

## VM509 Proposal:

### Solid Electrolyte Structural Modification for Battery Performance: Comb-like Polymer Electrolyte and Li<sub>9.6</sub>P<sub>3</sub>S<sub>12</sub> (LPS)

#### 1 Background

Rechargeable batteries have been developed to a great extent since they were first studied and developed. However, the organic liquid electrolytes commonly used for commercial applications are toxic and flammable and there are increasing occurrences of rechargeable batteries in cell phones or electric vehicles catching fire or exploding, causing great loss to the society. Recent developments of solid-state batteries provide the solution to the potential danger that the application of liquid electrolytes might cause because materials generally used for solid-state electrolytes are not organic thus not flammable. And the mechanical properties of the solid electrolyte can potentially prevent the dendrite formation within lithium liquid-electrolyte batteries and thus prevent the problem of short circuit [9].

For solid-state batteries to achieve the desirable energy density, there are still many difficulties and challenges. Basically, the challenges are in two fields. The first is the choice of electrolyte materials, which includes the consideration of the electrochemical stability voltage window of the solid electrolytes [10]. The interfacial stabilities between electrolyte and anode or electrolyte and cathode are both important (Figure 1). The solid electrolyte should maintain structurally good contact with the cathode material while being passivating against the side reactions with the cathode materials as well as its own decomposition reactions under high voltage conditions.

Apart from the thermodynamic aspect of the chemical or electrochemical reaction mechanism between the electrolyte-electrode-carbon interfaces, the kinetics of the ion transport across the solid-state electrolyte is difficult to investigate.

#### 2 Objective

The objective of this proposal is to investigate a possible solution to the improvement of the solid-state battery performance. By creating the mixture integrated with both inorganic ceramic electrolyte (LPS) and a kind of solid

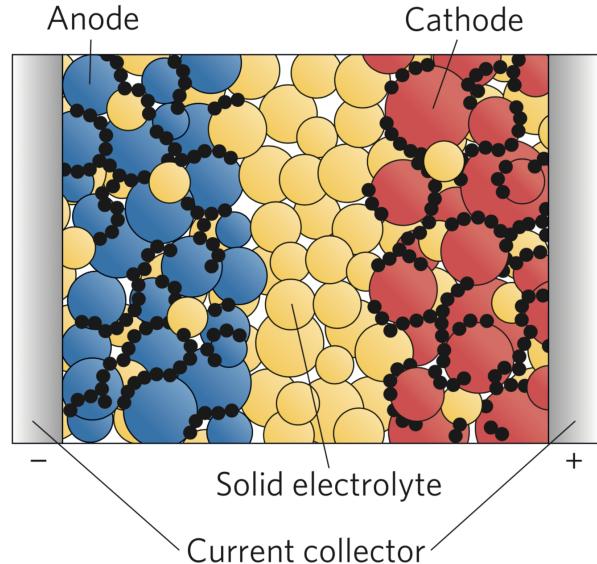


Figure 1: Solid-state battery single cell. [9]

polymer electrolyte with a special comb-like structure, the new composite material is expected to inherit some of the material merits of these different kinds of solid electrolyte and hopefully compensate the less favoured properties of each other.

For the LPS inorganic ceramic solid electrolyte, it has good interphase stability compared to LGPS with a columbic efficiency of 90%, which means only 10% of the solid electrolyte is consumed during the first chargedischarge cycle for the generation of the interface products [5][7][8]. Apart from that, LPS also has sufficient ionic conductivity within the temperature range of 0°C to 100°C [8]. Despite it does not have high ion-conducting ability as LPGS, the tradeoff between interfacial stability and ionic conductivity seems to favour LPS. However, we can see from Figure 2, the electrochemical stability window of LPS is comparably low (2.1V ~ 2.5V) [7], which we seek to compensate by the integration between the ceramic solid electrolyte and the polymer one.

