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## Effect of a layer-by-layer assembled ultra-thin film on the solid electrolyte and Li interface

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Advanced all-solid-state batteries are considered as the most preferable power source for the next generation devices. Such batteries demand consumption of electrode materials with high energy and power density. One of the excellent solutions is the utilization of Li metal as anode which provides opportunity to fulfill such requirements. Yet, obstacles such as interfacial impedance and reactivity of Li metal with promising solid electrolytes prevent the consumption of the Li anode. Despite its outstanding stability under ambient conditions, high ionic conductivity and facile synthesis methods, NASICON-type  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  also suffers from the above mentioned problems. In this work, these critical issues were resolved by applying an artificial protective interlayer. Herein, the layer-by-layer polymer assembly approach of the ultra-thin interlayer of (PAA/PEO)<sub>30</sub> on either side of solid electrolyte pellets simultaneously is presented. The introduction of the protective layer prevented a formation of mixed conduction interphase and effectively decreased the interfacial impedance. A symmetric cell with Li metal electrodes performed over 600 hours at 0.1 mA cm<sup>-2</sup>. Furthermore, an all-solid-state Li metal battery, assembled with the modified LTP solid electrolyte and  $\text{LiFePO}_4$  cathode, demonstrated an excellent electrochemical performance with an initial discharge capacity of 115 mA h g<sup>-1</sup> and a capacity retention of 93% over 20 cycles with a coulombic efficiency of almost 100%. The LTP with the (PAA/PEO)<sub>30</sub> coating exhibited electrochemical stability up to 5 V.

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## Introduction

Next generation batteries with prolonged cyclability, high energy density, safety and reliability along with a high operating potential are required to meet the performance properties of new devices and applications for further progress in portable electronics, ecological transport, communication devices and many other areas.<sup>1-7</sup> Along with high performance electrode materials, such advances of Li-ion and Li metal batteries mainly depend on the development of new types of solid ion conductors to replace commercial liquid electrolytes.<sup>8-13</sup> Despite the admirable benefits of commercial liquid ion conductors, these electrolytes have been facing dramatic safety problems and an inability to operate above certain potentials and at elevated temperatures causing their decomposition and fire.<sup>14-16</sup> These problems are worsened further due to their potential leakage and reaction with the electrode materials. On top of all these dramatic problems, incompatibility of lithium metal and liquid electrolytes due to uneven deposition of lithium causing

dendrite growth, raises another big issue.<sup>17-20</sup> Thus, new types of solid electrolytes should be developed to address these issues along with possessing high ionic conductivity, chemical and mechanical stability and simple handling. To date, potential candidates that satisfy most of these requirements are polymer and/or inorganic electrolytes. Solid electrolytes based on inorganic materials have gained popularity due to their safe operation, and sufficient ionic conductivity.<sup>18,21</sup> Currently there are several types of solid inorganic electrolytes available, namely argyrodite, garnet, Li-nitride, Li-halide, Li-hydride, perovskite, LISICON and NASICON.<sup>22-31</sup> Among them, the last mentioned ceramic material caught attention because of its stability towards air and moisture under ambient conditions.<sup>32-34</sup> Superior stability and a high ionic conductivity of 10<sup>-4</sup> to 10<sup>-3</sup> S cm<sup>-2</sup> at room temperature enabled the material to be the most suitable candidate for an all-solid-state battery.<sup>21,25,35,36</sup> Particularly, the composition  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  (LTP) demonstrated the most promising results. Within some doping limits, an aluminum dopant ( $\text{Al}^{3+}$ ) allows the accommodation of more lithium in interstitials to compensate for the charge balance; however, a dopant amount above 0.3 led to the formation of an undesired impurity phase of  $\text{AlPO}_4$ .<sup>32,37,38</sup> LTP ceramics can be fabricated through different synthesis routes depending on the requirements regarding the shape and size of particles.<sup>39-48</sup> Despite all these compelling advantages, LTP cannot tolerate

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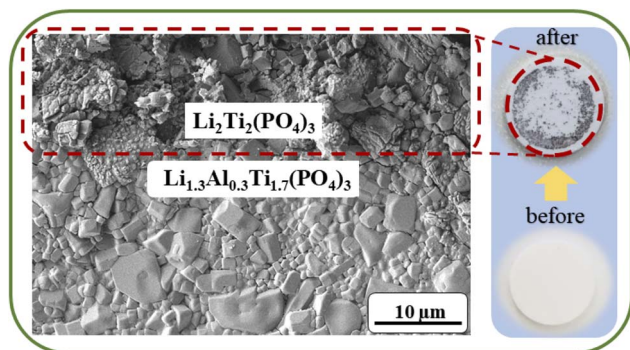


