

Full paper

Carbon paper interlayers: A universal and effective approach for highly stable Li metal anodes

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ABSTRACT

The Li metal anode is considered as one of the most promising candidates for next generation Li metal batteries (LMBs) due to the unique properties of high specific capacity, low potential and light weight. However, the crucial problems, including serious Li dendrite growth, undesired side reactions and infinite volume changes, are still big challenges for Li metal anodes, which can not only lead to the low Coulombic efficiency, but also can create short circuit risks. In this paper, we propose a novel and universal approach to achieve long life time and dendrite-free Li metal anodes by introducing carbon paper (CP) as an interlayer. As a result, the as-designed electrodes can deliver extremely high capacity (up to 3 mA h cm^{-2} and 5 mA h cm^{-2}), superior stable performances (620 h/265 cycles with 3 mA h cm^{-2}) and high operational current densities (3 mA cm^{-2} and 5 mA cm^{-2}). Meanwhile, the electrodes also can demonstrate high capacity and long life time in full cells using carbon-coated LiFePO_4 (C/LiFePO₄) as the cathode for lithium ion batteries (LIBs) and molecular layer deposition (MLD) coated C/S as cathode for Li-S batteries. These new findings could open a new window for the fabrication of safe, long life time and dendrite-free Li metal anodes.

1. Introduction

Lithium-ion batteries (LIBs) have been utilized for many applications over the past decades such as portable electronics, electric cars, and large scale energy storage stations [1–3]. Next-generation lithium-based batteries with high energy density, including Li-S, Li-air and solid-state Li batteries, have recently received increasing attention. Among all the anode candidates, Li metal is one of the most promising anodes for lithium-based batteries due to its high theoretical capacity (3860 mA h g^{-1}), low electrochemical potential (-3.04 V vs. the standard hydrogen electrode) and light weight (0.53 g cm^{-3}) [4–6]. The rechargeable Li-metal battery (LMB) was initially proposed in the 1970s, however, Li metal anodes hadn't been further applied in commercial batteries due concerns of safety. The safety issues of the Li metal anode are mainly caused by dendritic Li formation during the electrochemical plating/stripping process [7–9]. The main challenges of Li metal anode can be listed as follows: 1) during the electrochemical plating/stripping process, the mossy and dendritic Li grows. As a result, the Li dendrites may penetrate through the separators, causing short circuits and leading to safety issues [10,11]. Furthermore, Li dendrites can also become isolated from the bulk Li or current collector and become “Dead Li”, which is electrochemical inactive due to the loss of

electronic contact and thus shorten the cycle life of batteries [12]. 2) Side reactions between Li metal and organic electrolytes form unstable solid electrolyte interphase (SEI) layers, which continuously consume the liquid electrolyte and Li metal. This consumption results in rising resistance, lower Coulombic efficiency (CE) and reduced life time of the electrodes [13,14]. 3) More recently, the infinite volume change of Li metal electrodes during the Li plating/stripping is considered to be a huge problem due to the “hostless” nature [7].

In order to solve these above-mentioned issues and enhance the performances of Li metal electrodes for next-generation LMBs, different strategies have been developed. One of the major efforts focuses on stabilizing the SEI layer through in-situ or ex-situ procedures to achieve suppressed Li dendrite growth and improved life time. On the one hand, the in-situ formation of a stable SEI layer is dependent on the modification of electrolyte components, including organic solvents, Li salts and functional additives [9,15,16]. Alternatively, surface protective coating layers have been explored as artificial SEI films to improve the performances [15–18]. Among the reported methods for surface coating, atomic layer deposition (ALD) and molecular layer deposition (MLD) are utilized as the most promising techniques for Li metal surface modification due to their unique properties including excellent coverage, conformal depositions and highly controllable thicknesses [19].

