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Polar interaction of polymer host-solvent enables stable solid electrolyte interphase in composite lithium metal anodes

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ABSTRACT

The lithium (Li) metal anode is an integral component in an emerging high-energy-density rechargeable battery. A composite Li anode with a three-dimensional (3D) host exhibits unique advantages in suppressing Li dendrites and maintaining dimensional stability. However, the fundamental understanding and regulation of solid electrolyte interphase (SEI), which directly dictates the behavior of Li plating/ stripping, are rarely researched in composite Li metal anodes. Herein, the interaction between a polar polymer host and solvent molecules was proposed as an emerging but effective strategy to enable a stable SEI and a uniform Li deposition in a working battery. Fluoroethylene carbonate molecules in electrolytes are enriched in the vicinity of a polar polyacrylonitrile (PAN) host due to a strong dipole-dipole interaction, resulting in a LiF-rich SEI on Li metal to improve the uniformity of Li deposition. A composite Li anode with a PAN host delivers 145 cycles compared with 90 cycles when a non-polar host is employed. Moreover, 60 cycles are demonstrated in a 1.0 Ah pouch cell without external pressure. This work provides a fresh guidance for designing practical composite Li anodes by unraveling the vital role of the synergy between a 3D host and solvent molecules for regulating a robust SEI.

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1. Introduction

The expanding demands for portable electronics and electromobility have stimulated the intensive development of high-energydensity rechargeable batteries [1,2]. Lithium (Li) metal is considered as one of the most attractive anode materials, due to its ultrahigh theoretical specific capacity (3860 mAh g^{-1}) and the low electrode potential (-3.04 V vs. standard hydrogen electrode), far outperforming the conventional graphite anode (372 mAh g⁻¹) in Li-ion batteries [3]. Nevertheless, the practical applications of Li metal anode have been plagued for decades on account of dendrite growth and large volume fluctuations during repeated plating/stripping cycles which lead to an inferior lifespan and serious safety concerns [4-8].

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A large number of strategies have been explored to overcome the aforementioned challenges, such as liquid/solid electrolyte design [9–13], artificial protective layers [14–17], and composite Li anodes [18,19]. A large current density (>3.0 mA cm^{-2}) and a high cycle capacity (>3.0 mAh cm⁻²) are required under practical conditions in a working battery [20,21]. In this respect, the regular hostless Li metal experiences a virtually infinite volume fluctuation, resulting in enormous mechanical instability. A composite Li anode with a three-dimensional (3D) host can maintain dimensional stability because it can confine Li deposition in interconnecting pores, diminishing the volume fluctuation during repeated cycles [22-24]. In addition, the lithiophilic sites [25] and selfadaptable pressure [26,27] are effective in regulating behaviors of Li plating/stripping, endowing much promise to achieve stable composite Li anodes. Therefore, composite Li anodes have been strongly considered to promote the advances of Li metal batteries.

However, the cycle stability of composite Li anodes is still hindered by non-uniform Li deposition inside a 3D host. Although Li

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metal plates or strips inside host pores, the exposure of Li deposition to liquid electrolyte is necessary to maintain a stable ion transport in a composite Li anode [28–31]. The formation of solid electrolyte interphase (SEI) on Li metal is inevitable due to the well-known high reactivity of Li metal [32–34]. SEI plays a vital role in dictating the uniformity of Li deposition. Generally, the generation and function of SEI in a composite Li anode is similar to that in a routine Li anode without any host. However, the introduction of a host with distinctive physicochemical properties compared with Li metal can alter the formation process of SEI. Tuning the interaction between the polar polymer host and polar solvent molecules provides a lever to control the reaction with Li metal. Therefore, in addition to the design of electrolyte formulations, understanding and regulating the interaction between the host and solvent molecules provides a promising avenue to further regulate a stable SEI and enhance the uniformity of Li deposition in a composite Li anode.