Fig. 1 SEM image and visual illustration of the MCI.

direct contact with lithium metal.<sup>49–60</sup> There is an abrupt reduction process happening, where  $Ti^{4+}$  reduces to  $Ti^{3+}$  forming a secondary phase of a mixed conducting interphase (Fig. 1) that hinders lithium-ion conduction but facilitates the electron conduction.<sup>61–78</sup>

This issue can be resolved by applying a protective layer of lithium ion conducting substances. The most recent studies addressing this problem include deposition of artificial layers based on inorganic substances such as oxides, lithium salts, nanocomposites and other types of lithium conducting solid materials.<sup>79</sup> Liu *et al.* introduced  $Al_2O_3$  and  $Li_3PO_4$  materials as interface stabilizers using atomic layer deposition (ALD), while Bai *et al.* suggested depositing an  $Al_2O_3$  doped ZnO layer on LAMP using a magnetron sputtering tool.<sup>42,60</sup> Cheng *et al.* protected LAMP by depositing boron nitride nanocomposites *via* chemical vapor deposition (CVD).<sup>59</sup> In these studies, LAMP was physically protected from direct contact with Li metal. Nonetheless, this kind of material requires certain deposition techniques as well as inert atmosphere conditions and these processes are time consuming and not cost effective. Other perspective approaches involve polymer electrolyte films on LAMP or combining polymers with ceramics creating composite electrolytes. Yi *et al.* investigated a hybrid electrolyte of

poly(vinylidene fluoride) (PVDF), poly(ethylene oxide) (PEO) and LAMP.<sup>56</sup> Shi *et al.* fabricated a LAMP and PVDF composite electrolyte.<sup>52</sup> Yet, all these systems achieved improved electrochemical performance consuming a large amount of liquid electrolytes. There are also some studies that report coating the surface of LAMP with lithium ion conducting polymers, mostly PEO, which has insufficient ionic conductivity at room temperature. The thicknesses of these interlayers were from 10 to 100 micron and usually a thick film negatively affects charge transfer capability, creating additional barriers for lithium ion migration. Overall, the up-to-date status of various interlayers LAMP and LAGP with the results of Li stripping and plating performance duration is depicted in Fig. 2.<sup>79</sup>

It can clearly be seen that the interlayers designed from inorganic substances only operate at very low current densities, while the polymers showed very stable performance at higher current densities. It can be concluded from Fig. 2 that further developments on the solid electrolyte and Li metal interface are preferable to be carried out by utilizing artificial interlayers made of lithium ion conducting polymer materials.<sup>79</sup>

Therefore, in this report, we propose a 65–75 nm artificial interlayer of  $(PAA/PEO)_{30}$  through the layer-by-layer (lbl) assembly technique between LAMP and Li metal to prevent mixed conduction interphase (MCI) formation and to decrease the interface impedance as well. The lbl polymer coating method enabled achieving an ultra-thin texture with precise thickness control by manipulating the insertion numbers. A symmetric cell with Li non-blocking electrodes operated over 600 hours with a very low overpotential response as well as electrochemical stability up to 5 V. Furthermore, a simultaneous polymer coating on both sides of LAMP also improved the interface between the cathode and solid electrolyte resulting in significantly enhanced performance of an all-solid-state Li battery (ASSLB). The ASSLB with a commercial olivine  $LiFePO_4$  cathode displayed a highly reversible electrochemical behavior with an initial discharge capacity of  $115 \text{ mA h g}^{-1}$  and coulombic efficiency of about 100%.

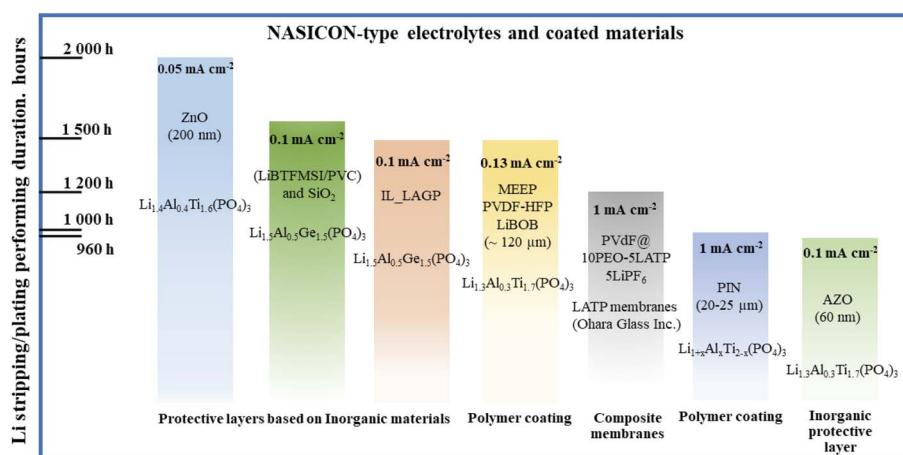


Fig. 2 Status of artificial layers on NASICON-type LAMP and LAGP solid electrolytes.<sup>79</sup>