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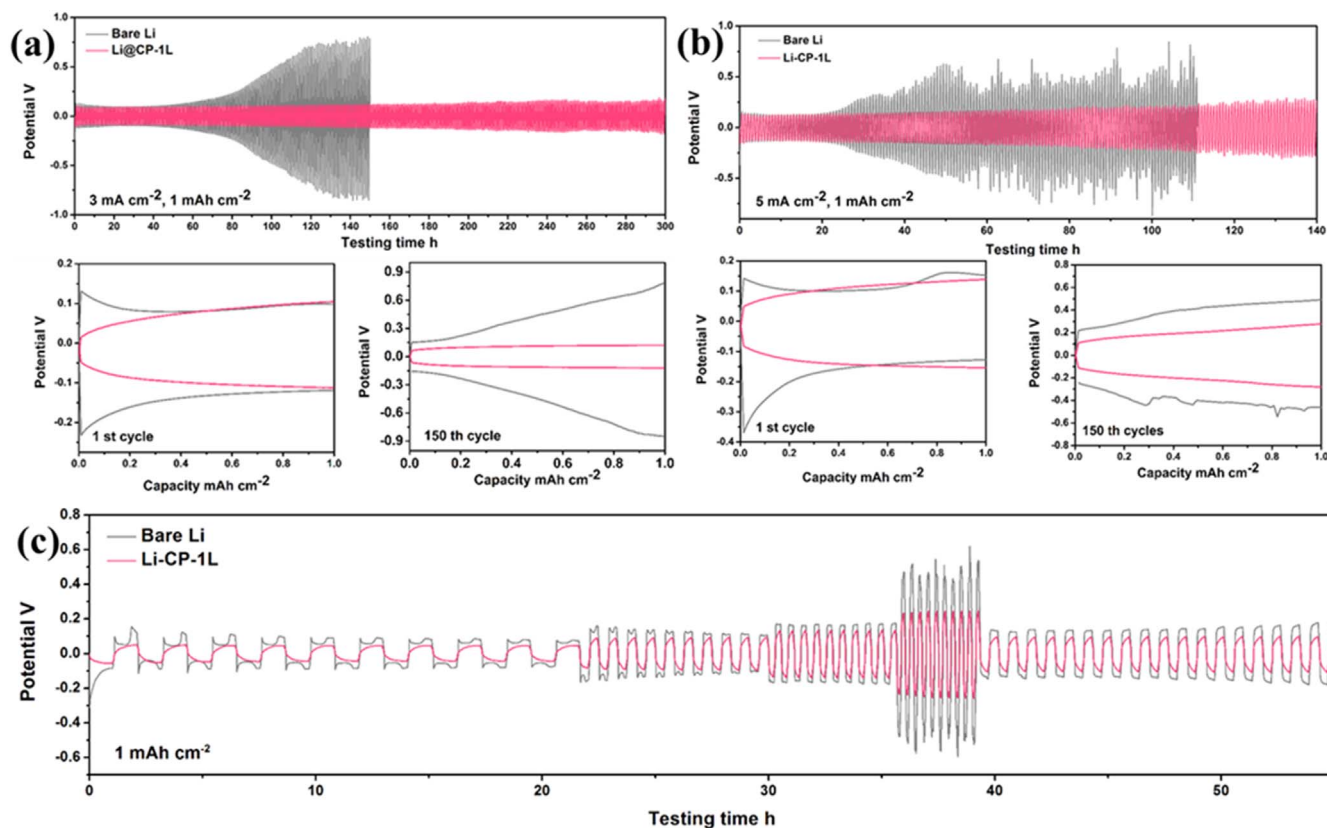


Fig. 1. Comparison of the cycling stability and voltage profiles of Li-CP-1L and the bare Li foil at a current density of 3 mA cm^{-2} (a), 5 mA cm^{-2} (b) and rate performances (c) with the capacity limit of 1 mA h cm^{-2} .

In 2015, two groups demonstrated ultrathin ALD Al_2O_3 thin film as a protective layer for metallic Li. From their results, the artificial SEI layer of Al_2O_3 can successfully prevent the side reactions between the Li metal anode and organic electrolytes and dramatically suppresses the Li dendrite growth [20,21]. Later in 2016, both our group and Hu's group had also applied this ALD Al_2O_3 coating for Na metal anodes and tested the performance in two different types of electrolytes (ether and carbonate, respectively), achieving very stable performances and further suppressed Na dendrite growth [22,23]. Moreover, MLD alucone protective layers, which were firstly reported by our group, have been deposited on Na metal, which exhibits superior electrochemical performances and long life time, especially in carbonate-based electrolyte [24].

Another prominent approach proposed by Cui's group is the use of thermal infusion to melt Li metal into 3D host structures, including reduced graphene oxide (rGO), porous carbon matrices, and polymeric matrices [25–27]. With this method, one of the major issues regarding the large volume change of lithium can be effectively relieved. Subsequently, other types of 3D hosts have been reported to obtain minimum volume change and longer life time of Li composite electrodes, such as Ni foam [28], Li-ion conductive matrix [29] and wood-derived carbon matrix [30]. However, there are still limitations for the thermal infusion method, in which one concern is the high temperature process required that makes it not easy to be operated and uneconomical. Another shortage is the stringent requirements of the Li wettability on the surface of hosts. Therefore, there are yet remaining challenges for 3D Li composites prepared via thermal infusion method for practical applications in future battery systems. Another interesting work has been reported by Lu's group, in which the 3D porous current collectors have been mechanically pressed on the Li foil to form 3D Cu/Li composites. As a result, the obtained 3D Cu/Li shows the improved electrochemical performances compared to planar Cu foil [31]. However, there is still large room for improvement from the achieved performances.

Meanwhile, the 3D metal current collectors are relatively heavy, and will lower the energy density of the batteries [32].

