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Natural protein as novel additive of a commercial electrolyte for Long-Cycling lithium metal batteries



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ABSTRACT

Keywords: Zein Electrolyte additive Lithium metal Carbonate-ester electrolyte Solid electrolyte interphase Suffering from critical instability of lithium (Li) anode, the most commercial electrolytes, carbonate-ester electrolytes, have been restrictedly used in high-energy Li metal batteries (LMBs) despite of their broad implementation in lithium-ion batteries. Here, abundant, natural corn protein, zein, is exploited as a novel additive to stabilize Li anode and effectively prolong the cycling life of LMBs based on carbonate-ester electrolyte. It is discovered that the denatured zein is involved in the formation of solid electrolyte interphase (SEI), guides Li⁺ deposition and repairs the cracked SEI. In specific, the zein-rich SEI benefits the anion immobilization, enabling uniform Li⁺ deposition to diminish dendrite growth; the preferential zein-Li reaction effectively repairs the cracked SEI, protecting Li from parasite reactions. The resulting symmetrical Li cell exhibits a prolonged cycling life to over 350 h from <200 h for pristine cell at 1 mA cm⁻² with a capacity of 1 mAh cm⁻². Paired with LiFePO₄ cathode, zein additive markedly improves the electrochemical performance including a higher capacity of 130.1 mAh g⁻¹ and a higher capacity retention of ~ 80 % after 200 cycles at 1 C. This study demonstrates a natural protein to be an effective additive for the most commercial electrolytes for advancing performance of LMBs.

1. Introduction

Rechargeable lithium metal batteries (LMBs) are attractive energy storage devices for future electric vehicles (EVs) due to their extremely high weight energy density [1–3]. However, the commercialization of LMBs is impeded by safety concerns and poor cycle performance [4]. The safety issues are caused by the growth of lithium (Li) dendrites during cycling process, which can lead to short circuit and trigger fire or even explosion. The serious energy density decay of LMBs is induced by multiple factors, that is, uneven Li ion deposition, enormous volume change of Li, Li dendrite growth, dead Li particle formation, unstable solid electrolyte interphase (SEI), etc. [5]. During the Li ion stripping and plating processes, uneven Li ion flux leads to the formation of Li dendrites [6]. The strain derived from the infinite volume change of Li anodes destroys Li dendrites and leads to the formation of dead Li particles [7]. The exposed fresh Li from cracked SEI layer causes continuous side reactions between Li and liquid electrolytes [8].

Over the past decades, numerous efforts have been reported to solve the above issues by applying protective films on Li anodes [9,10], solid electrolytes [11,12], separator coatings [13,14], nanostructured Li anodes/current collectors [15–17], or modifying electrolyte compositions

[18]. Endorsed by the well-developed battery manufacturing technology [19], modifying the compositions of liquid electrolytes by using appropriate solvents or functional additives is extremely attractive. Up to date, two classes of electrolyte solvents have been applied for LMBs [20]. The first category is based on ether solvents such as 1, 2-dimethoxyethane (DME) and 1, 3-dioxolane (DOL), which possess good stability against Li metal [21]. With the LiNO₃ additive, the ether-based electrolytes can exhibit an improved coulombic efficiency (CE) of \sim 98% in Li-S batteries [22]. However, because of the low oxidation potential (<3.5 V vs. Li/Li⁺), ether electrolytes are easy to be decomposed and corrode the aluminum current collector at high voltage, causing the incompatibility with commercial cathodes such as LiCoO₂ and LiMn_vNi_{1-x-v}Co_xO₂ (NMC) [23,24], and hence limited energy densities. The second category is based on carbonate-ester solvents such as ethylene carbonate (EC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), diethyl carbonate (DEC), etc. Carbonate-ester solvents with higher oxidation potentials (>4.2 V vs. Li/Li⁺) [25] are compatible with high-voltage commercial cathodes, making them more promising for the successful practical applications of high-energy LMBs. However, carbonate-ester electrolytes are plagued by critical instability against Li metal, causing a quite low CE (usually below 90 %) in LMBs [26].

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Received 30 November 2021; Received in revised form 31 January 2022; Accepted 12 February 2022 Available online 16 February 2022 1385-8947/© 2022 Elsevier B.V. All rights reserved. To improve the CE of carbonate-ester electrolytes, electrolyte additives that manipulate the SEI formation have been intensively studied. For example, fluoroethylene carbonate (FEC) is a widely used additive in carbonate-ester electrolytes for stabilizing the SEI [27]. It is found that FEC simultaneously changed the composition of SEI and the solvation sheath [28], but the decomposed toxic HF gas caused safety problems [29–32]. Additionally, other organic F-containing additives (e.g., Tris (2, 2, 2-trifluoroethyl) borate (TTFEB) [33], 2-Fluoropyridine (2-FP) [34], etc.) and S-containing additives (e.g., Dimethyl sulfate (DMS) [35]) also yielded unsatisfactory performance (CEs < 95 % [36]) in LMBs. Therefore, developing high-performance, harmless, and costeffective additives is significant for the practical applications of LMBs.

