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Article

An air-stable and waterproof lithium metal anode enabled by wax composite packaging

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ABSTRACT

The reviving use of lithium metal anode (LMA) is one of the most promising ways to upgrade the energy density of lithium ion batteries. In the roadmap towards the real use, besides the formation of the dendrite, various adverse reactions due to the high activity of LMA when exposed to air or the electrolyte limit its practical applications. Learning from the packaging technology in electronic industry, we propose a wax-based coating compositing with the ion conducting poly (ethylene oxide) by a simple dip-coating technology and the prepared LMA is featured with an air-stable and waterproof surface. The LMA thus remains stable for 24 h in ambient air even with the relative humidity of 70% while retaining about 85% its electrochemical capacity. More importantly, the LMA is accessible to water and when dipping in water, no obvious adverse reactions or capacity decay is observed. With the composite coating, a steady cycling performance for 500 h in symmetrical cells and a low capacity decay rate of 0.075% per cycle after 300 cycles in lithium-sulfur batteries assembled with the packaged anode have been achieved. This work demonstrates a very simple and effective LMA package technology which is easily scalable and is very promising for speeding up the industrialization of lithium-sulfur batteries and shows potentials for the large-scale production of air-sensitive electrode materials not limited to LMAs.

1. Introduction

The fast development of next-generation high energy density batteries, such as lithium-sulfur batteries (LSBs) and lithium-air batteries whose cathodes do not contain lithium sources, calls for the use of a lithium metal anode (LMA) with a high theoretical capacity (3,860 mAh g^{-1}) and a low potential (−3.040 V versus standard hydrogen electrode) [1]. Nevertheless, the LMA has failed to be commercialized because of the safety issues caused by lithium dendrite growth and uncontrolled interfacial reactions between the electrolyte and the lithium metal [2]. Considerable research effort has been dedicated to control lithium plating and stripping to suppress the dendrite formation, including the design of three-dimensional current collectors [3–5], the use of surface protective coatings (e.g. Al_2O_3 [6], graphene [7], Li_3N [8] or polymers [9–12]) and the electrolyte modification [13–18]. However, these techniques are complicated and need strict operating condition because the lithium metal has a very highly active surface, making them impractical.

Because it is an alkaline metal with high activity, various uncontrolled and adverse reactions will happen on the LMA surface when exposed to air, generating heterogeneous contamination and non-uniform nucleation and growth spots on the surface, and thus a deterioration in its electrochemical performance is inevitable [19]. Even worse, when contacted with water or humid air, the LMA tends to combust due to the production of a large amount of heat and hydrogen, leading to severe safety issues. Previous reports have shown some potential solutions for the above problems, such as forming a Li_3N coating [20], depositing Al_2O_3 by atomic layer deposition [6], stabilizing the surface by reacting it with CO_2 [21], and coating it with a graphene film [19]. These surface modification methods reduce surface corrosion in air to some extent, but none of these works addressed the stability of the LMA in the highly humid air or even in water, which is important for the

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safety of the LMA and as well more challenging. Thus, to simply build a coating that can not only protect the LMA in air and water but also restrain dendrite growth in the battery is an efficient way to simplify LMA processing and promote its practical use on a large scale.

If we can learn the knowledge from the packaging technology, which protects electronic components from physical damage and corrosion in humid air and water by a coating, an ideal design of the coating for LMA can be mapped. In this respect, wax, a commonly-used inert sealing material which has good water resistance and is easily coated on different surfaces, comes into our consideration. However, the ionic insulation of wax prohibits its use in batteries. Thus, introducing an ion-conductive network into wax to obtain a composite coating could be a promising way to build an air-stable LMA for real uses.

Here, we packaged the lithium metal in a wax-poly(ethylene oxide) (PEO) hybrid material by a simple dip-coating method to obtain an air-stable, waterproof and high-performance LMA. The functions of the composite coating are shown in Fig. 1a. The surface of an uncoated LMA becomes rough and contaminated when exposed to air or water because of the reactions of lithium with water or the oxidizing components in the air. Besides, the unstable interface between lithium and the electrolyte induce the formation of an unstable solid electrolyte interface (SEI) and dendrites that lower the electrochemical performance of the cells [22,23]. In contrast, the surface stability of LMAs with the wax-PEO coating (denoted Li-wax-PEO) is greatly improved in the air, water and batteries. In the air and water, this coating effectively retards the corrosion of LMA due to the good sealing of the wax, and in the battery the wax prevents the electrolyte from etching the LMA while the PEO provides ion diffusion paths [24], making the coating both interfacially protective and ion conductive. In addition, since electrostatic interaction between the polar segments of PEO and Li^+ in the electrolyte retard the fast Li^+ flux towards the LMA [25], the Li^+ flux is regulated more homogeneous by the PEO in the coating and lithium dendrite growth is limited [26]. Therefore with this wax-PEO coating, LMAs are stable in air (relative humidity: 70%) for 24 h with a high capacity retention of 85% compared with the original LMA. Even when Li-wax-PEO contacted water, no combustion or capacity decay occurred. A stable cycling performance of LMA in symmetrical cells for as long as 500 h and a low capacity decay rate of 0.075% per cycle in an LSB were achieved.