In 2012, Manthiram's group demonstrated microporous carbon paper (CP) as interlayer between cathode and separator for Li-S batteries. The significant enhancement can be achieved on the active material utilization and capacity retention [33]. Subsequently, different carbon fiber-based interlayers have been applied into Li-S batteries to trap soluble intermediate polysulfides, provide space to store electrolyte and reaction production [34–37]. Meanwhile, it has been proven that this kind of carbon fiber-based interlayers also play the positive role in terms of the protection Li metal anodes in Li-S batteries. However, the detailed electrochemical performances and mechanism of Li plating/stripping have not been studied in detail, especially using carbon interlayer on Li metal anode. Herein, we propose a novel and universal approach to achieve long life time and dendrite free Li metal anodes by introducing CP as an interlayer. As a result, the as-designed electrodes can deliver extremely high capacity (up to 3 mA h cm^{-2} and 5 mA h cm^{-2}), superior stable performances (620 h/265 cycles with 3 mA h cm^{-2}) and high operational current densities (3 mA cm^{-2} and 5 mA cm^{-2}). Meanwhile, the electrodes also can demonstrate high capacity and long life time in full LMB cells using carbon-coated LiFePO_4 (C/LiFePO₄) as the cathode for LIBs and MLD coated C/S as cathode for Li-S batteries. The influence of the number of CPs used for the Li anode interlayer on their electrochemical performance has been investigated. The role of CP in Li deposition/dissolution mechanisms have been further illuminated in detail. These new understandings could open a new window for the fabrication of safe, long life time and dendrite-free Li metal anodes.

2. Results and discussion

The configuration of the designed Li electrodes with CP interlayers is shown in Fig. S1. Firstly, the CP was cut into a disk shape with the

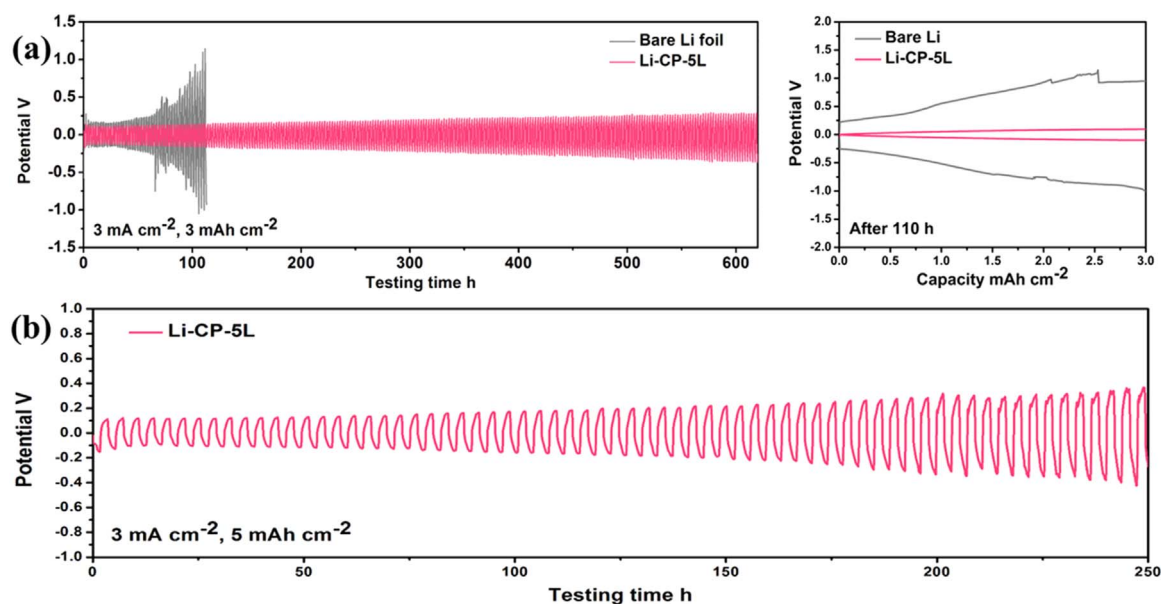


Fig. 2. Cycling stability and voltage profiles of Li-CP-5L and bare Li foil at a current density of 3 mA cm^{-2} with capacity limits of 3 mA h cm^{-2} (a) and 5 mA h cm^{-2} (b).