In this contribution, the interaction between a polar host and solvent molecules was investigated and proposed as an effective strategy to tailor a stable and uniform SEI and thus improved the uniformity of Li deposition inside a composite Li anode. Fluoroethylene carbonate (FEC) was selected as a representative polar solvent molecule and the electrospinning polyacrylonitrile (ELPAN) was employed as a polar host. There is a strong dipole-dipole interaction between ELPAN and FEC. Consequently, FEC molecules tend to be enriched in the vicinity of ELPAN fibers in Li-containing composite anodes (Li/ELPAN), which results in a LiF-rich SEI on Li metal (Fig. 1a). The LiF-rich SEI enhances the uniformity of Li deposition and further retards dead Li accumulation. In contrast, a routine SEI forms if there is a weak interaction between the host and solvent molecules, which cannot further improve the uniformity of Li deposition (Fig. 1b). Under practical conditions, the full cell with a Li/ELPAN maintains 145 stable cycles with a capacity retention of 80% in comparison to a common composite Li anode only retains 90 cycles. Moreover, a 1.0 Ah pouch cell performs 60 cycles without external pressure, demonstrating the practical potential of the proposed approach.

2. Experimental

2.1. Fabrication of ELPAN, ELPS, Li/ELPAN and Li/ELPS electrode materials

ELPAN and ELPS: solution of 12 wt% PAN (M_w = 150 000, Aldrich) was employed as the electrospinning precursor for spin-

ning on an electrospinner (ET-2535H, Beijing Ucalery Technology Development Co., Ltd) and the solvent is dimethyl sulfoxide (DMSO, 98% purity, Alfa). A high voltage of 12.9 kV was adopted and the distance between the needle and drum collector was fixed at 18 cm. The flow rate of the solution maintained at 0.52 mL h⁻¹ using a needle with a diameter of 0.51 mm and a constant rotational speed of drum collector at 80 rpm. The same method and parameters were applied to fabricate ELPS materials.

Li/ELPAN and Li/ELPS: the hosts were shelved in the Ar-filled glove box with the content of O₂ and H₂O below 0.1 ppm for drying. The composite anodes were fabricated by rolling method. The ELPAN and ELPS hosts were cut into strips with the same width of 5.0 cm as ultrathin Li foils (33 μ m, 99.9%, China Energy Lithium Co., Ltd.). The hosts and ultrathin Li foils were stacked and rolled in a roller press (Shenzhen Kejing Star Technology Co., Ltd.). The rolling process was carried out in the dry room with a dew-point temperature of -40 °C.

2.2. Material characterization

A scanning electron microscope (JSM 7401F, JEOL, Japan) was employed to characterize the morphology of electrode materials and deposited Li. The deposited Li sample obtained from disassembled cells were firstly cleaned by 1,2-dimethoxyethane (DME) solvent three times, and then dried until the solvent was thoroughly volatilized in a glove box with the content of O_2 and H_2O below 0.1 ppm.

Additionally, the inner structure of pristine Li/ELPAN was observed by a focus ion beam-scanning electron microscope (FIB-SEM, S9000, Tescan, Czech Republic). The samples were sealed in an Ar-filled bottle before transferring into the vacuum chamber. The Xe ion source was employed and the SEM images were taken at the voltage of 5 kV.

Fourier-transform infrared spectra of the hosts and solvents were obtained by employing the Nicolet 6700 (Thermo Fisher Scientific Inc., USA). The hosts were directly measured and the solvents were dropped into the potassium bromide slice and then the solvents were dropped onto the hosts to detect the interaction.

An Al K_{α} radiation (72 W, 12 kV) at a pressure of 10^{-9} torr was applied to obtain X-ray photoelectron spectroscopy (XPS) spectra on ESCALAB 250Xi (Thermo Fisher Scientific Inc., USA). The diameter of the analyzed area was 400 μ m. The Ar ion sputtering rate of the XPS depth-profiling calibrated on SiO₂ surface was approximately 20 nm min⁻¹. The 1.0 M lithium perchlorate (LiClO₄, 99% purity, Alfa) in fluoroethylene carbonate (FEC, 98% purity, Suzhou Duoduo Chemical Technology Co. Ltd)/dimethyl carbonate (DMC,



Fig. 1. Schematic illustration of the polar interaction between the polymer host and solvent molecules in a composite Li anode. (a) Polar polyacrylonitrile (PAN) and (b) nonpolar polystyrene (PS) host. The strong dipole-dipole interaction between FEC molecules and a PAN host enables the formation of LiF-rich SEI on Li metal to achieve uniform Li deposition.

