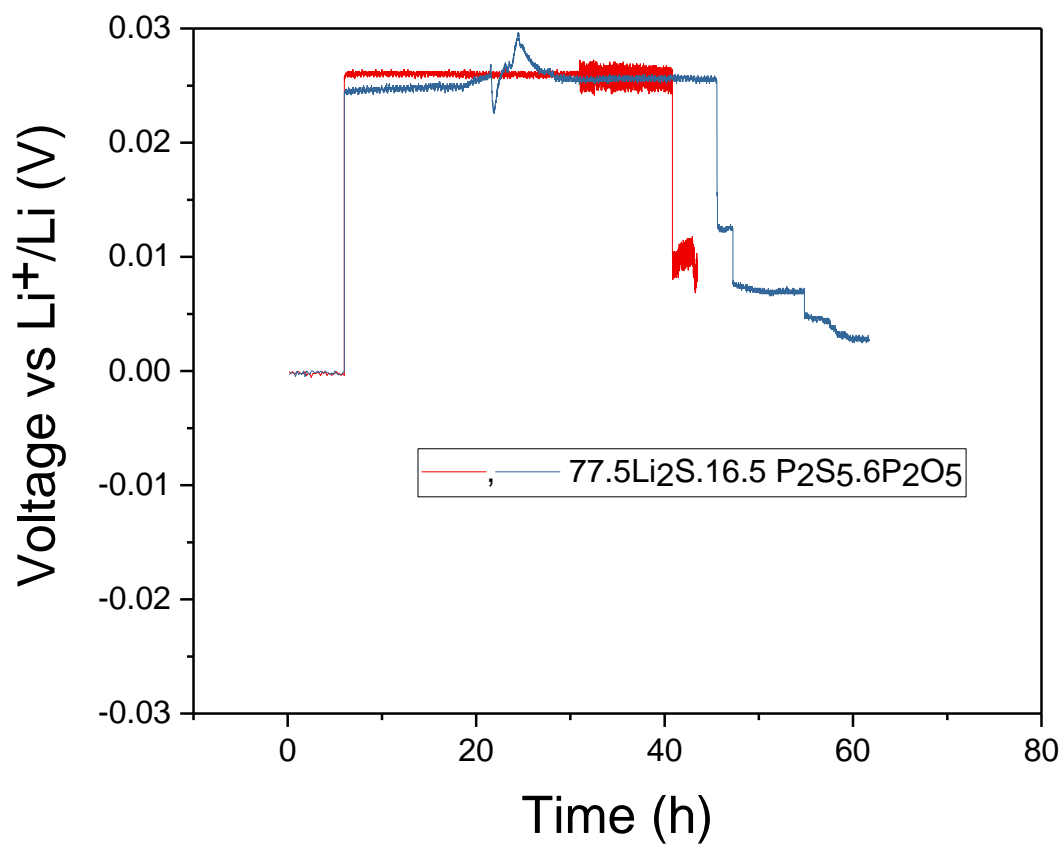


Figure 21. Galvanostatic plating of lithium in a metal cell using the $77.5\text{Li}_2\text{S} \cdot (22.5 - x) \cdot \text{P}_2\text{S}_5 \cdot x\text{P}_2\text{O}_5$ (mol %) SSE with 6 mol% P_2O_5 substitution.