2. Materials and methods

2.1. Chemicals and materials

Wax was purchased from the Aladdin Company. Poly(ethylene oxide)was purchased from Aldrich-Sigma Company. Toluene was purchased from Sinopharm Company. Lithium sheets were purchased from China Energy Lithium Co., Ltd.

2.2. Preparation of the Li-wax-PEO

A simple dip-coating method was used to fabricate the wax-PEO coated LMA (Fig. S1 online). All the chemicals used were treated to remove any residual water. Different amounts of PEO and wax were added to toluene and stirred for 2 h at 80 °C until a clear solution was obtained (Fig. S2 online), revealing they can uniformly mix together to ensure the formation of homogeneous composite coating. Usually, the PEO concentration was fixed at 25 mg mL^{-1} to ensure its dissolution. The coating of PEO and wax onto the lithium was conducted at 80 °C, at which temperature PEO and wax could be dissolved in toluene. Lithium sheets were soaked in the toluene solution of PEO and wax for several seconds, and then removed to evaporate the solvent at 60 °C. After drying, the Li-wax-PEO was available for use.

2.3. Preparation of Li-PEO and Li-wax

The preparation methods of Li-PEO and Li-wax were the same as for the Li-wax-PEO. The concentrations of PEO and wax in toluene were 25 and 100 mg mL^{-1}, respectively.

2.4. Stability tests in air and water

The air stabilities of Li and Li-wax-PEO wax were tested by placed the samples in the air with a relative humidity of about 70%. Water dripping experiment was conducted in air by dripping 20 μL water on Li and Li-wax-PEO. To guarantee the stability of Li-wax-PEO in water, a thicker coating with thickness of about 30 μm was used. The thickness of the coating can be controlled by changing the concentrations of wax and PEO in toluene shown in Fig. S3 (online). The stripping curves were obtained by stripping lithium from Li and Li-wax-PEO at the rate of 0.02 C.

2.5. Electrochemical performance assessment

To assess the electrochemical performance of the samples, symmetric 2032 coin cells were assembled. Both electrodes were made from the same material. Celgard 2400 was used as the separator. 1 mol L^{-1} Lithium bis(trifluoromethanesulphonyl)imide (LiTFSI) in 1,3-dioxolane (DOL):1,2-Dimethoxyethane (DME) (1:1 vol%) with 1 wt% lithium nitrate ($LiNO_3$) was used as the electrolyte. All cell measurements were made on a LAND multi-channel battery testing system. The electrochemical impedance spectroscopy of the cell was evaluated using a BioLogic VMP3 electrochemical workstation. The frequency range was from 100 kHz to 100 mHz.

2.6. Li-S cell assembly

Graphene nanosheets (GNs) were prepared according to previous report [27]. Sulfur and GNs were mixed in a mass ratio of 7:3 and then heated in an argon atmosphere at 155 °C for 12 h to obtain a sulfur-GN composite. Sulfur-GN, conductive additives (SuperP) and polyvinylidene fluoride (PVDF) were then added to N-methylpyrrolidone (NMP) in mass ratios of 8:1:1, and the mixture was stirred for 6 h to obtain a sulfur-containing slurry which was then blade-coated onto aluminum foil. The sulfur electrode was obtained after removing the solvent from the slurry. The mass loading of the electrode was about 2.5 mg cm^{-2}. Li-S cells were assembled with 1 mol L^{-1} LiTFSI in DOL:DME (1:1 vol%) with 1 wt% $LiNO_3$ as the electrolyte and Celgard 2400 as the separator. Li and Li-wax-PEO were used as the anodes for the comparison.