## Experimental section

### Preparation of LATP solid electrolyte

$\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  ceramic material was fabricated *via* the molten flux method. The procedure was slightly modified where a flux ( $\text{CO}(\text{NH}_2)_2$ ) was first dissolved in deionized water (DIW). Then, water soluble chemicals such as  $\text{LiNO}_3$  (98%) and  $\text{NH}_4\text{H}_2\text{PO}_4$  (98%) were added in a stoichiometric ratio. The remaining insoluble components,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ , were introduced into the solution after 10 minutes of mixing. The mixture was stirred for 4 hours and dried at  $120^\circ\text{C}$  for 12 hours. The solid residue then was crushed in an agate mortar and heated at  $500^\circ\text{C}$  for 8 hours. The resulting powder was mixed in a ball-mill at 450 rpm for 4 hours in acetone (Pulverisette, FRITSCH,  $\text{ZrO}_2$  ball, 6 mm in diameter). The ball-milled powder was pelletized with an 8 mm die and calcined at  $900^\circ\text{C}$  for 6 hours in air in a muffle furnace (ELF 11/6B, Carbolite Gero Ltd.). To mitigate the evaporation/loss of lithium during high temperature calcination, an extra 5% lithium salt was added while preparing the solution.

### Preparation of aqueous polymer solutions

Branched poly(ethylenimine) (PEI; MW = 750 000, 50 wt% in  $\text{H}_2\text{O}$ ), poly(ethylene oxide) (PEO; MW = 100 000), and poly(acrylic acid) (PAA; MW = 450 000) were used as received and dissolved in deionized water with a concentration of  $0.2\text{ g dm}^{-3}$ . The pH values of polymer solutions were 6 and 2.6 for PEI and PAA, PEO, respectively. Adjustments of pH were carried out by using diluted HCl and NaOH solutions.

### Layer-by-layer assembly of polymers

The lbl process was carried out using a dip coating robot DR-3 (Riegler & Kirstein GmbH) by programming insertion processes. Prior to the coating procedure, pellets of LATP were treated with 5% of  $\text{H}_2\text{O}_2$  to create charge on the surface and then rinsed in DI water. Then, the pelletized samples were immersed in a positively charged solution of PEI for 5 minutes

to form a precursor layer. Next, the pellets were dipped in PAA and PEO solutions with a pH of 2.6 for 5 minutes and washed with 0.01 M Trizma® buffer solution with the same acidity (Fig. 3). Alternate insertion of pellets into these polymer solutions was assigned as  $(\text{PAA}/\text{PEO})_n$  and the process was carried out for 30 times with the final composition of  $(\text{PAA}/\text{PEO})_{30}$ .

### Characterization techniques

The structure and morphology of the synthesized and  $(\text{PAA}/\text{PEO})_{30}$  coated LATP were investigated by using an X-ray diffractometer (XRD, Rigaku SmartLab XRD system) equipped with a Cu X-ray tube, a D-Tex detector and a scanning electron microscope (SEM, Crossbeam 540, FeSEM Auriga). The thickness of the layer was measured using an ellipsometer (SENre-search 4.0, Sentech) and the polymers were coated on one side of a polished Si wafer.

### Electrochemical characterization techniques

Prior to electrochemical measurements, the  $\text{LiPF}_6$  commercial liquid electrolyte ( $0.5\ \mu\text{l}$ ) was dropped onto a thin polymer layer as a Li-ion source for ion conduction. Electrochemical impedance spectroscopy (EIS) using lithium (non-blocking) electrodes in a frequency range of 1 Hz to 1 MHz (potentiostat/galvanostat, Metrohm AutoLab 204) was used to measure the ionic conductivity. A continuous stripping and plating test of Li-ions in symmetric cells with lithium metal electrodes was carried out by using a potentiostat/galvanostat (Bio-Logic SAS VMP3) at  $0.1\text{ mA cm}^{-2}$  current density. Linear sweep voltammetry (LSV) was conducted using a potentiostat-galvanostat (VMP3, Bio-Logic Inc.) between  $-0.5$  to  $5.5\text{ V}$  using blocking (stainless steel, SS) and non-blocking (lithium metal) electrodes. A full all-solid-state Li metal battery was assembled and investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge tests.  $\text{LiFePO}_4$  (LFP) olivine-type commercial material was used as the cathode. All cells were prepared using polished pristine and  $(\text{PAA}/\text{PEO})_{30}$  coated LATP pellets.