same diameter of commercial Li foil. Before the battery assembly process, the CP interlayers were put onto the surface of Li foil (between Li and separators) and used together as the anode. To evaluate the influence of CP on the electrochemical performance of Li foil, symmetrical coin cells (2032-type) were assembled using a carbonate-based electrolyte (1 M LiPF₆ in EC/DEC/DMC) with CP interlayers on the Li foil. The overpotential between the two electrodes in the galvanostatic testing can be separated into two parts: (1) the overpotential associated with the mass-transfer resistance throughout the plating/stripping, and (2) nucleation at the initial stages of deposition, which is affected by the lithiophilicity of the electrode surface [38]. Fig. 1 shows the electrochemical plating/stripping performances of the Li foil with one layer of CP as an interlayer (named Li-CP-1L) under different current densities with a capacity limit of 1 mA h cm^{-2} . Fig. 1(a) exhibits the cycling stability and detailed voltage profiles of Li-CP-1L and bare Li foils at a current density of 3 mA cm^{-2} . From the voltage profiles in the 1st cycle, a sharp voltage drop to -250 mV (versus Li⁺/Li) for the bare Li foil is observed at the initial stage of Li plating, which corresponds to the nucleation process. Afterwards, the voltage increases to a stable platform at -100 mV (versus Li⁺/Li). With a more promising electrochemical performance, Li-CP-1L shows a much smaller voltage drop at the initial stage of Li plating ($\sim -50 \text{ mV}$), indicating homogeneous nucleation with the CP interlayers. Upon further plating, a similar stable platform at 100 mV (versus Li⁺/Li) can be obtained for Li-CP-1L. That the carbon fibers in CP are initially inserted with Li⁺ during the first plating process and the stable SEI are induced to form on the surface of CP. In this case, the SEI layers can prevent penetration of solvent molecules and allow interfacial transfer of Li⁺, which can provide the homogeneous deposition of Li. From the cycling stability tests, the overpotential of bare Li foil starts to increase after 70 h (70 cycles) and rises to over 700 mV (versus Li⁺/Li) after 150 h (150 cycles) with large polarization in the voltage profiles. In comparison, Li-CP-1L can maintain superior stability and lower overpotentials of 100 mV (versus Li⁺/Li) after 150 h (150 cycles). Even after 300 h (300 cycles), the overpotential of Li-CP-1L is only about 150 mV (versus Li⁺/Li), illustrating the enhanced electrochemical performance enabled by the CP interlayer. Fig. 1(b) shows the cycling stability and the detailed voltage profiles of Li-CP-1L and bare Li foil at a current density of 5 mA cm^{-2} . When applying a higher current density, the voltage drop for the initial nucleation process is below -350 mV (versus Li⁺/Li) in the 1st cycle for bare Li foil, which is even larger than that of the cells

cycled at 3 mA cm^{-2} . However, with the CP interlayer, Li-CP-1L shows an initial nucleation potential of -80 mV (versus Li⁺/Li) which stabilizes at -150 mV (versus Li⁺/Li) in the first cycle. During electrochemical cycling at this current density, the stability of bare Li foil is very poor, in which the overpotential starts to increase after only 35 h and rises up to 600 mV after only 50 h with large fluctuations in overpotential voltage. The fluctuating voltage profiles are related to the Li dendrite (mossy) growth, dead Li layer formation and soft short circuiting. For Li-CP-1L, a more stable performance with less polarization is observed during cycling, in which the overpotential after 140 h is only 240 mV (versus Li⁺/Li). To further explore the performances under different current densities, the rate behavior of symmetrical cells are presented in Fig. 1(c). Li-CP-1L demonstrates a significantly lower and more stable voltage polarization at the current density of 1, 3, 5 and 10 mA cm^{-2} . In contrast, the bare Li foil presents a larger overpotential at all current densities, particularly when cycled at 10 mA cm^{-2} . The obvious difference at high current densities can be attributed to the high specific kinetic obstacles, in which the CP interlayer can provide effective pathways for electron/ion transport with favorable electron/ion conductivity.

One of the major advantages of using Li metal as the anode for LMBs is the large capacity. It is widely accepted that the areal capacity of a commercial electrode needs to reach at least 3 mA h cm^{-2} for practical application [7]. Therefore, a capacity limit of 1 mA h cm^{-2} , which is the most popular parameter for demonstrations in the reported literatures, may not meet the requirements for the future batteries applications. In this case, we are also trying to achieve high capacity with enhanced stability by using the CP interlayer with Li foil. Firstly, the bare Li foil is tested at the current density of 3 mA cm^{-2} with the capacity limit of 3 mA h cm^{-2} . As expected, the overpotential increases after only 60 h and grows to 1000 mV (versus Li⁺/Li) after 110 h (Fig. 2(a)). Compared to the behavior of symmetric cells with a lower capacity of 1 mA h cm^{-2} , a larger and faster polarization can be observed at the same current density, indicating the significant amount of mossy and dendritic Li growth during the deposition process. Very interestingly, when using one layer CP as interlayer (Li-CP-1L) with capacity of 3 mA h cm^{-2} , the cycling stability can also be improved with a stable overpotential after 110 h (Seen in Fig. S2).

In order to further improve the electrochemical performance of the Li anode at large capacity, we apply a simple strategy of increasing the number of CP interlayers. This approach will be shown to be very