3. Results and discussion

The scanning electronic microscope (SEM) image (Fig. 1b) shows that the surface of the Li-wax-PEO is smooth and the magnified image (Fig. 1c) suggests that the wax-PEO coating is compact and seamless. The thickness of the coating is approximately 4 μm according to cross-sectional SEM image in Fig. 1d. The X-ray diffraction (XRD) pattern of the Li-wax-PEO (Fig. 1e) shows peaks of both wax and PEO indicating the chemical composition of the coating. An infrared (IR) spectrum also suggests the existence of PEO according to the large amount of $-CH_2-$ and C–O–C in the coating (Fig. 1f). Since oxygen only exists in the PEO, the homogeneous mixing of wax and PEO is confirmed by energy dispersive spectroscopy (EDS) mapping which shows a uniform distribution of oxygen in the coating (Fig. 1g, h). The coating with the homoge-

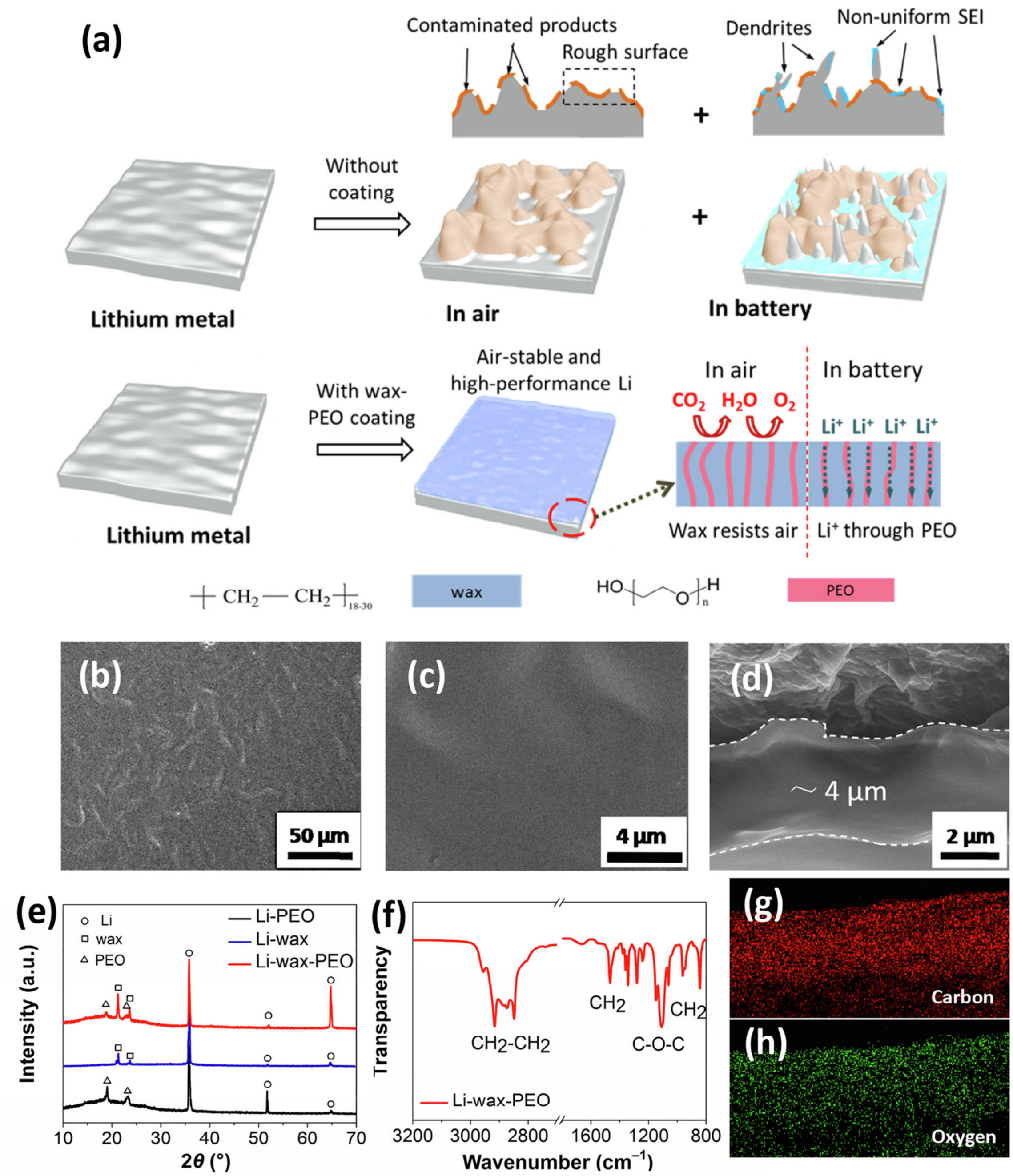

Fig. 1. The diagram and characterizations of the wax-PEO coating. (a) Diagram of the functions of the wax-PEO coating; SEM images of the Li-wax-PEO surface (b) and its magnified area (c); (d) the cross-section image of the Li-wax-PEO; (e) XRD patterns of Li-PEO, Li-wax and Li-wax-PEO; (f) IR spectrum of Li-wax-PEO; (g, h) elemental distributions in the wax-PEO coating for carbon and oxygen.

neously distributed PEO is thus expected to achieve uniform Li ion transport through the diffusion channels on the electrode surface and thus suppress the growth of lithium dendrites. The thermogravimetric analysis (TGA) shows the mass loss of the composite coating mainly starts from about 200 °C (Fig. S4 online), which is much higher than the temperature of batteries working, indicating its good thermal stability in battery.

