In-situ constructing slow-release Li-Al-O interface layer for lithium metal batteries to enhance interface stability and suppress lithium dendrite growth

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ABSTRACT

Composite polymer electrolytes (CPEs) have shown extraordinary promise for use in all-solid-state lithium metal batteries (LMBs) because of their tunable merits in ionic conductivity and mechanical flexibility. Their practical application is however hindered by the poor interface stability and the uncontrollable Li dendrite formation. Addressing these two issues, we report an in-situ formed Li-Al-O interface layer between CPEs and Li metal anode by introducing Al_{2}O_{3} nanoparticles in CPEs. X-ray photoelectron spectroscopy results indicated that the CPE-Al_{2}O_{3} could slowly release Al atoms which react with Li metal to form the current Li-Al-O interface layer. We highlight that the Li-Al-O interface layer can stabilize lithium deposition/stripping over 1400 h in lithium symmetric batteries, and afford an impressive cycle life of 300 cycles in LiFePO_{4}-Li batteries with almost no capacity loss. The present findings demonstrate that in-situ constructing a slow-release Li-Al-O interface layer is an easy and effective approach to stabilize the solid electrolyte interface and suppress the Li dendrites growth. Furthermore, the obtained batteries show excellent cycling stability, indicating the strategy with in-situ formed CPEs shed light on improving the processability of fabrication of high-performance electrolytes.

1. Introduction

Lithium metal batteries (LMBs) have been considered as one of the most promising power sources for numerous applications such as consumer electronic products, energy storage devices, and electric-drive vehicles [1-3]. However, LMBs using liquid electrolytes usually suffer from unstable solid electrolyte interface (SEI) and safety issues associated with the high chemical reactivity of Li metal and the formation of irregular metallic Li electrodeposits [4-6]. LMBs with composite polymer electrolytes (CPEs) have attracted extensive attention as one of the most sought-after solutions due to their outstanding merits: (i) they are non-vaporizable and nonflammable, and (ii) they exhibit promising electrochemical stability and mechanical performance [7]. However, the poor CPEs/Li interface stability and the formation of lithium dendrites across the CPEs/Li surface in LMBs (i.e., inhomogeneous stripping and plating reaction of metallic lithium anode during cycling) hinder the practical application of CPEs in LMBs [8-11].

Many efforts have been made to address these issues, such as constructing an artificial SEI layer, which is considered to be an effective method to stabilize the CPEs/Li interface [12,13]. Huang et al. in situ constructed a Li_{3}N layer between electrolyte and Li anode, which enhanced the interfacial stability [14]. Hu et al. made a Li-rich artificial SEI layer in the PEO-based CPEs, which improved the cycle performance in batteries [15]. Among the artificial interface layers, the thermodynamically stable Li-Al-O interface was created to reduce the contact resistance and increase the interface stability between CPEs and Li metal anode [16]. Therefore, many efforts have been made to construct the Li-Al-O interface. Huang et al. synthesized a polycrystalline Li-Al-O electrolyte via chemical reaction aiming to protect the Li anode and elongated the cycle life of Li symmetric batteries. But the electrolyte consisted of complex composition, and the Li-Al-O electrolyte lacked of flexibility [17]. Chen et al. constructed a Li-Al-O composition through

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2.2. Preparation of CPEs

The condition of preparation of CPEs were shown in Figure S3. CPEs were prepared by a solution casting procedure [20]. The PCL and nano Al2O3 fillers were dried in a vacuum drying oven for 12 h to remove the absorbed water from the atmosphere. Then the PCL and LiTFSSi in an optimized mole ratio of 20:1 were dissolved in 15 mL DMC (Aladdin, 99%) solution and continuously stirred at 60 °C for 2 h [21]. Then different amounts of nano Al2O3 with contents of 0%-30% were added. The solution was finally mixed for 24 h with continuous heating. Especially, during the stirring process, the solution was ultrasonic dispersed per 2 h. The solution was cast on a glass plate using a doctor blade when a significant homogenization has taken place. Residual solvent was completely removed by drying the electrolyte film in a vacuum oven at room temperature for another 24 h. The thickness of the residual solvent. For simplification, CPEs with different amounts of Al2O3 were dried in a vacuum oven for 12 h.