effective for addressing the challenges of large capacity Li metal anodes, in which the cell configurations are presented in Fig. S1(b) and the electrochemical performances are shown in Fig. S2(a) and Fig. 2(a). The layers of CP are named as Li-CP-3L, Li-CP-4L and Li-CP-5L with 3, 4, and 5 CP interlayers, respectively. It can be seen from Fig. S2 that after 180 h, the overpotential of Li-CP-1L, Li-CP-3L and Li-CP-4L are ~ 500 mV, 300 mV and 250 mV (versus Li^+/Li), respectively. Moreover, with 5 CP interlayers, the Li-CP-5L delivers very stable plating/stripping performances and the lowest overpotential of ~ 240 mV after more than 620 h (Fig. 2(a)), which is almost 10 times longer life time than that of the bare Li foil. In order to prove the great potential and advantages of multilayer CP for the Li metal anode, a larger capacity of 5 mA h cm^{-2} is further explored with 5 layers of CP. It can be seen from Fig. 2(b) that even with a higher capacity of 5 mA h cm^{-2} , the overpotential of Li-CP-5L is still lower than 200 mV (versus Li^+/Li) after 130 h. Even after 250 h of electrochemical plating/stripping, the Li-CP-5L electrodes still deliver stable performances with a maximum overpotential of 350 mV (versus Li^+/Li). The electrochemical impedance spectroscopy (EIS) results are shown in Fig. S3 where the spectra show Nyquits plots before cycling and after 50 cycles for different samples (bare Li, Li-CP-1L, Li-CP-3L, Li-CP-4L, and Li-CP-5L) under the current density of 3 mA cm^{-2} with the capacity of 3 mA h cm^{-2} . It is believed that two distinct semicircles is associated with both the SEI/electrode (high frequency) and the charge transfer (CT)/electrical double layer (EDL) (lower frequencies). Promisingly, even before electrochemical cycling, the resistances have been reduced with the conductive CP interlayers. After 50 cycles of Li plating/stripping, the resistance of bare Li rapidly increases and the Li-CP-5L shows the smallest resistance, which corresponding to the most stable electrochemical performances. The Impedance parameters calculated by equivalent circuits for different samples are shown in Table S1. From Table S1, the results indicate that the R_{SEI} of bare Li foil is much larger than the designed electrodes with CP interlayer after 50 cycles Li plating/stripping process. These results indicate that the CP interlayers have a significant influence on the high capacity Li metal anode. Meanwhile, the thickness of CP can be controlled to meet the requirements of the desired capacities. All of the battery testing was carried out in conventional carbonate based electrolyte (1 M LiPF_6 in EC/DEC/DMC of 1:1:1 volume ratio), which is considered to be more challenging because of the more serious side reactions and unstable SEI formation compared to ether-based electrolyte systems [9,26]. To the best out knowledge, our design yields the best performances in symmetric Li/Li cells in carbonate-based electrolyte in term of the large capacity, high current density and longest life time (Table S2).

In order to understand the effects of the CP interlayer on the process of Li dendrite growth, the morphologies of deposited Li in different designs are characterized by SEM. As a comparison, the Li deposition behavior of bare Li foil is presented in Fig. 3 and Figs. S4–5. The first plating and stripping processes of bare Li foil with a capacity of 1 mA h cm^{-2} are shown in Fig. S4. During the first stripping process (Fig. S4(a)), Li is stripped from the surface randomly, generating pits of variable size on the surface. In the first plating process (Fig. S4(b)), Li is preferentially deposited as mossy-like dendrites due to the inhomogeneous nucleation and growth. When increasing the stripping/plating capacity of Li to 3 mA h cm^{-2} , the holes become larger and the surface of Li becomes rougher during the first stripping process (Fig. S5(a)). Likewise, thicker and denser mossy-like Li dendrites can be observed from the first plating process (Fig. S5(b)). It has previously been shown that the mossy-like Li will produce a dead Li layer and become electrically isolated during cycling and results in low CE, increased polarization and resistance in addition to depletion of the Li inventory [39,40]. The morphologies of Li deposition for bare Li foil after cycling (10 cycles) is presented in Fig. 3(a, c). When the capacity of Li is 1 mA h cm^{-2} , a relatively rough surface can be observed from the top-view SEM images and dead Li layers with a thickness of $20 \mu\text{m}$ can be seen from cross section pictures (Fig. 3(e, g)). After increasing

the capacity to 3 mA h cm^{-2} , large cracks on the top surface of bare Li evolve and thick dead Li layers of $\sim 45 \mu\text{m}$ are formed after 10 cycles, which is an indication of more serious side reactions and Li dendrite growth.

The influence of CP interlayers on the morphology of Li deposition have also been studied via SEM, as displayed in Fig. 3 and Figs. S6–9. Firstly, the Li plating/stripping behaviours during the initial cycle are tested with a capacity of 1 mA h cm^{-2} . From Fig. S6, it can be observed that the morphologies of CP are almost identical in the first cycle. This observation is clearly different compared to the case with bare Li foil, in which there is no pitting behavior after stripping and mossy-like Li dendrite growth has also been avoided during Li plating (Fig. S6(a, b)). The indentations on the surface of Li are caused by the carbon fibers of CP, which aid in delivering uniform local current distributions resulting in homogeneous nucleation and growth of Li during plating and stripping. The phenomenon observed from the SEM results are highly consistent with the first cycle electrochemical potential profiles discussed above. After 10 cycles, the top-view images of CP and the cross-section images of the whole electrode are presented in Fig. 3(b) and (d), respectively. As exhibited in Fig. 3(b), there is still no mossy-like or dendritic Li deposition after 10 cycles, and the Li is plated on the surface or the gaps between the carbon fibers in CP. The cross section images give consistent evidence, in which Li is filled in the porous spaces between carbon fibers without any dendrite growth, and the dead Li layers are prevented through the use of CP interlayers (Fig. 3(d)).