Due to the different roles of wax and PEO, their ratio will affect the ion conductivity and waterproof property of the composite coating. If the lithium was coated with only PEO (denoted Li-PEO), it turned black in air almost as fast as did the uncoated lithium metal (Fig. S5a online) and some micro cracks were formed in the PEO coating (Fig. S7a–d online). The reason for this is that PEO is a water-soluble polymer and cannot stop moisture from corroding the lithium metal. The electrochemical performance also deteriorates due to the lithium consumption and the production of inactive and ion-insulating LiOH (Fig. S5b online) [28,29]. Therefore the electrochemical performance of symmetric cells using Li-PEO was not improved compared to cells using Li because of the lack of interfacial protection (Fig. S5c online). Thus, Li-PEO does not meet the requirement for an air-stable LMA. In contrast, a wax coating produced an LMA with high air stability after 24 h exposure because it prevents the air from permeating to the lithium surface underneath it (Fig. S6a online), and the micromorphology remains smooth (Fig. S7e–h online). However, wax provides no channels for lithium ion passing through which greatly increases the impedance of the cells (Fig. S6b online) and makes the cells not work normally (Fig. S6c online). Thus, compositing PEO and wax is of great importance, and the electrochemical impedance spectra (EIS) and morphology changes in air of LMAs with different coatings were used to assess the influence of different PEO/wax ratios on the performance. As shown in Fig. S8 (online), when the PEO/wax ratio is 1:2, the air stability of the LMA is as poor as Li-PEO. As the ratio decreases, the air stability of LMA increases but the impedance of the cells also increases because of the low ion conductivity of wax. To balance both the stability in air and the low impedance, a coating with a PEO/wax ratio of 1:4 was chosen for the further test according to the results in Fig. S5 (online).

Contact angle tests in Fig. S9a–c (online) show the contact angles of water on wax, PEO and wax-PEO. They are 101.2° for wax, and 98.4° for the wax-PEO coating, indicating their high hydrophobicity. As a result, the dense structure and the hydrophobicity of the wax-PEO coating give it excellent water resistance. To prove that, lithium metals with or without coating were exposed to air with a high relative humidity of about 70% to access their air stability. The color of uncoated lithium metal changed immediately, and the whole surface turned into blue with the increased exposure time (insets of Fig. 2a, b). SEM images show that the lithium metal changed from a smooth to a particle-covered surface (Fig. 2a, b), and both XRD and infrared spectra indicate the formation of LiOH (Fig. S10a, b online) [29]. In sharp contrast, the surface of the Li-wax-PEO remained the same for 24 h, as indicated by the unchanged color (insets of Fig. 2d, e) and an almost unchanged flat surface during the exposure (Fig. 2d, e), while the chemical components also did not change (Fig. S10a, b online). The dense coating of wax composite guarantees the air-stable property of the lithium metal. The electrochemical behaviors of the LMAs after exposure to air were investigated too. The stripping voltage-specific capacity curves of lithium metal and Li-wax-PEO after exposure to air for