2.3. Sample characterization

The crystal structure was determined by a D8-ADVANCE X-ray diffractometer (XRD) using Cu Kα radiation. The morphology and microstructure of CPEs were studied by scanning electron microscopy (SEM, HITACHI SU8010). X-ray photoelectron spectroscopy (XPS) was measured utilizing the Thermo Scientific K-Alpha system to measure elemental species and the chemical valence of the CPEs.

2.4. Electrochemical characterization

Coin cells SS/CPEs/SS (SS, stainless-steel plate electrodes) were assembled to determine the ionic conductivity (σ) of the CPEs by alternating current (AC) impedance measurements over the frequency range 10 MHz to 0.1 Hz with a potential amplitude of 10 mV using a Zahner electrochemical workstation. The value of σ of the CPEs can be calculated by Eq. (1) [22]:

\[ \sigma = \frac{I_0}{RS} \]  

where I0 is the thickness of the electrolyte membrane, R represents the impedance of the symmetrical stainless blocking batteries and S is the electrode area. Coin cells Li/CPEs/SS were assembled to measure the electrochemical window of CPEs by linear sweep voltammetry (LSV) technique at a scanning rate of 0.1 mV s⁻¹ using CHI660E. The Li-ion transference number (tLi⁺) can be calculated by the Bruce-Vincent formula in Eq. (2) [23]:

\[ t_{Li^+} = \frac{I_{0s} - I_{0r}}{I_{0s} - I_{0r} - \Delta V/R}\ ]

where I0s and I0r represent the initial and stable current obtained from the DC polarization curves of symmetrical Li/CPEs/Li battery (ΔV = 10 mV), respectively. R0 and R0s correspond to the impedance before and after polarization, respectively. The galvanostatic test of both Li/CPEs/Li batteries and LiFePO4/CPEs/Li full solid-state batteries were carried out on a Land battery testing system at 60 °C.

3. Results and discussion

It is reported that a loose layer consisting of LiF and C-F containing layer may form between CPEs and Li metal anode during cycling [24]. The formation process of a Li-Al-O interface in CPE-A20 is illustrated in Fig. 1. The Al2O3 nanoparticles in the CPEs are expected to slowly release Al atoms and react with Li metal to form a Li-Al-O interface layer between CPEs and Li metal anode during battery cycling. This interface layer is expected to stabilize the CPEs/Li interface and make a uniform Li deposits process over the Li surface, as well as suppress the Li dendrite growth.

To verify whether a Li-Al-O interface layer is formed between the CPE-A20 and the Li metal anode during battery cycling, we characterized the Li electrode before and after 10 cycles in LFP/CPE-A20/Li battery through XPS. Fig. 2(a) shows the full XPS spectra on the Li surface before and after 10 cycles. Both Li surfaces before and after 10 cycles in LFP/CPE-A20/Li battery contained C, O, and F. It was worth noting that in the F1s spectrum, peaks at 684.6 and 688.7 eV (Figure S4) were assigned to LiF and CF3. The LiF and CF3 originated from the decomposition of lithium salts. After 10 cycles, Al existed on the Li surface after cycling in LFP/CPE-A20/Li battery, indicating the slow release of Al atoms during cycling in batteries. The deconvolution of the Al2p peak, as shown in Fig. 2(b, c), was fitted with two peaks at 75.1 and 73.6 eV, corresponding to γ-Al2O3 [19] and Li3AlO6 [18], respectively. The obtained results indicated the formation of the Li-Al-O compound on the Li surface. And the formation process of the Li-Al-O interface can be concluded as follows: Al2O3 nanoparticles exposed on the interface between the Li metal anode and CPEs electrolyte are prone to react with Li to form a stable Li-Al-O composition spontaneously during charging/discharging. Then slow released Al atoms continue to react with Li metal during cycling. And Li atoms could be delivered by this interface layer to the CPEs while maintaining this structure.