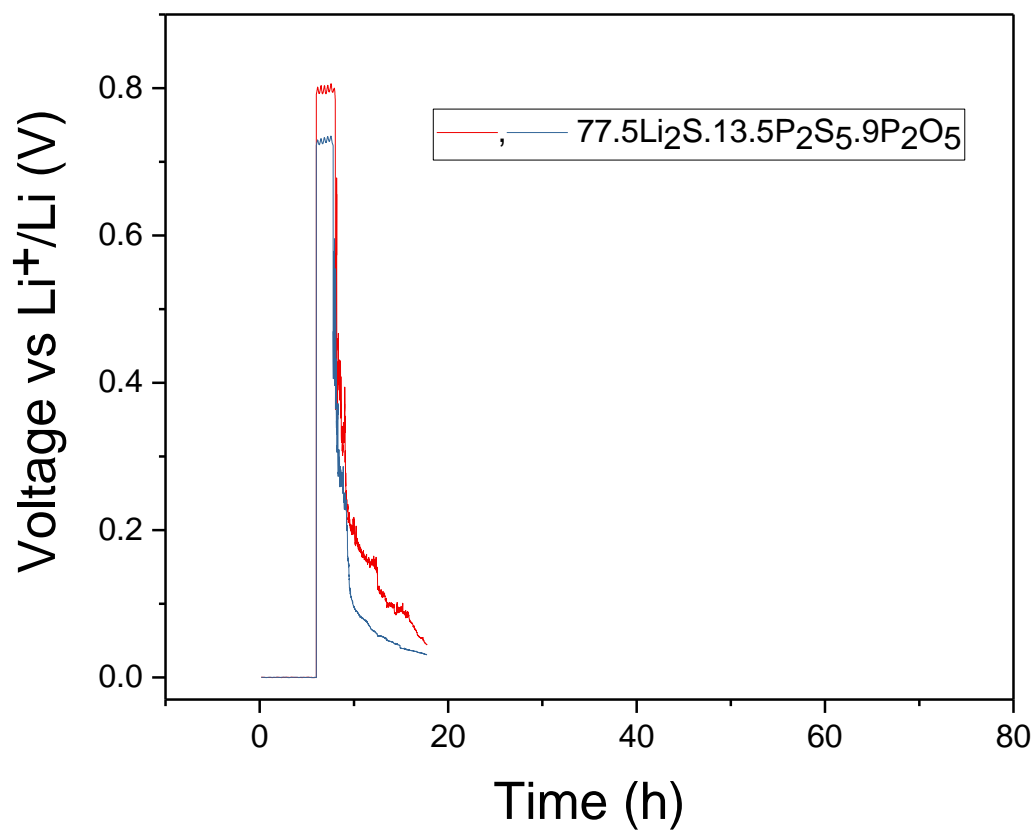


Figure 22. Galvanostatic plating of lithium in a metal cell using the $77.5\text{Li}_2\text{S}.(22.5-x).\text{P}_2\text{S}_5.x\text{P}_2\text{O}_5$ (mol %) SSE with 9 mol% P_2O_5 substitution.

4. Conclusions

The $77.5\text{Li}_2\text{S}.22.5\text{P}_2\text{S}_5$ glassy SSE and $77.5\text{Li}_2\text{S}.(22.5-x)\text{P}_2\text{S}_5.x\text{P}_2\text{O}_5$ (mol %) glassy electrolyte systems with varying composition of P_2O_5 were prepared by the mechanical milling method. Adding a small amount of P_2O_5 to $77.5\text{Li}_2\text{S}.22.5\text{P}_2\text{S}_5$ glassy electrolyte led to increase in conductivity, and density of the pellet. 0.25 mol % P_2O_5 substitution reveals the highest conductivity of $6.5 \times 10^{-4} \text{ Scm}^{-1}$ and the longest cycling performance of 54 cycles. This would be a result of the enhanced conductivity, and increased density of the pellet. Moreover, $\text{Li}/77.5\text{Li}_2\text{S}.(22.5-x).\text{P}_2\text{S}_5.x\text{P}_2\text{O}_5$ (mol %)/Li metal cells with P_2O_5 substitution of $x < 9$ displayed longer cycling performance without short circuiting compared to cells with pure $77.5\text{Li}_2\text{S}.22.5\text{P}_2\text{S}_5$ (mol %) SSE. The increase of the cycling performances could be from enriched conductivity and P_2O_5 substitution. Furthermore, the $77.5\text{Li}_2\text{S}.(22.5-x)\text{P}_2\text{S}_5 .x\text{P}_2\text{O}_5$ (mol %) glassy electrolyte with 0.5 mol% P_2O_5 displayed the highest short circuit capacity. This could be from enhanced conductivity, and increased density of the pellet. Hence, in the case of this study, the conductivity, density and a small amount of P_2O_5 addition to the $77.5\text{Li}_2\text{S}.22.5\text{P}_2\text{S}_5$ electrolyte could be the main concepts of diminished uncontrolled dendritic and moss lithium growth.

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