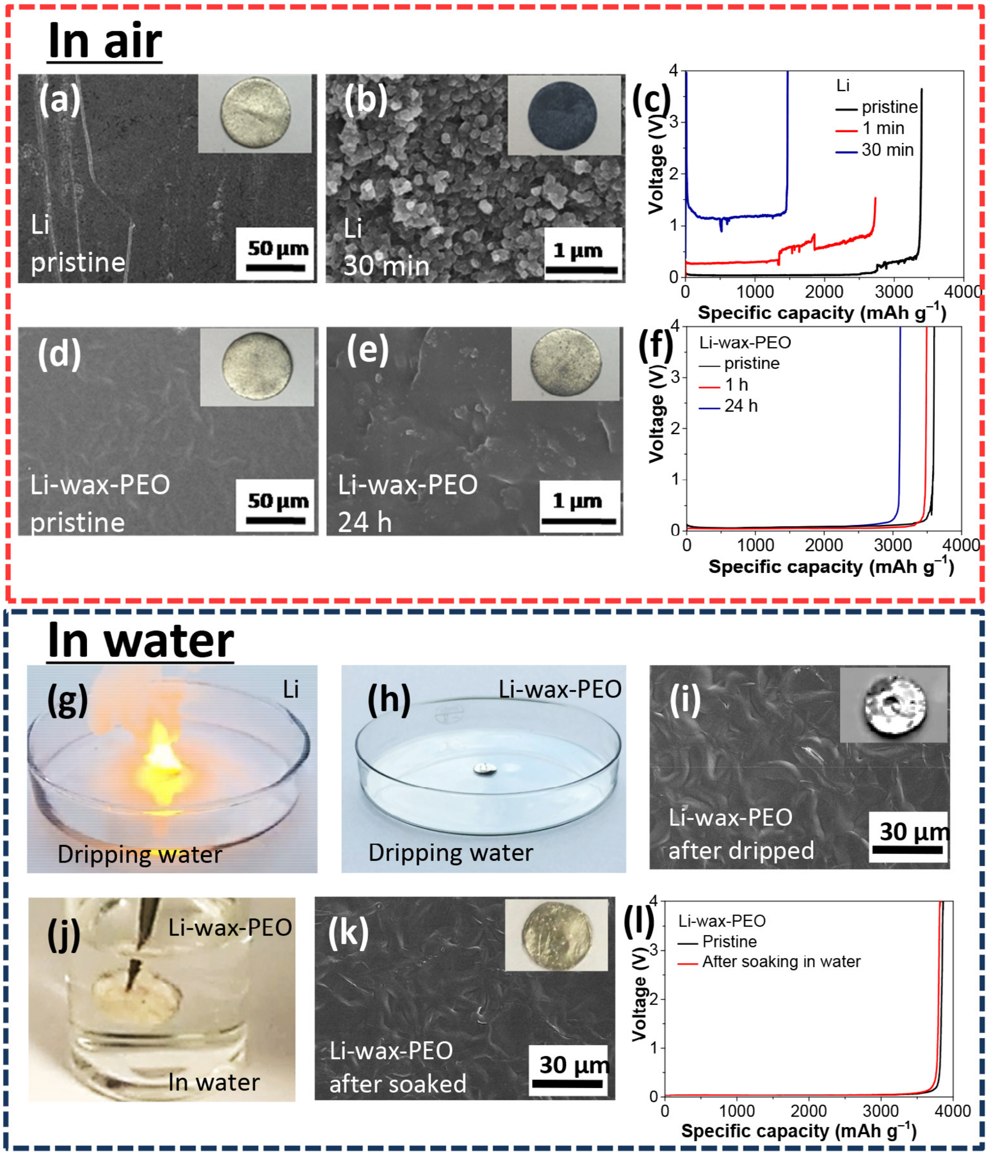

Fig. 2. The stability of Li-wax-PEO and Li in air and water. (a, b) The morphologies of Li before and after exposure to air for 30 min (insert: the optical photos), and (c) the corresponding stripping curves; (d, e) the morphologies of Li-wax-PEO before and after exposure to air for 24 h (insert: the optical photos) and (f) the corresponding stripping curves; the optical photos of (g) Li and (h) Li-wax-PEO when water was dripped on the surface; (i) the morphology of Li-wax-PEO after water dripped (insert: the optical photo); (j) the optical photo when Li-wax-PEO was soaked in water and (k) the morphology of Li-wax-PEO after soaked in water (insert: the optical photo); (l) the stripping curves of Li-wax-PEO before and after soaked in water; The relative humidity of the air was about 70%.

various times are shown in Fig. 2c, f. In the lithium stripping process, the overpotential of the LMA increases from about 40 mV to about 1.2 V after a 30 min exposure to air (Fig. 2c). The specific capacity decayed rapidly to about 44% that of the original lithium metal. The consumption of lithium metal in air caused this decay, and the formation of ion-insulating and electrochemically inactive LiOH on the surface causes the increased impedance resistance [28,29]. In sharp contrast, the electrochemical behavior of Li-wax-PEO after one day exposure to air was almost unchanged (Fig. 2f). The overpotential remained stable at about 68 mV, while the specific capacity retention was as high as 85% of the original one.

To further prove the viability of the coating, the waterproof property of Li-wax-PEO was assessed. When a small amount of water was dripped onto the Li and Li-wax-PEO, the Li caught fire when contacting with water due to the drastic reaction between lithium and water, after which its morphology totally changed (Fig. 2g, Video S1 online). There were no visible changes on the surface of the Li-wax-PEO (Fig. 2h, i, Video S2 online). Moreover, when the Li was soaked in water, the production of hydrogen bubbles was obviously observed immediately (Video S3 online), after which the surface of the Li changed into a rough and black one (Video S3 online). In sharp contrast, no obvious gas production or a change of the surface morphology was observed when soaked Li-wax-PEO in water (Fig. 2j, k, Video S4 online). The electrochemical behaviors of Li-wax-PEO before and after soaked in water have also been tested, and the stripping curves are shown in Fig. 2l, which suggest that the water contact hardly change the overpotential and specific capacity of Li-wax-PEO. The dense structure and hydrophobicity of wax-PEO composite coating ensure its resistance to water and other oxidants in the air that might come into contact with the surface of the LMA.