99% purity, Suzhou Duoduo Chemical Technology Co. Ltd) (1:4, by volume) was employed as the electrolyte in order to make sure that the components containing fluorine in SEI were totally from the decomposition of FEC. The results were obtained after etching for 1, 3, and 5 mins on different composite Li anodes.

2.3. Electrochemical measurements

All coin cells were assembled with standard CR2032 coin-type cells in an Ar-filled glove box with O₂ and H₂O content below 0.1 ppm. The polypropylene film (Celgard 2400) was employed as the separator. The electrodes were punched into 13 mm diameter for coin cells, such as Li/ELPAN and Li/ELPS. They were employed as working electrodes in half cells in which the counter electrode was Li foil (600 µm in thickness). Li | Li/ELPAN half cells were assembled to observe the location and morphology of deposited Li at a current density of 1.0 mA cm⁻² with a high capacity of 2.5 mAh cm⁻². The 1.0 M hexafluorophosphate (LiPF₆, 99% purity, Suzhou Duoduo Chemical Technology Co. Ltd) in FEC/DMC (1:4, by volume) was employed as the electrolyte. Moreover, the 1.0 M LiPF₆ in vinylene carbonate (VC, 98% purity, Alfa)/DMC (1:4, by volume) was employed as electrolyte to demonstrate the fundamental understanding and regulation of SEI in composite anodes are general instead of specific.

The LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ (NCM523, 2.5 mAh cm⁻²) cathode and 33 μ m ultrathin Li metal with a diameter of 15.0 mm were employed in full cells. The NCM523 full cells were monitored in galvanostatic mode within a voltage range of 2.8 to 4.3 V, which were firstly cycled at 0.1 C and then cycled at 0.4 C. The charge/discharge tests of all coin cells were performed on a Neware multichannel battery tester (CT-4008 T-5 V10 mA-164, Shenzhen, China) in a testing room with a constant temperature of 25 °C. The amount of electrolyte is 50 μ L in the symmetrical and full coin cells. And the electrolyte uptake of ELPAN host is 8.75 mg cm⁻².

Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 10^{-2} – 10^{5} Hz with a perturbation of 10 mV in amplitude, performing on a Solartron 1470E

electrochemical workstation (Solartron Analytical). The software of ZView was employed to fit the resistance.

The pouch cells were assembled in dry room with a dew-point temperature of -40 °C. A layer-by-layer process has been employed to alternate the cathodes and anodes with the polyethy-lene separator in pouch cells. All pouch cells were tested on a Land CT2001 multichannel battery tester (Wuhan Land Electronic Co., Ltd.) in the environmental oven (SEG-021, Espec, Environmental Equipment Corp., Ltd.) with a constant temperature of 25 °C and under a fixing device to prevent the pouch cells from moving randomly.

2.4. Theoretical calculations

The first-principles calculations were conducted in Gaussian (G09) program with Becke's three-parameter hybrid method using the Lee–Yang–Parr correlation functional (B3LYP) at the 6–311++G (d, p) level. The universal solvation model of SMD was used to describe the solvation effects in DMC environment with a dielectric constant of 3.107. A trimer and monomer of PAN and PS polymers were adopted to interact with electrolyte solvents based on a cluster model, respectively. Frequency analysis was performed to ensure the ground state of optimized molecules. The binding energy (E_b) between polymer and solvent is defined as following:

$$E_{\rm b} = E_{\rm polymer-solvent} - E_{\rm polymer} - E_{\rm solvent} \tag{1}$$

where $E_{\text{polymer-solvent}}$, E_{polymer} , and E_{solvent} are total energy of polymer–solvent, polymer, and solvent clusters, respectively. The dipole moments of molecules are calculated by the same method.