For the solid polymer electrolyte with the comb-like structure, it has the general material properties of flexibility and elasticity, which could help maintain a good contact between the solid electrolyte and the solid cathode during lithium-ion deposition and intercalation process. From the manufacturing perspect, solid polymer electrolyte can enable the bipolar stacking, which can consequently improve the energy density of the batteries [12]. Specifically, the polymer electrolyte we will use showed good thermal stabiltiy, considerable ionic conductivity at ambient temperature, a wide electrochemical

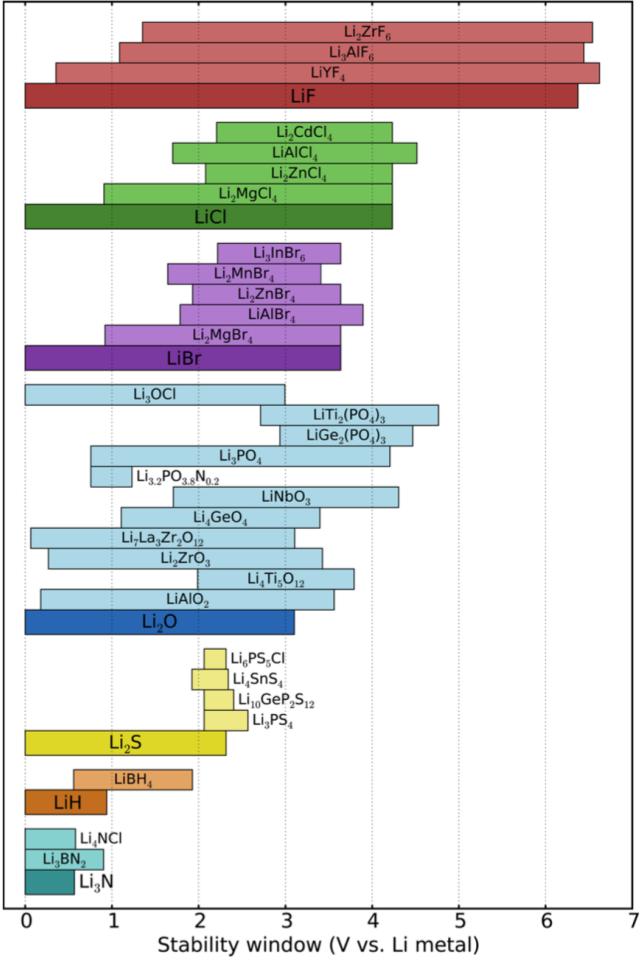


Figure 2: Electrochemical stability windows of selected materials [7].

window ( $0 \sim 5.05\text{V}$ ) as well as good compatibility with lithium metal anode [12].

### 3 Previous Related Research

#### 3.1 3D garnet nanofiber networks for lithium batteries [3]

The work describes a lithium-ion-conducting membrane (Figure 3). The membrane is composed of ceramic garnet nanofibers and ion-conducting polymers. The ceramic garnet nanofibers can provide reinforcement and improvement of the mechanical properties of the composite material [3]. The polymers within the composite can provide shape versatility as well as flexibility to the electrode. The composite material is proved to have high electrochemical stability to high voltage as well as good mechanical stability that can prevent the generation of lithium dendrites [3].

The garnet nanofiber for the composite material is prepared by a method called electrospinning of

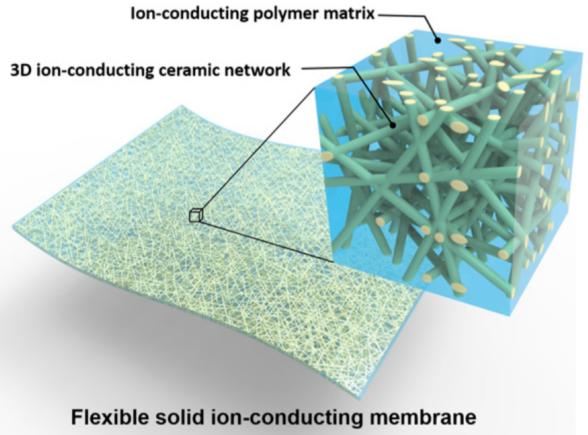


Figure 3: The 3D garnet nanofiber networks schematics [3].

polyvinylpyrrolidone (PVP) polymer mixed with relevant garnet LLZO salts (Figure 4). The fibers were then annealed at high temperature in air for 2 hours [3]. The polymer is PEO-LiTFSI, which was then infiltrated between the 3D garnet fiber networks at about  $60^\circ\text{C}$  [3].