Symmetrical coin cells were assembled to further evaluate the electrochemical viability of the wax-PEO coating. Cycling tests (Fig. 3a–c) show that the stability of the Li-wax-PEO cells was better than that for lithium metal cells. The overpotentials of Li-wax-PEO cells in the first few cycles were slightly larger than those of lithium metal cells, due to the coating layer restricting lithium ion transport to some extent, but they remained stable even after a large number of cycles. The electrochemical performance of the

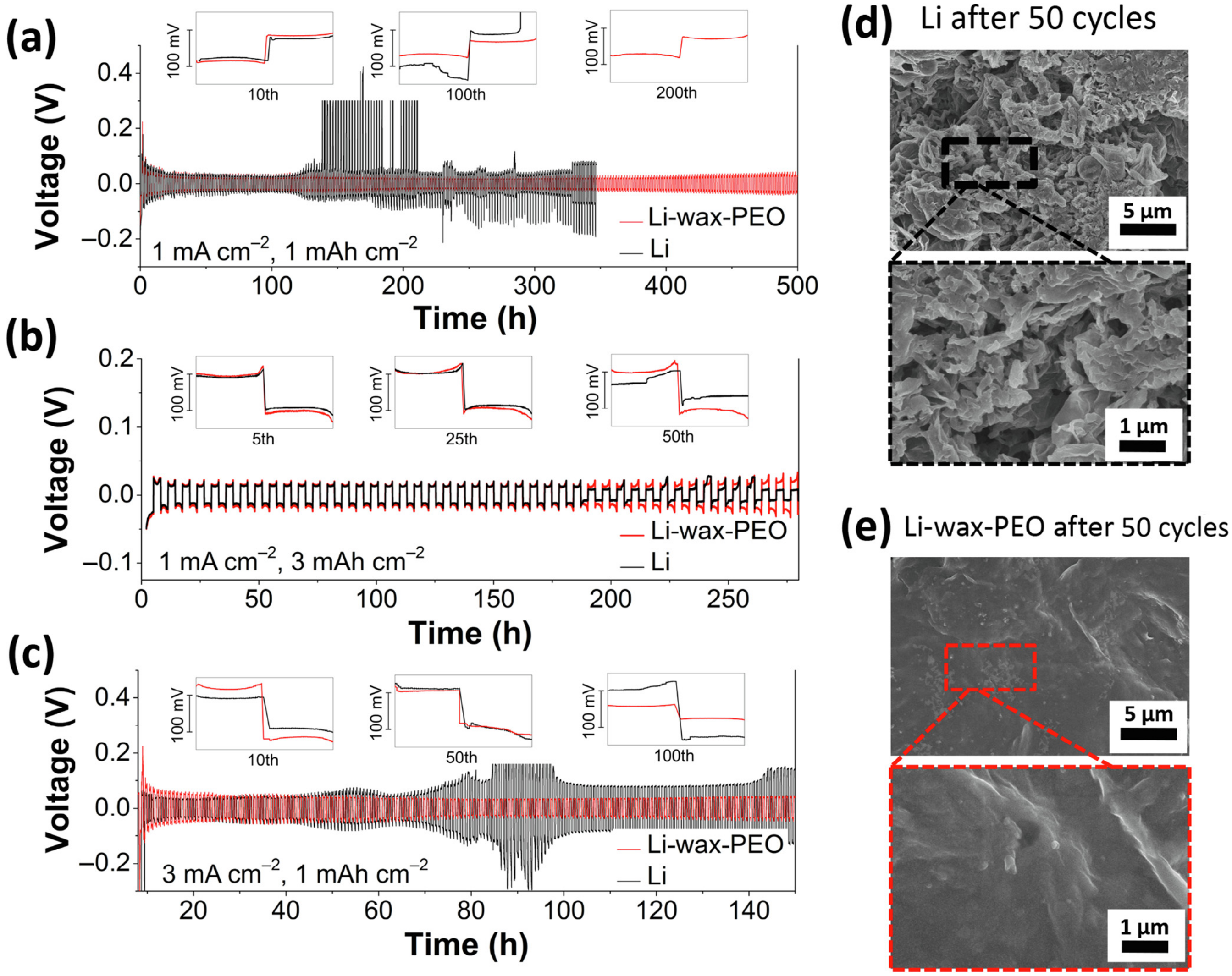

Fig. 3. The test results for Li and Li-wax-PEO in symmetric cells. (a–c) Comparison of the cycling performance of symmetric cells of Li-wax-PEO and Li. (a) Voltage-time curve of the cells cycling at a rate of 1 mA cm^{-2} with a plating/stripping capacity of 1 mAh cm^{-2} (insert: charge/discharge curves at different cycles); (b) voltage-time curves of the cells cycling at a rate of 1 mA cm^{-2} with a plating/stripping capacity of 3 mAh cm^{-2} (insert: charge/discharge curves at different cycles); and (c) voltage-time curves of the cells cycling at a rate of 3 mA cm^{-2} with a plating/stripping capacity of 1 mAh cm^{-2} (insert: charge/discharge curves at different cycles). (d–e) Optical microscope images of the morphologies of (d) Li and (e) Li-wax-PEO after the cycling tests.