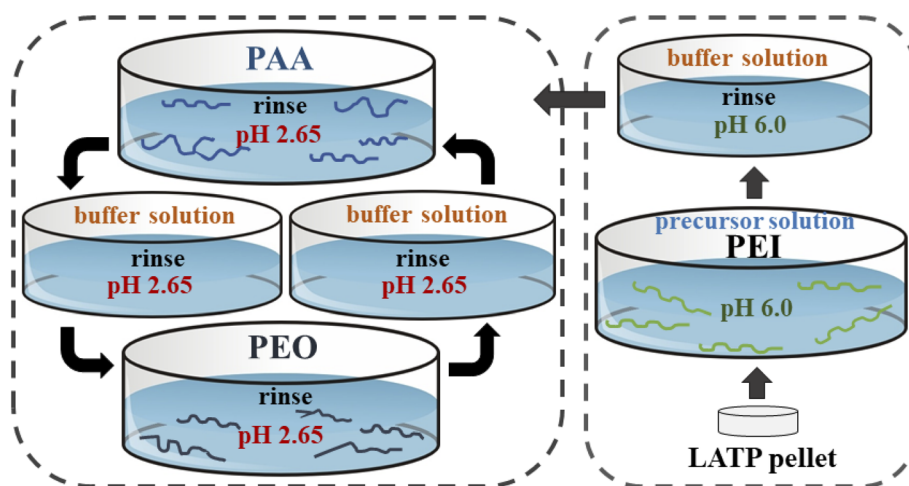


Fig. 3 Visual illustration of the lbl assembly process on LATP pellets.



## Results and discussion

The elementary molten flux preparation method demonstrated that single phase L ATP can be fabricated without any impurities. Introduction of the flux, additional lithium inclusion and optimal calcination temperature not exceeding 900 °C facilitated production of pure L ATP ceramic which was confirmed *via* an X-ray diffractometer. The synthesized powder had a rhombohedral structure with a  $R\bar{3}c$  space group. This again confirms the importance of the synthesis method and its parameters we discussed in the earlier work.<sup>80</sup> Furthermore, for the advancement of the solid electrolyte/electrode interface and to protect L ATP from reduction by Li metal, the ceramic pellets were successfully coated with ultra-thin (PAA/PEO) multilayers by the lbl technique. This was achieved by creating a negatively charged surface by treating the pellets with  $H_2O_2$ , and this facilitated the adhesion of positively charged PEI on L ATP as a precursor layer. It was followed by deposition of a negatively charged PAA layer to form a strong electrostatically bonded initial bilayer with the composition of (PEI/PAA) (Fig. 4a). Generally, the thin layer consists of two main polymers of PAA and PEO, and the samples were dip coated consequently for 5 minutes.

The lbl assembly was carried out using polymer solutions with pH 2.65. Following each polymer deposition step, the L ATP pellets were washed with Trizma® buffer solution (0.01 M) with the same pH for 2 minutes. Completion of (PAA/PEO) insertions was considered to be one bilayer (bl) and the dipping procedure was repeated 30 times (30 bls). Initially, the link between PAA and PEO is based on intermolecular hydrogen bonding as illustrated in Fig. 4a. The structural stability of the ceramic after continuous immersion in mild acidic solutions was also validated by XRD after the lbl coating technique. Fig. 4b depicts the XRD patterns of the samples and shows that the structure of L ATP did not change upon the treatments, proving chemical durability of the ceramic material. Afterwards, heating at 130 °C enabled transition of the intermolecular forces such as electrostatic and hydrogen bonds to covalent bonds, precisely, and PEI and PAA links through amine and carboxylic groups while PAA and PEO, through carboxylic and terminal groups as previously reported.<sup>81–83</sup> Despite the thinness, the polymer

coating provided high durability and cohesion due to the covalent bonding. The mechanical stability and ionic conductivity of the  $(PEO/PAA)_n$  thin film as solid polymer thin film electrolyte was examined by Hamed *et al.*<sup>83</sup> It was found that a cross-linked texture had mostly an amorphous phase, which greatly favored high lithium ion conduction achieving  $2.3 \pm 0.8 \times 10^{-4} \text{ S cm}^{-1}$ .<sup>83</sup>