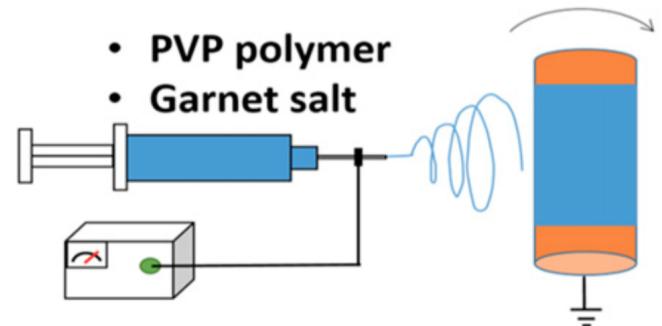


Figure 4: Schematics of preparation of the garnet fiber by electrospinning [3]

The conclusion of this work is that the garnet nanofiber provide lithium-ion transfer pathways as well as structural reinforcement [3]. The final composite membrane showed an ionic conductivity of  $2.5 \times 10^{-4} \text{ S/cm}$  at room temperature [3]. The work shows a possibility of using method of composite material design to reinforce the mechanical strucuture as well as maintaining the electrochemical performance of the solid electrolyte for lithium batteries.

#### 3.2 Ion-conducting polymer electrolyte with comb-like structure [12]

A series of solid polymer electrolytes (SPEs) with comb-like structures were prepared by UV curing and the ionic

conductivity of the different types of SPE was investigated. The comb-like shape of the polymers and the synthesis schematics of the polymers is shown in Figure 5. From the schematics, we can see that the lithium

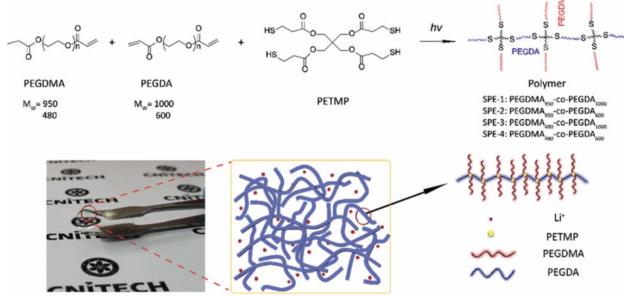


Figure 5: Synthesis of the copolymers [12].

ions can travel through the vacancies between the intertwined branches of the cured polymers. After investigating the interface stability with the lithium metal anode, the comb-like polymers showed good capacity retention of around 75% even after 200 hours (Figure 6). This result means that polymer electrolyte can effectively prevent lithium dendrites and show good interface stability for lithium metal anode.

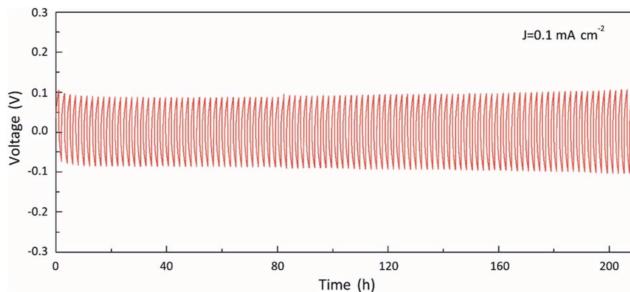


Figure 6: Li/SPE/Li symmetrical cell at 60°C at current density of  $0.1 \text{ mA cm}^{-2}$ .

Comparing the electrochemical stability window of the four SPE materials with different ratios between PEGDMA and PEGDA, we can see that SPE-1: PEGDMA(950)-co-PEGDA(1000) showed a good electrochemical stability until around 5.05 V (Figure 7).