Li-wax-PEO cells remained steady even after 500 h at a rate of 1 mA cm^{-2} with a plating/stripping capacity of 1 mAh cm^{-2}. In contrast, the overpotential of lithium metal increased and the electrochemical behavior became abnormal in cycling. Increasing the plating/stripping capacity to 3 mAh cm^{-2} and the rate to 3 mA cm^{-2}, the cycling performances of Li-wax-PEO was much better than those of the uncoated lithium metal. When the thickness of the coating increased to 30 μm to achieve the better waterproof performance, although the coating resistance increased (Fig. S12 online), the symmetrical cells still showed a steady cycling performance (Fig. S12b online). The improved electrochemical performance of Li-wax-PEO is ascribed to the wax preventing the electrolyte etching lithium metal and thus providing stable interface between the electrolyte and the lithium metal. To prove this, the Li-wax-PEO was soaked in the electrolyte for 5 days, and its surface had hardly changed as shown in Fig. S11 (online). After cycling tests, the surface morphology of the uncoated lithium metal was much rougher than that of Li-wax-PEO, and lithium dendrites were observed (Fig. 3d and e), clearly showing the advantages of the wax-PEO coating. Another reason for the improved performance is that the PEO in the coating provides sufficient diffusion channels for lithium ions and regulates regulate the lithium ion flux and thus realize homogeneous lithium deposition [26,30].

LMA is ideal for matching the needs of high energy density systems with a lithium-free cathode [31,32]. Here, lithium sulfur batteries were assembled to evaluate the potential for the practical use of the Li-wax-PEO anode. The sulfur cathode was prepared with a composite of sulfur and graphene by the slurry coating method. The sulfur content in the cathode was 56 wt%, and the mass loading of sulfur was about 2.5 mg cm^{-2}. In Li-S batteries, surface corrosion of the bare LMA often occurs due to the shuttling of lithium polysulfides (LiPSs) from the cathode to the anode and the resulting reactions with Li to form Li_2S_2/Li_2S [32–34]. With the protection of the wax-PEO coating, the above reactions between polysulfides and the LMA are inhibited. This protecting function is proven by SEM images of the electrode surfaces after 50 cycles (Fig. 4a and b). Corrosion is clearly observed on the uncoated Li surface while the surface of the Li-wax-PEO is hardly changed. EIS tests show that the impedance of the cells with the Li-wax-PEO is smaller, suggesting a better interfacial state of the Li-wax-PEO as well (Fig. 4c). During galvanostatic tests, the initial overpotential of the Li-wax-PEO cells was slightly higher than that of the Li cells due to the slight restriction of ion conduction by the