The SEM image of pristine L ATP revealed that particles have a cubic shape with a grain size of up to  $\sim 9 \mu\text{m}$  (Fig. 5a). A previous report clearly showed that well-defined cubic shape L ATP particles with larger crystals are more favorable due to their high compactness. Onwards, the lbl assembled polymer on L ATP image from the top view is depicted in Fig. 5b.<sup>80</sup> The lbl coating technique enabled obtaining an ultra-thin and uniform texture that covered the whole surface of a pellet without any breach (Fig. 5b). The growth of the nanofilm was also followed by ellipsometry when the cleaned and polished Si wafer was utilized as a substrate. The thickness of the first PEI layer was estimated to be  $1.7 \pm 0.2 \text{ nm}$ , while the (PAA/PEO) bilayer had a thickness of  $2.5 \pm 0.5 \text{ nm}$  which increased linearly with the bilayer numbers. The final thickness of the polymer interlayer was estimated to be between 65 and 75 nm, which is also well matched with a value from SEM cross-sectional image (Fig. 5c).

Prior to the electrochemical performance studies, the L ATP pellets were visually tested for the reactivity with the negative electrode of the Li metal disc by making them come into contact. The results certainly indicated the formation of an MCI on top of pristine L ATP. Zhu *et al.* believed that the MCI began to form between the electrolyte and electrode interface during the lithiation process.<sup>84</sup> However, our examination clearly demonstrated that the reaction between L ATP and Li metal proceeds instantly when they came into contact, as both components are highly reactive. Evidently, the experiment confirmed the instant reduction of L ATP while in contact with Li metal (Fig. 6). This reaction creates obstacles to combining this electrolyte with Li metal, which restricts its consumption in Li batteries. Apparently, the pellet with a protective layer demonstrated durability towards Li metal even after 24 hours of physical contact.

In the nick of time, this side reaction can be prevented by an artificial buffer layer of  $(PAA/PEO)_{30}$ . This physical barrier not

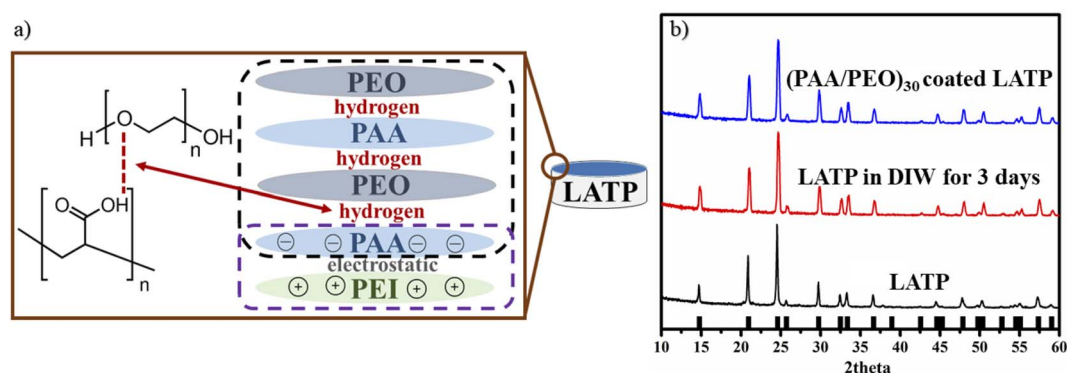


Fig. 4 (a) Film growth mechanism between polymers and (b) the XRD pattern of pristine, deionized water treated and  $(PAA/PEO)_{30}$  coated L ATP.



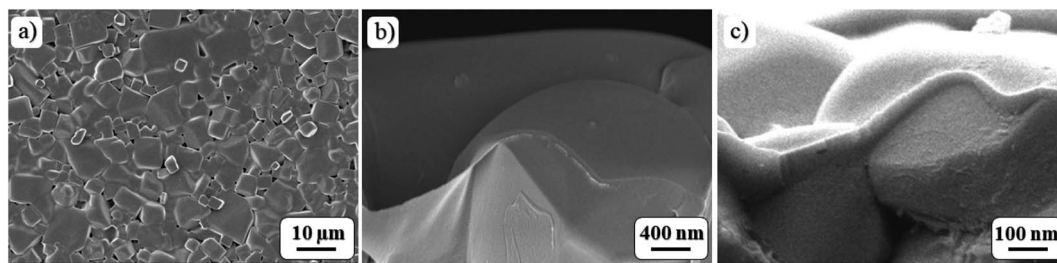


Fig. 5 SEM images, (a) top and (b and c) cross sectional views of (PAA/PEO)<sub>30</sub> coated LATP pellets.