Furthermore, more detailed studies on the morphology of 5CP interlayers have been carried out when the capacity is increased to 3 mA h cm^{-2} (Fig. 3(f, h) and Figs. S7–9). In the first cycle, a similar phenomenon can be observed on the surface of Li metal, in which indentations of carbon fibers exist without any holes/pits or mossy-like lithium during stripping and plating. Meanwhile, the morphologies of CP in different layers (1st, 3rd and 5th) are also presented, in which they show near identical structures. After 10 cycles, the Li metal can retain a smooth surface without mossy-like and dendritic Li growth (Fig. S7(c)). Obvious differences in the plating behavior can be seen on the different layers of CP after 10 cycles. The inner layers of CP show very similar morphology with the CP in Li-CP-1L, indicating the similar process of SEI formation and Li deposition. However, more pancake-like Li deposition can be observed on the top CP layer in Li-CP-5L with increasing of the capacity. It demonstrates that the extra amount of Li tends to deposit on the top layer of CP and then diffuses into the inner layers, finally reaching the Li metal surface [41–43].

The performance of the Li foil with and without CP interlayers as an anode is further investigated in a full cell using C/LiPF₆ as the cathode. The loading of C/LiFePO₄ is over 8 mg cm^{-2} corresponding to an areal capacity of $\sim 1.36 \text{ mA h cm}^{-2}$. Accordingly, we have chosen Li-CP-2L to match this areal capacity, at the same time avoiding an unnecessary increase in weight due to an excessive number of CPs. Fig. 4 and Fig. S10 shows the cycling performances of full cells using bare Li foil and Li-CP-2L as anodes at a rate of 1 C, in which the configuration of the cell is shown in Fig. S1(c). In the battery using bare Li foil, the discharge/charge capacity starts fading after 100 cycles, decreasing to about 40 mA h g^{-1} after 300 cycles. However, with an interlayer of CP, the cell maintains an extremely stable capacity of $\sim 130 \text{ mA h g}^{-1}$ after 380 cycles. Fig. 4(c) shows the potential profiles of the cells using bare Li foil and Li-CP-2L as anode after 150 cycles. An obvious increase in overpotential can be seen for the bare Li electrode, which can be attributed to an increase of surface passivation/pulverization of the lithium. Promisingly, there is almost no change in the overpotential after 150 cycles for the cell with CP interlayers.

Moreover, in our previous study on Li-S batteries, we have successfully developed alucone coated C-S cathode electrodes used in conventional carbonate-based electrolytes with high sulfur loading [44]. The as-prepared sulfur cathodes in carbonate electrolyte have been demonstrated to undergo a solid-phase Li-S redox reaction