For the manufacturing method of the comb-like polymer, a UV lamp was used to cure the precursor [12]. The solution containing PEGDA, PEGDMA, LiTFSI and a photoinitiator was in liquid before the curing and then polymerized into a solid state [12]. The resulting polymer electrolyte membrane was about 150  $\mu\text{m}$  and was transparent [12]. The preparation process of this kind of polymer was rather simple and straight-forward.

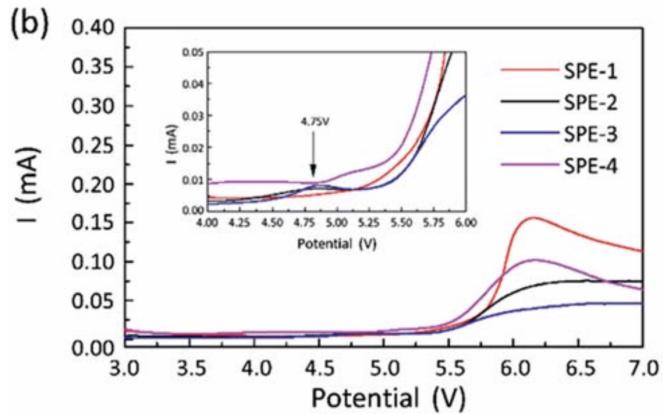


Figure 7: Electrochemical Stability Window for SPE [12].

In a more recent research of this team, a new kind of polymer electrolyte was synthesized by UV-polymerization method and exhibited a capacity retention of about 80% [13] after 50 cycles. The polymer synthesized is of cross-linked structure (Figure 8). However, the incapability of good capacity retention was explained to be the failure of remaining good contact between the solid polymer electrolyte and the cathode interface [13].

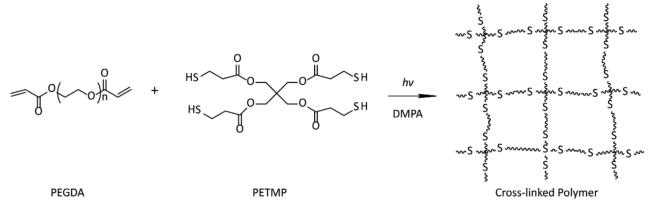


Figure 8: Cross-linked polymer synthesis route [13].

The comparably good capacity retention capability of the comb-like polymer instead of the cross-linked polymer might be due to the polymer strucutre. Since there were more available versatile branches in the comb-like polymers, these branches might be able to keep better contact with the cathode material. Instead, for the cross-linked polymers, since the branches are already "connected" with each other, they primarily contribute to the structural mechanical properties of the mateiral itself instead of structural "interaction" with the cathode.

### 3.3 Interface Stability of LPS [8]

The electrochemical properties of the LGPS family were investigated and  $\text{Li}_{9.6}\text{P}_3\text{S}_{12}$  (LPS) was reported to have a high stability [8]. From the CV curve (Figure 9), we can see that the least loss of capacity of LPS compared to other materials in the LPGS family.