3. Results and discussion

The lightweight polymer host with excellent mechanical property is a promising candidate of 3D hosts for composite Li anodes towards practical applications [24,34–37]. Electrostatic spinning is a simple and important way for processing polymers to obtain a free-standing structure with moderate specific surface and porous structure [38]. The ELPAN and electrospinning polystyrene



Fig. 2. Bird-view SEM images of the pristine (a) Li/ELPAN (top panel) and Li/ELPS (bottom panel). (b) FIB-SEM images of a Li/ELPAN and the partial enlarged image (bottom panel). (c) Electrostatic potential maps of PAN and FEC molecule. (d) FT-IR spectra of hosts, solvents or combinations: ELPAN and FEC (left panel), ELPAN and DMC (centre-left panel), ELPS and FEC (centre-right panel) and ELPS and DMC (right panel). (e) Summary of the calculated binding energy between two polymers and solvent molecules.

(ELPS) were employed as the hosts due to the distinctive difference in polarity. The dipole moment of PAN and PS monomer is 9.25 and 0.22, respectively (Table S1). The Li-containing composite anodes (Li/ELPAN and Li/ELPS) were fabricated by a facile method of rolling a host with an ultrathin Li foil (33 μ m, Fig. S1). The role of FEC in forming a stable LiF-rich SEI has been extensively investigated in other recent works (Scheme S1) [39,40]. Therefore, the mixture of FEC/dimethyl carbonate (FEC/DMC, the volume ratio is 1:4) was selected as the representative carbonate solvent in this contribution.

The morphologies of polymer hosts and composite Li anodes were recorded by scanning electron microscopy (SEM) and focused ion beam-scanning electron microscopy (FIB-SEM). The ELPAN and ELPS hosts possess similar pore structure by adjusting the parameters of electrospinning. The diameter of the fiber and the average size of pores distribute around 200 nm and 10 µm, respectively (Fig. S2). Li metal is extruded into a 3D host and little Li metal can be observed from the bird view (Fig. 2a and S3). The thickness of two composite anodes is around 40 µm (Fig. S4) and the Li/

ELPAN delivers a large specific capacity of 2660 mAh g^{-1} based on the weight of the whole composite anode (Fig. S5) [41]. The internal structure of the Li/ELPAN was obtained by employing FIB (Fig. S6). Li metal conformally contacts with host fibers inside the composite anode and the surface of Li metal is completely covered by the fibers (Fig. 2b). Consequently, solvent molecules enriched in the vicinity of host fibers can directly touch with Li metal in the Li/ELPAN.

There are a large number of polar cyano-group (C \equiv N) in an ELPAN host. The relatively positive charge is localized on the carbon atom of C \equiv N group. Similarly, the negative charge is localized on the oxygen atom of carbonyl-group (C=O) in an FEC molecule (Fig. 2c) [42]. Due to the local dipoles composed of atoms carrying opposite charges, the C \equiv N group of PAN interacts with the C=O group of FEC, forming a dipole–dipole interaction, which is much stronger than that with an acyclic carbonate of DMC. The interaction between the polymer host and solvent molecules is probed by fourier transform infrared spectra (FT-IR). The peak of 2240 cm⁻¹ is attributed to the C \equiv N group in the spectrum of ELPAN (Fig. 2d)



Fig. 3. XPS spectra of the SEI formed in a Li/ELPAN (left panel) and Li/ELPS (right panel) after 5 cycles in symmetric cells. (a) Li 1s spectra and (b) F 1s spectra. The corresponding peak area ratio retrieved from (c) Li 1s and (d) F 1s spectra. Bird-view SEM images of Li plating on the (e) Li/ELPAN and (f) Li/ELPS after 5 cycles in symmetric cells.