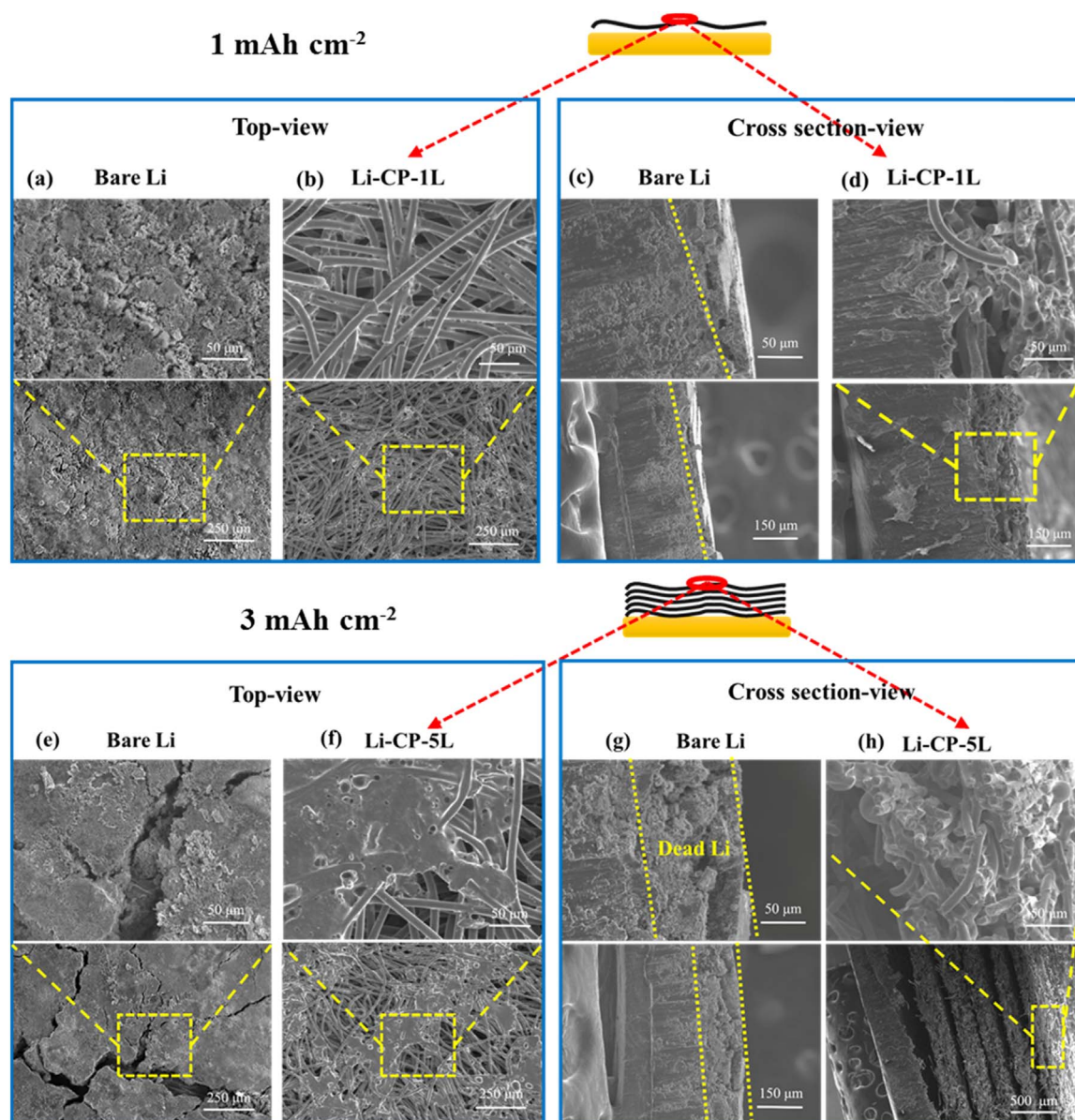


Fig. 3. Top view SEM images of bare Li foil (a) and Li-CP-1L (b) as well as the cross section view of bare Li foil (c) and Li-CP-1L (d) after 10 cycles with a 1 mA h cm^{-2} capacity limit. Top view SEM images of bare Li foil (e) and Li-CP-5L (d) and cross section views of bare Li foil (g) and Li-CP-5L (h) after 10 cycles with a 3 mA h cm^{-2} capacity limit.

and therefore the performance of Li metal anode and fast Li/Li^+ transport are crucial for these types of batteries [44]. The C-S composite loading is around $2.8\text{--}3.0 \text{ mg cm}^{-2}$, corresponding to an areal capacity of $\sim 2.5\text{--}2.7 \text{ mA h cm}^{-2}$. Fig. 4(d) shows the cycling performances of full cells using bare Li foil and Li-CP-2L. Interestingly, with the use of Li-CP-2L, the Li-S battery exhibits excellent cycling stability and reversibility. The battery exhibits an initial capacity of over 1200 mA h g^{-1} and maintains 600 mA h g^{-1} after 150 cycles. On the contrary, with the use of bare Li anode, the cycling capacity of the Li-S battery drops very fast, which illustrates the importance of the interlayer to improve the stability of Li-S batteries. Comparison of discharge-charge profiles of the two Li-S batteries are shown in Fig. 4(e) and (f). Impressively, the Li-S battery with the carbon paper interlayers demonstrates stable, flat, and highly reversible discharge-charge potential plateaus, while the potential plateaus of the Li-S cell without an interlayer gradually reduce during cycling. The Li-S full cell demonstration illustrates the excellent performance by the interlayer design and shows potential for use in next-generation lithium metal batteries.

The CP is demonstrated as an interlayer to significantly improve the

stability and life time of Li metal anodes. In our design and concept, materials of CP and Li foil are commercialized with an affordable price. Furthermore, the fabrication of the Li-CP composite electrode is facile and easily realized, and can potentially be combined with previously reported approaches including chemical surface modification, electrolyte additives and 3D Li structures. Then, the strong mechanical properties and flexibility of CP make it very promising not only in coin cells but also for use in larger devices without significant changes to the fabrication procedure of commercial batteries. Finally, this approach also can be considered as a universal method by using different materials as interlayers. Another two types of materials (including carbon cloth and Ni foam) are used as interlayer for Li metal anode (shown in Fig. S11), demonstrating very stable electrochemical plating/stripping performances compared with Li foil.

The morphologies of Li deposition with and without CP interlayers have been characterized to understand the mechanism and functions of CP during Li-S the Li plating/stripping process. Fig. 5 shows the schematic illustration of the Li stripping/plating behavior occurring on the surface of the different electrodes. As shown in Fig. 5(a), the mossy and