Particularly for the manufacturing method, LPS was

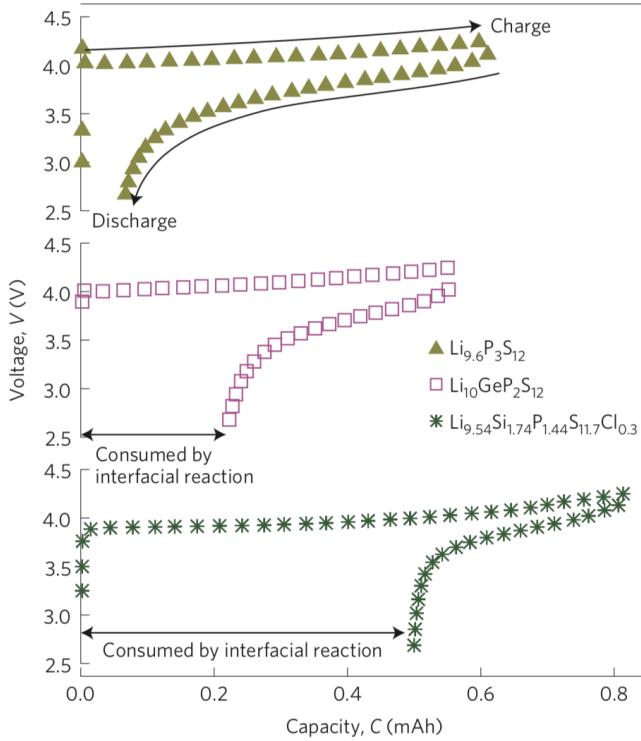


Figure 9: CV Curve of the LGPS Family

prepared by a ball milling process of  $Li_2S$  and  $P_2S_5$  and phosphorus [8]. The procedures were conducted within an argon glove box. The milled products were then pressed and put into a furnace at high temperature for curing.

## 4 Methods

### 4.1 Material synthesis

For the comb-like polymer, the synthesis method is UV-polymerization [12]. For the LPS, the synthesis method is ball milling of start products and then furnace curing at high temperature [8]. Due to the different conditions of these two processes. We will first synthesize the LPS by ball milling and furnace curing at high temperature. After we get the LPS, we will then again use ball milling method so that LPS is milled into small particles. Adding these LPS small particles into the solution start products for the comb-like polymers, we use UV-polymerization procedure to synthesize the polymer with LPS particles distributed evenly inside.

Also, we should prepare LPS and the comb-like polymers separately for comparison purpose.

### 4.2 Synthesis product validation

After the synthesis of the material, we should validate the product. By performing X-ray diffraction on the specimen, we should see corresponding peaks of both LPS and the comb-like polymers. Also, we should check the FT-IR spectra of the specimen to see the corresponding patterns of the comb-like polymers. Microphotograph should also help with the validation of the distribution of LPS particles within the polymer matrix.

### 4.3 Compatibility with Li Anode

To see the compatibility with Li metal anode, we perform the lithium plating/stripping cycles. We can investigate the galvanostatic cycling profile of the specimen at different current density  $J$ .

Since separately, both materials exhibited good interfacial stability versus lithium metal anode [8] [12], we expect good performance of the synthesized specimen as well.

### 4.4 Ionic conductivity

We should also measure the ionic conductivity of the specimen. Under an argon atmosphere, we can carry out the a.c. impedance method [8] at different temperature starting from the room temperature.

For the comb-like polymers, the previous research suggested that the ionic conductivity is contributed by the length of and the space between the side chains of the comb-like polymer [12]. Therefore, the existence of the LPS particles might help with the ionic transfer between the main chains of the polymers if the LPS particles are surrounded and intertwined by several main chains of the polymers, which would improve the ionic conductivity further.

### 4.5 Capacity retention capability

Another important electrochemical property of the specimen, the capacity retention capability, is examined by the CV curve of the Li/electrolyte/LiClO<sub>2</sub>. In the previous research, how the comb-like polymer performs during the first charge/discharge cycle was not clearly stated [12]. However, while good capacity retention of LPS was shown, around 10% of the capacity is still lost due to the interfacial reactions during the first cycle [8]. Inserting LPS particles into the tangled structure of the comb-like polymer might create some restrain in the kinetics of the interfacial reaction between the LPS and the cathode, which can eliminate some of the capacity loss. Also, we should examine the cycling characteristics of the specimen as well.

## 4.6 Electrochemical stability window

Note that LPS has a rather narrow electrochemical stability window of  $2.1 \sim 2.5V$  [7] while the polymer has a wide window up to  $5.05V$  [8]. By analyze the LSV curve for the specimen, we might find the anodic peak suggesting the stability window value of the specimen. The scanning range should be between  $0V$  and  $5.05V$  at least.

## 4.7 Charge/Discharge product

This is particularly important due to the different stability window range of the LPS and the comb-like polymer. Since LPS is not stable above  $2.5V$  itself, there should be side products generated due to the existence of LPS within the comb-like polymer. We should also see what kind of side products are generated in order to determine the effectiveness of the synthesized material.

## 4.8 Other Aspects

Based on the preliminary results of experiment, we might also be interested in the influences of the thickness of synthesized electrolytes or the size ratios between the LPS particles and the electrolyte thickness on battery performance. The mechanical or structural sizing, positioning might be influencing the kinetic aspects of the battery reaction.