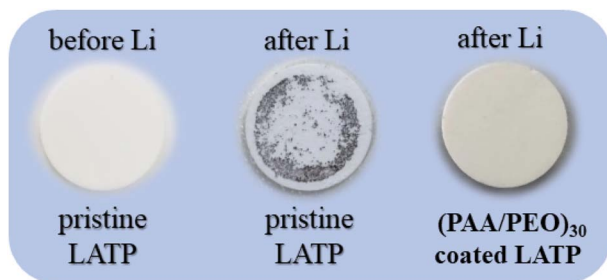


Fig. 6 Visual test for pristine and modified LATP with Li metal.

only hinders the direct contact between LATP and Li metal preventing their reaction, but it also allows high lithium-ion transfer through its matrix. Besides, the protective interlayer was one of the most efficient approaches towards decreasing the interfacial impedance between the solid electrolyte and electrodes. The current work was not an exception, as this very thin interlayer designed from polymer material created soft intermedia for these two materials by providing a continuous path for Li-ion migration. This also positively influences the overall kinetics of charge transfer and the electrochemical reaction.

Further electrochemical studies were conducted with pristine and (PAA/PEO)<sub>30</sub> coated LATP. The ionic conductivity measurements of different cell configurations were conducted in a cell with Li metal non-blocking electrodes and the electrolytes sandwiched between them. The electrochemical impedance spectrum of sandwiched polished pristine LATP with Li electrodes is obviously depicting a large charge transfer

resistance due to the reduction of the ceramic electrolyte and formation of an MCI (Fig. 7a). As an extension of this, a lack of confined contact of surfaces between LATP and Li metal also contributed to high impedance. In contrast, the LATP pellet with a (PAA/PEO)<sub>30</sub> film showed a lower interfacial impedance with a charge transfer resistance two times smaller than that for the pristine LATP sample, resulting from a smooth transfer of Li-ions through the electrolyte to the electrode (Fig. 7a) by the provided profound contact with the interlayer. The ionic conductivity of Li/LATP/Li and Li/(PAA/PEO)<sub>30</sub>/LATP/(PAA/PEO)<sub>30</sub>/Li, systems were  $1.8 \times 10^{-5} \text{ S cm}^{-1}$  and  $1.6 \times 10^{-4} \text{ S cm}^{-1}$ , respectively, demonstrating that the use of the interlayer allows a conductivity of one order higher to be achieved. Along with protection from the side reaction, this layer provided definite connection without limiting Li-ion transfer<sup>85,86</sup>. In both cases, the Warburg impedance was not observed in a lower frequency region due to the non-blocking electrode's nature. An identical cell configuration was also tested for thw stripping and plating test at  $0.1 \text{ mA cm}^{-2}$  (Fig. 7b). As the results show, the Li/LATP/Li system operates for only around 40 hours with a very large overpotential response. Abrupt decline in resistivity that could be seen from the potential response data is related to the interface degradation leading to a large electrolyte/electrode interface impedance between the electrolyte and electrode.

The introduction of an artificial interlayer enabled the formation of a lithium-deficient layer for interdiffusion that significantly improved the interfaces as (PAA/PEO)<sub>30</sub> was coated on both sides of LATP simultaneously. The Li/(PAA/PEO)<sub>30</sub>/

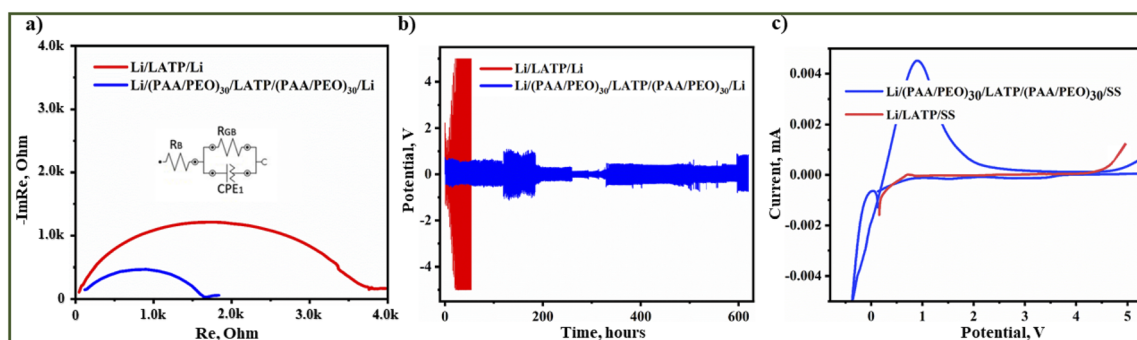


Fig. 7 Results of electrochemical performance of pristine and (PAA/PEO)<sub>30</sub> coated LATP pellets; (a) EIS spectra; (b) stripping and plating behavior; (c) LSV profile.