[43]. The explicit evidence of polymer–solvent interaction is exhibited by an additional band around 2350 cm⁻¹ in the ELPAN–FEC spectrum. In contrast, neither peak shift nor additional peak is observed related to the peak of 2240 cm⁻¹ in the ELPAN–DMC spectrum, indicating that there is no polar interaction between ELPAN and DMC. When employing a non-polar host of ELPS, the peaks in the range of 1450–1650 cm⁻¹ are assigned to the vibration of the benzene in ELPS. There is little polar interaction between ELPS and solvent molecules, which is confirmed by the comparison of the peak of functional groups in ELPS, pure solvent, and ELPS– solvent (FEC or DMC).

The interaction between the polymer and solvent molecules was quantitatively described based on theoretical calculations (Fig. S7). The binding energy which represents the interaction strength between the polymer and solvent molecules is summarized in Fig. 2e. The binding energy of PAN–FEC is more than twice than that of PAN–DMC ($-9.07 \text{ vs} - 4.22 \text{ kJ mol}^{-1}$), confirming FEC molecules tend to be enriched in the vicinity of ELPAN fibers. In contrast, PS has no priority for FEC and DMC molecules since PS has a weak interaction with FEC and DMC (-1.04 and $-1.81 \text{ kJ mol}^{-1}$, respectively). Therefore, FEC molecules tend to aggregate in the vicinity of ELPAN instead of ELPS. The enriched FEC can directly contact and react with Li metal [44], becoming the ingredients of SEI. Therefore, the SEI in a Li/ELPAN is adjusted

due to the alteration of species and number of solvent molecules in the vicinity of ELPAN compared with ELPS.

X-ray photoelectron spectroscopy (XPS) was conducted to reveal the chemical features of SEI in the composite Li anode with an ELPAN or ELPS host. Lithium perchlorate (LiClO₄) was employed as the Li salt in order to make sure that the components containing fluorine totally stem from the decomposition of FEC. The average content of LiF is 46.9% in the whole SEI of a Li/ELPAN compared to 22.5% in a Li/ELPS according to the ratio of peak area in Li 1s spectra, confirming that more FEC molecules decompose on Li metal in a Li/ELPAN due to the strong interaction (Fig. 3a and c). LiF is generally regarded as an effective component in SEI for uniform and fast Li ion transport [45–50] and thus the SEI formed in a Li/ELPAN is in favor of uniform Li plating/stripping. In addition, the proportions of various components have a little change as the sputtering time increases in the SEI of the Li/ELPAN but a large variation of the Li/ELPS, indicating that a uniform SEI is achieved by the strong interaction between the ELPAN and solvent molecules. A similar result can be obtained in F 1s spectra. The two peaks of 685.1 and 686.6 eV are assigned to LiF and species with C-F bond, respectively (Fig. 3b). The average proportion of LiF is 83.9% in the SEI of a Li/ELPAN compared to 58.7% in a Li/ELPS (Fig. 3d), further indicating the attached Li has more opportunities to react with FEC, which renders the increase of LiF in SEI on the surface of Li metal.



Fig. 4. The cycling performance of full batteries under practical conditions. (a) The cycling performance of coin cells with an NCM523 cathode and different anodes at 0.4 C. (b) The corresponding voltage profiles of coin cells at the 10th and 100th cycle with a Li/ELPAN or Li/ELPS. (c) The cycling performance of a 1.0 Ah pouch cell at 0.1 C. (d) The voltage–capacity profiles of the pouch cell at the 3rd and 30th cycle.