## 5 Conclusion

This proposal seeks to investigate the electrochemical properties of a prepared material of solid polymer electrolyte integrated with inorganic ceramic solid electrolyte LPS. After the synthesis of the material, standard investigation methods of solid electrolyte properties will be carried out.

The proposed idea of synthesizing these two particular materials is just an attempt to structurally modify solid electrolyte so that the favourable material properties of different solid electrolytes might be integrated for better battery performance. However, with more detailed research, better synthesis methods, composition of materials or pre-treatment methods of the synthesized materials should be purposed based on the analysis of the experimental results and conclusions or proposed theories on reaction mechanisms.

## References

- [1] B. Chen, Q. Xu, Z. Huang, Y. Zhao, S. Chen, X. Xu. One-pot preparation of new copolymer electrolytes with tunable network structure for all-solid-state lithium battery. *J. Power Sources*. 2016, 331, 322-331.
- [2] J. H. Lee, J. Y. Lim, J. T. Park, J. M. Lee, J. H. Kim. Polymethacrylate-comb-copolymer electrolyte for solid-state energy storage devices. *Materials and Design*. 2018, 149, 25-33.
- [3] K. Fu, Y. Gong, J. Dai, A. Gong, X. Han, Y. Yao, C. Wang, Y. Wang, Y. Chen, C. Yan, Y. Li, E. D. Wachsman, L. Hu. Flexible, solid-state, ion-conducting membrane with 3D garnet nanofiber networks for lithium batteries. *PNAS*. 2016, 113(26), 7094-7099.
- [4] P. Verma, P. Maire, P. Novak. A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries. *Electrochimica Acta*. 2010, 55(22), 6332-6341.
- [5] S. Wenzel, S. Randau, T. Leichtweiß, D. A. Weber, J. Sann, W. G. Zeier, J. Janek. Direct Observation of the Interfacial Instability of the Fast Ionic Conductor  $Li_{10}GeP_2S_{12}$  at the Lithium Metal Anode. *Chem. Mater.* 2016, 28, 2400-2407.
- [6] T. P. Heins, N. Harms, L-S. Schramm, U. Schroder. Development of a new electrochemical impedance spectroscopy approach for monitoring the solid electrolyte interphase formation. *Energy Technol.* 2016, 4, 1509-1513.
- [7] W. D. Richards, L. J. Miara, Y. Wang, J. C. Kim, G. Ceder. Interface Stability in Solid-State Batteries. *Chem. Mater.* 2016, 28, 266-273.
- [8] Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba, R. Kanno. High-power all-solid-state batteries using sulfide superionic conductors. *Nature Energy*. 2016, 1, 16030.
- [9] Y.-S. Hu. Batteries: getting solid. *Nature Energy*. 2016, 1, 16042.
- [10] Y. Tian, T. Shi, W. Richards, J. Li, J. C. Kim, S.-H. Bo, G. Ceder. Compatibility issues between electrodes and electrolytes in solid-state batteries. *Energy Environ. Sci.* 2017, 10, 1150.
- [11] Y. Tian, Y. Sun, D. C. Hannah, Y. Xiao, H. Liu, K. W. Chapman, S.-H. Bo, G. Ceder. Reactivity-Guided Interface Design in Na Metal Solid-State Batteries. *Joule*. 2019, 3, 1037-1050.
- [12] Z. Wei, S. Chen, J. Wang, Z. Wang, Z. Zhang, X. Yao, Y. Deng, X. Xu. Superior lithium ion conduction of polymer electrolyte with comb-like structure via solvent-free copolymerization for bipolar all-solid-state lithium battery. *J. Mater. Chem. A*, 2018, 6, 13438-13447.
- [13] Z. Wei, S. Chen, J. Wang, Z. Wang, Z. Zhang, X. Yao, Y. Deng, X. Xu. A large-size, bipolar-stacked and high-safety solid-state lithium battery with integrated electrolyte and cathode. *J. Power Sources*. 2018, 394, 57-66.