LATP/(PAA/PEO)<sub>30</sub>/Li cell exhibited 600 hours of cyclability with the lowest overpotential response (−1 to 1 V) (Fig. 7b). Due to the formation of intrinsic resistivity, the cell showed a slightly higher potential response for about 50 hours, and further stabilized with even lower response. Still, the cell depicted some resistivity after 600 hours due to intrinsic microstructural fractures which could be explained by chemomechanical stress. The cells with configurations such as SS/LATP/Li and SS/(PAA/PEO)<sub>30</sub>/LATP/(PAA/PEO)<sub>30</sub>/Li were assembled for the electrochemical stability measurements by linear sweep voltammetry (LSV) in a potential range of −1 to 5.5 V with a scanning rate of 0.1 mV s<sup>−1</sup>. According to the obtained voltammograms lithium intercalation and deintercalation are significantly well defined in LATP with a polymer coating while peaks related to these reactions are negligible in the pristine sample. In addition, the cell with bare LATP has electrochemical stability up to 4.4 V (Fig. 7c) while the modified LATP with a (PAA/PEO)<sub>30</sub> coating was stable up to 5 V with slow decomposition at a potential exceeding 5 V (Fig. 7c). Furthermore, this promising feature of the advanced polymer coated LATP solid electrolyte was further examined in the all-solid-state Li metal battery (ASSLB) with a commercial olivine structured LiFePO<sub>4</sub> (LFP) cathode. The cathode composite casting was carried out in a non-traditional way by brush painting a cathode slurry with a composition of LFP : AB : PVdF in a ratio of 65 : 20 : 15 (weight) on well-polished pristine and (PAA/PEO)<sub>30</sub> coated LATP. This method of applying the electrode and a high amount of PVdF was

chosen to enhance the cathode adhesion on the surface of the electrolyte pellets. We compared this technique with the traditional doctor-blade method of casting a cathode on the Al current collector but it did not show any electrochemical response due to the lack of proper contact between the electrode and electrolyte. In contrast, our painting technique allowed very reproducible high performance data to be obtained for our polymer coated LATP electrolyte.

Two ASSLB systems, namely, Li/LATP/LFP and Li(PAA/PEO)<sub>30</sub>/LATP/(PAA/PEO)<sub>30</sub>/LFP with the addition of 0.5 μl commercial liquid electrolyte to wet the polymer matrix for lithium ion transport, were assembled in an inert atmosphere glovebox. Prior to cycling, the EIS technique was applied to examine the overall resistivity of the cell. The ASSLB with bare LATP had the highest resistivity due to the known reasons of the reduction side reaction (Fig. 8a). In contrast, the lowest resistivity of the modified electrolyte pellets was because of a thin polymer layer with Li-salt in it. The role of the liquid electrolyte in the performance of solid electrolyte also was tested, and the results revealed that wetting bare LATP does not aid in decreasing the charge transfer resistance as its resistivity was still higher than that of with the polymer film (Fig. 8a). Next, the CV measurements showed the reversible reactions related to the redox process of LFP, but with high polarization due to poor kinetics and the presence of accompanying resistivity mostly within the ceramic electrolyte (Fig. 8b). The CV profile of Li/LATP/LFP demonstrated a weak response to the oxidation