The corresponding raw materials, i.e., CPEs, were characterized through XRD, SEM, and EDS, and the obtained results were shown in Figure S5. Then the electrochemical performances of the CPEs were
characterized. In Fig. 3(a, b), the ionic conductivities of CPEs membranes at different temperatures (from 30 to 60 °C) were presented. The σ of CPE-A0 was only 6.32 × 10⁻⁶ S·cm⁻¹. After Al₂O₃ nanoparticles adding to the CPEs, the σ increased firstly as the σ reached to 1.72 × 10⁻⁵ S·cm⁻¹ for CPE-A10 and 1.94 × 10⁻⁵ S·cm⁻¹ for CPE-A20 at 60 °C. When the content of Al₂O₃ reached to 30%, the σ decreased to 1.23 × 10⁻⁵ S·cm⁻¹, which may be ascribed to that excess Al₂O₃ nanoparticles likely to agglomerate, leading to the elimination of effective interaction interfaces as well as the lowering of polymer free-volume [25]. Therefore, the conductivity in turn decreased. The LSV measurements from 1.0 to 7.0 V at 0.1 mV s⁻¹ were carried out, and the obtained results were shown in Fig. 3(c). The CPEs membranes were relatively stable below approximately 6.0 V (vs Li/Li⁺). The calculated Li-ion transference number (tₐLi⁺) was shown in Fig. 3(d). CPE-A20 had a tₐLi⁺ value of 0.65 at 60 °C, and the tₐLi⁺ value of CPE-A10 and CPE-A30 are 0.56, and 0.51 (Figure S6), respectively. These results showed that CPEs with Al₂O₃ nanoparticles exhibited a relatively high tₐLi⁺, which could mean a good battery property for the CPEs.

Cycling performance heavily relied on the electrode/electrolyte interface stability. Here we investigated the battery cycle performance of LFP/CPEs/Li to further assess the interface stability. The rate performance and charge/discharge profiles of CPEs were shown in Figure S7, respectively. The LFP/CPE-A20/Li battery delivered the specific capacities of 140.7, 135.1, 127.4, 121.3 and 118.1 mAh·g⁻¹ at different discharge rates of 0.1, 0.2, 0.5, 0.8 and 1.0C, respectively. And the specific capacities of LFP/CPE-A30/Li battery were 128.6, 122.9, 110.9, 105.7 and 100.0 mAh·g⁻¹ at the same rate. Note that LFP/CPE-A20/Li and LFP/CPE-A30/Li batteries showed the initial capacity of 120.7 and 102.4 mAh·g⁻¹, and both of them exhibited outstanding capacity retention of 98% and 100%, after 300cycles at 1.0C, as shown in Fig. 4 (a, b). The excellent cycle stability for the LFP/CPE-A20/Li and LFP/CPE-A30/Li batteries might originate from the in-situ Li-Al-O interface layer, which facilitated interfacial charge transport, and shorten the ion diffusion pathway [26]. However, the LFP/CPE-A10/Li battery suffered from a sudden capacity fading, this might come from the poor thermal stability for CPE-A10 because of the low content of Al₂O₃ nanoparticles [27]. The thermal shrinkage properties of the CPEs were investigated as shown in Figure S8. It should be mentioned that the battery performance of the present CPE-Al₂O₃ compares favorably with many reported CPEs (Table S2). As a result, the excellent cycle stability of the LFP/CPE-A20/Li and LFP/CPE-A30/Li batteries indicated that a slow-release Li-Al-O interface layer was formed and this interface layer was concluded to be responsible to enhance the battery performance.

SEM images of the cross-section of the LFP/CPE-A20/Li battery after cycles was shown in Figure S9(a). There was no obvious boundary between the electrolyte and electrodes, indicating a tight integration. The morphology of Li metal anode before cycling was shown in Figure S9(b). For the Li metal anode with CPE-A20 and CPE-A30 at 1.0C in LFP/CPE/Li batteries after 300cycles, a flat and compact surface morphology was observed (Fig. 4(c-f)) with packed and plate-like Li, indicating a uniform and stable lithium deposits during cycling. Furthermore, the Li-Al-O interface layer could ameliorate the intimate contact between the electrolyte and electrode and promote the lithium ions transport, thus obtaining a smooth surface structure on the Li metal anode. Moreover, no Li dendrites can be observed on the surface of the Li metal anode, which suggested the Li-Al-O interface layer was favorable to inhibit Li dendrites penetration. The results indicated that the slow-release Li-Al-O interface layer effectively improved the stability of the CPEs/Li interface and significantly inhibited the formation and growth of lithium dendrites on the surface of lithium metal.