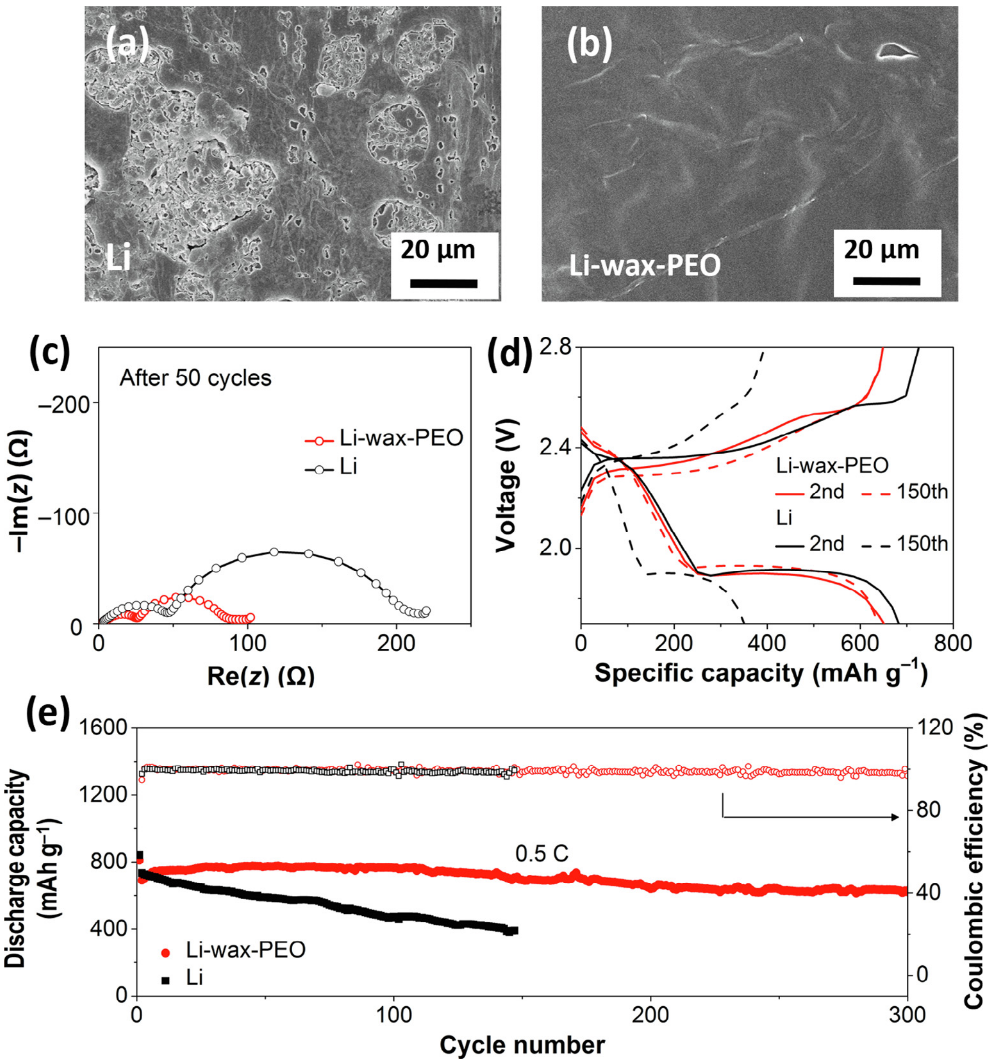

Fig. 4. Test results for Li and Li-wax-PEO in lithium-sulfur cells. The surface morphologies of (a) the Li anode and (b) the Li-wax-PEO anode after 50 cycles; (c) EIS of the two anodes after 50-cycles; (d) the charge and discharge curves of cells with a Li anode and a Li-wax-PEO anode at the 2nd and 150th cycles; (e) comparison of the cycling performance of cells with Li and Li-wax-PEO anodes.

coating, but after a few cycles, the overpotentials of the Li cells increased greatly and changed more than those of Li-wax-PEO cells (Fig. 4d and S9a, b online). The better electrochemical behavior is due to the aforementioned surface protection of the wax-PEO. When the rate was increased to 1C, the capacity of the Li-wax-PEO cells remained at 607 mAh g^{-1} (Fig. S9c online). For a long-cycle test, the discharge capacity of Li cells decreased to 390 mAh g^{-1} after 150 cycles at a charge/discharge rate of 0.5 C. But the discharge capacity of Li-wax-PEO cells was as high as 776 mAh g^{-1}, and a stable cycling performance of 300 cycles with decay rate of 0.075% per cycle was achieved (Fig. 4e).

4. Conclusion

In summary, we have developed a method of improving both the stability in air and even in water and electrochemical performance of lithium metal by applying a composite coating of wax and PEO. This dense thin coating is hydrophobic and ionically conductive, for the combination of properties of wax and PEO. It packages the lithium metal to avoid adverse surface-related reactions, and this makes it possible for lithium metal anodes with this coating to remain stable in air with relative humidity of 70% for more than one day, and no combustion happens even in contact with water. From the perspective of electrochemical performance, wax inhibits adverse interfacial reactions between the electrolyte and the LMA, while the PEO provides conducting paths for the Li^+ and regulates the ion flux. Therefore, in symmetric cells, increased cycling stability of more than 500 h was achieved. When paired with a sulfur cathode, the wax-PEO coating allows Li^+ ions to access the LMA while inhibiting polysulfides from corroding it, and as a result the capacity decay of the cells was as low as 0.075% per cycle after 300 stable cycle tests. This simple method of modifying the surface of lithium metal also has potential for use with other air-sensitive electrode materials or structures in future research and large-scale production.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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Author contributions

Q.H.Y. and W.L. managed the project and guided the research; W.L. conceived and Y.Z., G.Z. and Q.H.Y. developed the concept. W.L. and Y.Z. designed the experiment. Y.Z. carried out the material synthesis, characterizations and electrochemical measurements with the helps from Z.H., C.Z. and J.Z. G.Z. gave many important inputs to the air stability and water proof tests. Q.Q. and B.H. conducted lithium-sulfur battery tests. Y.-B.H. and F.K. involved in the discussion. Y.Z. wrote the manuscript with the supervision of W.L. and Q.H.Y. and all authors have approved the final manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scib.2019.05.025.

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