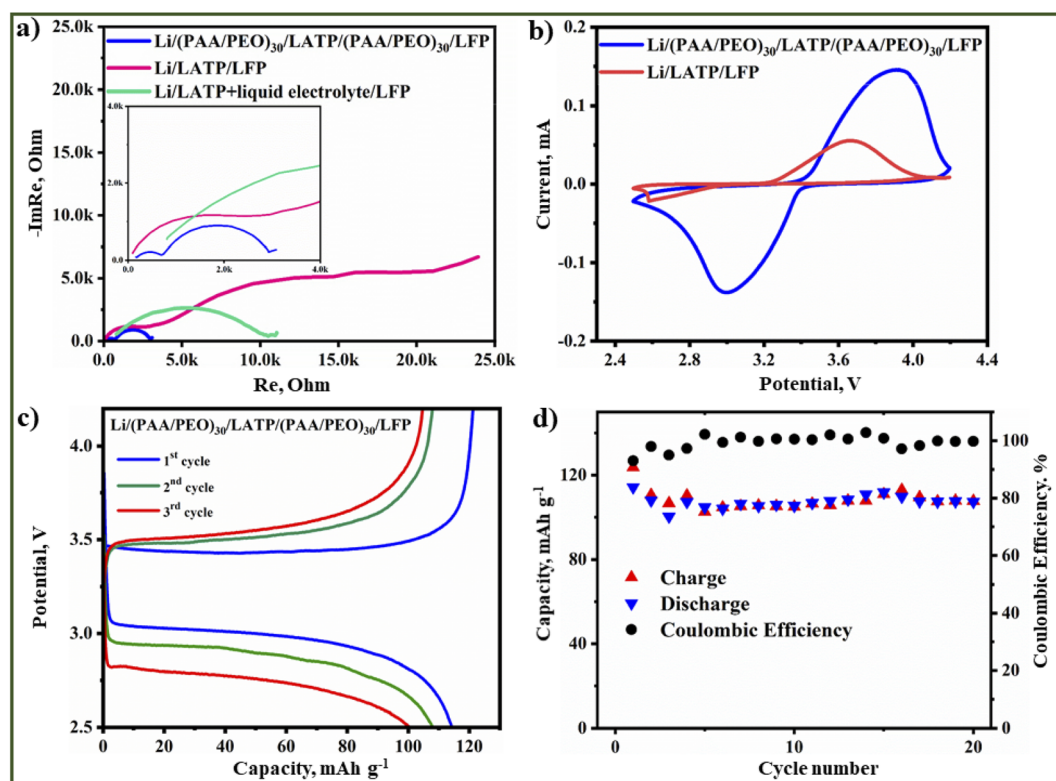


Fig. 8 Results of electrochemical performance of the ASSLB with pristine and (PAA/PEO)<sub>30</sub> coated LATP pellets: (a) EIS spectra; (b) CV and (c) galvanostatic charge and discharge profiles; (d) cyclability and coulombic efficiency.



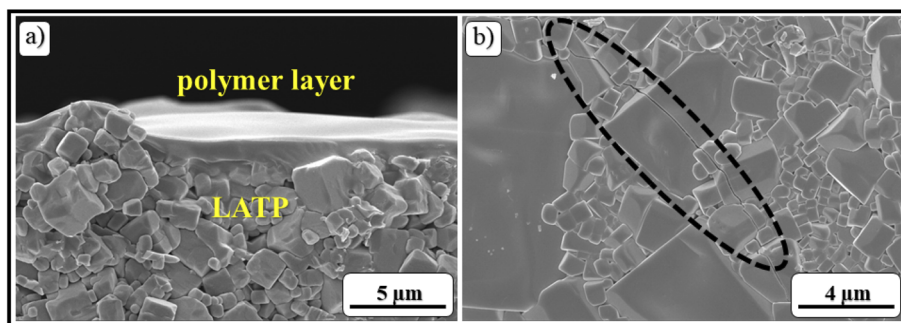


Fig. 9 SEM images of a disassembled ASSLB with a (PAA/PEO)<sub>30</sub> film after 20 cycles; (a) cross-section of LAMP and (PAA/PEO)<sub>30</sub>; (b) fracture of LAMP grains.

process of the cathode material, and the reduction process was not equivalent, which is due to the lithium ion blocking in the interface caused by a side reaction of Li metal with LAMP. In the case of LAMP with a polymer film, it exhibited very intense reversible peaks related to the redox of LFP. An ASSLB with polymer texture performed 20 cycles at 0.1C with an initial discharge capacity of 115 mA h g<sup>-1</sup> and a coulombic efficiency of 93% (Fig. 8c and d). In the subsequent cycles, the coulombic efficiency increased to 100% with stable discharge capacities from 107 to 102 mA h g<sup>-1</sup>.

The morphology of LAMP and the polymer film after 20 charge–discharge cycles was observed by using the SEM images (Fig. 9). The cross-sectional image in Fig. 9a clearly shows that the film has not changed maintaining its uniformity. However, other observations revealed that the ceramic grains have large fractures of different sizes from 10 to 200 μm. The limited operation of the ASSLB could be explained by these fractures that occurred because of chemomechanical stress upon cycling. This kind of outcome was found in many reports on solid electrolyte research.<sup>85–98</sup> Regardless of the chemomechanical fractures, the lbi assembled ultra-thin polymer significantly improved the interfaces in a solid-state cell and conserved its morphology and uniformity over 20 galvanostatic charge discharge cycles. Importantly, the formation of the MCI layer was not observed for this system which was confirmed by the cross-section image in Fig. 9a.

## Conclusion

The research presented a thin artificial protective texture of (PAA/PEO)<sub>30</sub> as an interlayer between LAMP and Li metal through the layer-by-layer polymer assembly technique. Firstly, the ultra-thin interlayer assisted in preventing the formation of the mixed conductive interphase. Secondly, the artificial polymer texture decreased the interfacial impedance at the electrolyte/electrode border by providing intimate contact between solid electrolyte and electrodes for non-disruptive lithium ion insertion and extraction for 600 hours at 0.1 mA cm<sup>-2</sup>. Thirdly, simultaneous polymer coating on both sides of the LAMP pellets enabled the design of an all-solid-state Li metal battery with a commercial LFP cathode that demonstrated a highly reversible electrochemical behavior.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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