Lithium stripping and plating experiments were further performed to analyze the cycling stability of the CPE-A20 and CPE-A30 against lithium metal. The lithium plating/stripping cycling in the Li/CPE-A20/Li, and Li/CPE-A30/Li symmetric batteries at different current densities from 0.01 to 0.2 mA·cm⁻² were shown in Figure S10. Both CPE-A20 and CPE-A30 in symmetric batteries exhibited stable rate performances until the current up to 0.2 mA·cm⁻². To further investigate the cycle stability
Fig. 3. (a) Impedance plots of the CPEs at 60 °C, (b) Arrhenius plots for the ionic conductivity of the CPEs, (c) LSV curves of CPEs and (d) steady state polarization curve and the impedances of the Li/CPE-A20/Li battery before and after polarization.

Fig. 4. Cycle performance of (a) LFP/CPE-A20/Li and (b) LFP/CPE-A30/Li batteries. SEM images of Li surface after 300 cycles in (c, d) LFP/CPE-A20/Li battery and LFP/CPE-A30/Li battery, respectively.
between the CPEs with Li metal, the galvanostatic lithium stripping and plating measurements were carried out at 60 °C at 0.05 mA cm⁻². As shown in Fig. 5(a), the CPE-A20 showed a stable voltage initially, suggesting an interface formed between electrolytes and Li metal anode [28]. Especially, the Li/CPE-A20/Li battery can be charged and discharged for over 1400 h with a small voltage polarization of about 0.071 V at 0.1 mA cm⁻², and about 0.083 V after 200 h at 0.1 mA cm⁻², as shown in Fig. 5(b). Similar phenomenon was shown in Li/CPE-A30/Li battery shown in Figure S11, as the voltage polarization is about 0.046 V at 0.05 mA cm⁻² after 500 h and 0.124 V after 200 h at 0.1 mA cm⁻². Such high stability of Li/CPE-A20/Li battery even after 1400 h cycles indicated that the addition of nano Al₂O₃ in PCL-based CPEs generated a more stable and higher quality Li-Al-O interface layer. Though a few vibrations appeared in the voltage profile in Li/CPE-A20/Li symmetric battery, the battery maintained a stable overpotential in the following cycles, indicating no uncontrolled increase of resistance caused by the degradation of the Li-Al-O interface layer on the Li metal anode [29].

The impedance associated with time in symmetric Li batteries was calculated. It is clear from Table S3 that the CPE-A20 and CPE-A30 showed stable impedance during cycling, which indicated that the Li-Al-O interface layer could greatly improve the Li stripping/plating stability in Li symmetric batteries. This explained why the cycle performances of CPE-A20 and CPE-A30 in the symmetric battery were stable.

To further explore the interfacial stability of Li-Al-O between the CPE-A20 and Li metal anode, and the inhibition of Li dendrites, we disassembled the cycled symmetric batteries to observe the Li/CPE-A20/Li interface layer on the Li metal surface [31]. From the above analysis of both symmetric batteries and full batteries, the Li-Al-O interface layer can effectively improve the cycle stability and inhibit the Li dendrites.

4. Conclusions

In summary, a Li-Al-O interface layer was in-situ formed between Al₂O₃-based CPEs and Li anode during battery cycling. The formation of the Li-Al-O interface layer resulted from the reaction between the slowly released Al atoms and the Li metal anode. Benefiting from the stabilized Li-Al-O interface layer, the symmetrical battery with CPEs-Al₂O₃ electrolyte can be cycled over 1400 h with a small voltage polarization of ~0.071 V. Besides, excellent capacity retention reaching ~100% can be achieved in LFP/CPE-A20/Li batteries after 300cycles at 1.0C. The remarkable results confirmed the effectiveness of the in-situ formed Li-Al-O interface layer in improving the interfacial stability between CPEs and Li metal anode. SEM and XPS characterizations confirmed a smooth and stable Li-Al-O interface layer even after 1400 h in Li symmetric batteries and 300cycles in LiFePO₄-Li batteries. Our work provided a facile and effective strategy to stabilize the electrode/electrolyte interface and suppress the Li dendrite growth in LMBs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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