The morphologies of Li plating/stripping were investigated in different composite anodes to evaluate the uniformity of SEI. There are few Li dendrites on the surface of the Li/ELPAN and the Li deposition in pores is dense and smooth with a capacity of 2.5 mAh $\rm cm^{-2}$ at the 5th plating, which demonstrates the uniformity of Li deposition is significantly enhanced with a uniform LiF-rich SEI (Fig. 3e). In contrast, dendrites and protrusions are observed in pores of a Li/ ELPS, performing inhomogeneous Li deposition (Fig. 3f). Additionally, there is little dead Li in a Li/ELPAN during Li stripping in comparison to a Li/ELPS with considerable dead Li (Fig. S8). The behaviors of Li plating/stripping have been prominently improved, which is contributed by the uniform LiF-rich SEI induced by the interaction between ELPAN and FEC. Electrochemical impedance spectroscopy (EIS) measurements were carried out to reveal the resistance of the SEI in different composite anodes [51–54]. The semicircle of high frequency can be attributed to the resistance of Li ion transport through SEI (Fig. S9) [55,56]. The cell with a Li/ELPAN exhibits evidently lower transport resistance than that with a Li/ELPS (60.5 vs 85.5 Ω). Consequently, the LiF-rich SEI induced by the interaction between ELPAN and FEC can reduce transport resistance of Li ion in SEI and promote the uniform Li plating/stripping in a Li/ELPAN.

To further demonstrate the potential of the regulation of SEI in composite anodes under practical conditions, the full cells were assembled combining with a high loading LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ (NCM523, 2.5 mAh cm⁻²) cathode and a low N/P ratio (~2.6) [57]. The capacity of planar Li | NCM523 coin cell rapidly fails after 60 cycles at 0.4C under the benchmark of 80% capacity retention (Fig. 4a). The cycle life of the cell employing a Li/ELPS is prolonged to 90 cycles and the cell with a Li/ELPAN delivers 145 cycles, significantly demonstrating the preponderance of the Li/ELPAN with a LiF-rich SEI. In addition, the initial middle voltage is 3.77 V in the cell with a Li/ELPAN, which is similar to 3.76 V of the cell with a Li/ELPS (Fig. 4b). However, the overpotential with a Li/ELPS appreciably increases from the 10th to 100th cycle, indicating that significant amounts of dead Li accumulate in the pores of the 3D hosts due to the unstable SEI and thus increasing the Li ion transport resistance. In contrast, the small overpotential of Li/ELPAN | NCM523 cells illustrates the uniform morphology of Li deposition and decreased dead Li owing to the LiF-rich SEI in the Li/ELPAN. The Li/ELPAN was further employed in a pouch cell with a highloading cathode of 4.0 mAh cm⁻², lean electrolytes of 3.0 g Ah⁻¹, and a low N/P ratio of 1.6. The specifications of the pouch cell are exhibited in Table S2 [58]. The first discharge capacity of the pouch cell is 0.92 Ah and it can achieve 60 cycles when the capacity declines to 80% at 0.1 C with a minor polarization (Fig. 4c and d).

To demonstrate the extensibility of the above fundamental understanding and regulation of SEI, vinylene carbonate (VC) with C=O group was employed to substitute FEC. VC has been regarded as an effective film-formation additive to improve the cycle stability of Li metal anode [59]. The interaction between C=O group in VC and the C=N group of ELPAN is reasonable. The cycle life of the cell with a Li/ELPAN is twice longer than that with a Li/ELPS (160 vs. 79 cycles, Fig. S10). Therefore, the fundamental understanding and regulation of SEI in composite anodes are general instead of specific.

4. Conclusions

The polar interaction between polymer hosts and solvent molecules is proposed as an effective strategy to render a stable and uniform SEI inside a composite Li anode. There is a strong dipole–dipole interaction between $C \equiv N$ group of ELPAN and the C = O group of FEC. Consequently, FEC molecules tend to be enriched in the vicinity of ELPAN host fibers and then decompose to form a LiF-rich SEI on Li metal. The LiF-rich SEI formed inside a Li/ELPAN enhances the uniformity of Li deposition and further retards electrolyte consumption and dead Li accumulation. The full coin cell with a Li/ELPAN undergoes 145 cycles under practical conditions while the cell with a Li/ELPS rapidly fails after 90 cycles. Moreover, a 1.0 Ah pouch cell achieves 60 cycles without external pressure, demonstrating the practical potential of the proposed approach. This work uncovers the fresh but vital role of the interaction between hosts and solvent molecules in tailoring SEI and provides a fresh guidance for designing practical composite Li anodes.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jechem.2021.04.045.

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