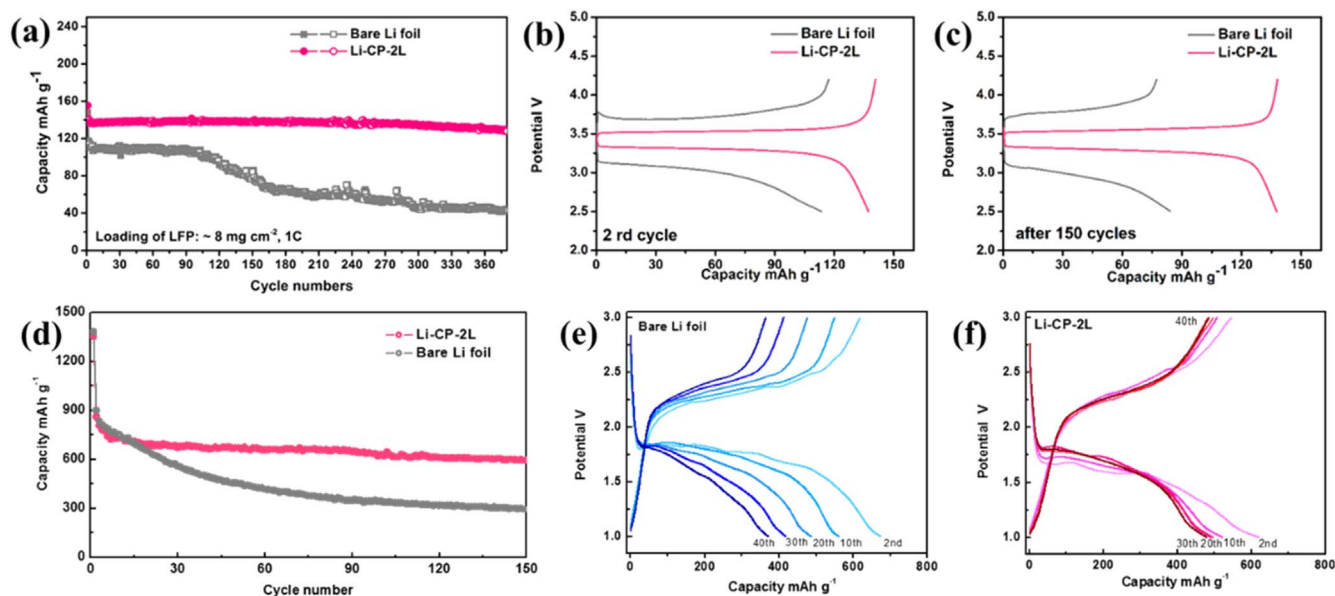


Fig. 4. (a) Cycling performance of full cells (C/LiFePO_4 as cathode) using bare Li foil and Li-CP-2L at 1 C; (b, c) Voltage hysteresis profiles of charge/discharge of bare Li foil and Li-CP-2L in 2nd cycle and after the 150th cycle. (d) Cycling performance of full cells (modified C/S as cathode) using bare Li foil and Li-CP-2L; Voltage hysteresis profiles of bare Li foil (e) and Li-CP-2L (f) in various cycles.

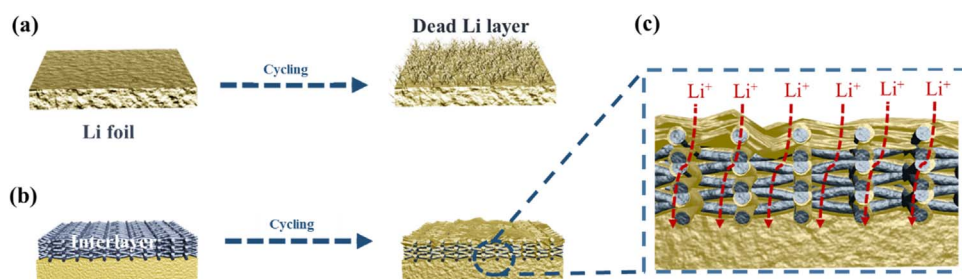


Fig. 5. Schematic illustration of the Li stripping/plating behavior occurring on the surface of bare Li foil (a), Li foil with CP interlayers (b); the detailed mechanism of Li deposition on the CP (c).

dendritic Li is formed during cycling of the bare Li foil, resulting in a thicker dead Li layer on the surface. As a result, an increased resistance, lower CE and reduced life time is observed. In contrast, the CP interlayer enables uniform Li deposition without mossy and dendritic growth, which can be attributed to the homogeneous distribution of local current on the CP. Meanwhile, the porous structure of CP provides a transport path for liquid electrolyte and buffer space for Li plating/stripping (Fig. 5(b-d)).

3. Conclusion

In summary, we have firstly demonstrated the concept of using carbon paper (CP) used as an interlayer for highly stable Li metal anodes. In this novel design, we highlight multiple advantages and performance enhancements including; 1) the fabrication of the Li-CP composite electrode is very facile and easy to be realized, which can be applied for large-scale production. 2) The as-prepared Li-CP-5L electrode shows superior and stable plating/stripping performances for up to 620 h, which is almost 10 times longer than that of the bare Li foil. To the best of our knowledge, our design presents the best performances in symmetric Li/Li cells in carbonate-based electrolyte in terms of the highest capacity, highest current density and longest life time. 3) Ultra-long cycling life and high capacity retention is realized by introducing CP interlayers for Li foil paired with C/LiFePO_4 as the cathode for LIBs and MLD-coated C/S as the cathode for Li-S batteries. 4) There is no observable mossy or dendritic Li formation during the Li deposition process, in which the mechanism and functions of CP during Li plating/stripping process have been highlighted in detail. Herein, our

achievement is very promising and provides a facile approach to stabilize Li metal anodes with superior long life time, large capacity and high current density. It is believed that our design of CP interlayers opens up new opportunities to the realization of next-generation high energy density Li metal batteries.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2017.11.032>.

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