Proteins are composed of numerous amino acids that embed various kinds of polar functional groups (–CO-NH-, –COOH, –OH, –NH₂) inside. These groups can potentially generate various interactions with electrolyte solvent molecules and Li salts [37], inspiring the applications of proteins for binders [38,39], separator coatings [40,41] and Li-anode protective layers [42–44]. Recently, fibroin protein was applied as the additive for ether-based electrolytes and improved the cycle performance of Li||Li₄Ti₅O₁₂ full cells [45]. However, protein additives have not been reported for protecting Li anode in carbonate-ester electrolytes that are the most broadly used electrolytes in the battery market currently.

We report here that zein protein can be applied as an additive for liquid carbonate-ester electrolyte to improve the cycling performance in LMBs. The zein additive not only induces a homogenous Li ion deposition to alleviate the Li dendrite growth, but also repairs the cracked SEI to prevent the Li anode from the corrosion of liquid carbonate-ester electrolyte. Additionally, the zein additive changes the functional groups of SEI for Li anode, which induces the low polarization of cells in the cycling process. With the optimized ratio of zein additive, the symmetrical Li cells show the best cycle life of 350 h at the current density of 1 mA cm⁻² with a capacity of 1 mAh cm⁻². Moreover, the effectiveness of zein additive for protecting Li anode is demonstrated in Li|LiFePO₄ (LFP) full cells.

2. Results and discussion

2.1. Properties of electrolyte with zein

Natural proteins are macromolecules with quaternary structures that hide considerable functional groups inside. To unfold the quaternary structure and transform it into the secondary structure or primary structure for exposing more functional groups, zein is denatured in EC/EMC/LiPF₆ electrolyte and the conception is depicted as Fig. 1a. It is note that the electrolyte with the optimized concentration of zein (0.05 wt%, Fig. S1a) is marked as w/ zein in the main text. A high concentration of LiPF₆ (1 M) in EC/EMC solvents can disrupt the salt bridge and hydrogen bonding of zein and expose abundant polar functional groups [46–48]. As shown in Fig. S1b, zein fully dissolves in the electrolyte of EC/EMC/LiPF₆, but does not dissolve in EC, EMC or their mixture EC/EMC. The high-frequency regions of Fourier-transform infrared





Fig. 1. (a) Schematic illustration of the denaturation process of zein and the change of inter-/intra-molecular interactions during the dissolving process. (b) Fourier-transform infrared spectroscopy (FTIR) spectra of pure zein and the electrolytes with and without zein in the high-frequency region [49]. (c) FTIR spectra of the electrolytes with and without zein in the low-frequency region. Note that the electrolyte with 0.05 wt% zein is marked as w/ zein in the main text.

spectroscopy (FTIR) results are presented in Fig. 1b and Fig. S2. After zein dissolves in the electrolyte, the peak (3288 cm^{-1}) of H-boding of zein disappears in the electrolytes with various zein concentrations (5 wt %, 1 wt% and 0.05 wt%), indicating the H-boding disruption of protein molecules in the liquid electrolyte. A new peak of H-bonding at 3479 cm^{-1} can be found, which can be attributed to the intramolecular interaction between protein and the organic solvents. Furthermore, the exposed functional groups on the main chains and side chains of zein can potentially generate various interactions with Li ions, anions, EC, and EMC. In the electrolyte system, Li ions generate complex interactions with the electrolyte solvents and additives. Therefore, Li ions may aggregate with solvent molecules or additive molecules and generate solvation sheath [36]. The FTIR spectra of the electrolytes with and without zein in low-frequency region are shown in Fig. 1c. The peaks at \sim 1800 cm⁻¹ and 1745 cm⁻¹ are correspondent to the C=O stretching mode of EC and EMC, respectively. The peak at $\sim 1769 \text{ cm}^{-1}$ can be assigned to the Fermi resonance (F.R.) in EC. The peak at 1270 cm^{-1} is correspondent to the C-O stretching mode of EMC [50]. It can be seen that the relative intensity between the peaks at 1745 cm^{-1} and 1270 cm^{-1} has a significant decrease after zein is added, which implies that the interaction of Li ion-solvating EMC is significantly affected by zein. This may be induced by the charged functional groups $(-COO^{-}, -NH_3^{+},$ $=NH_2^+$) in the R group of specific amino acids (Asp, Lys, Glu, Arg) (Table S1 and Fig. 1a) and peptide bonds (-CO-NH-) of the protein backbone [51,52]. The molecular weight range of zein was determined by sodium dodecyl sulphate-polyacrylamide gel electrophoresis (SDS-PAGE) in our previous study, which is 20–25 kDa for the α , γ -zein and 37–50 kDa for γ-zein [53].

The change of solvation state affects the electrolyte ionic conductivity as shown in Fig. 2a. When soaking in the polypropylene (PP) separator, the electrolyte with zein shows a slightly decreased ionic conductivity but still maintains at the same order of magnitude as the pristine electrolyte. Furthermore, the wetting behavior of electrolytes on the components of batteries (Li plate, separator, and LiFePO₄ sheet) was determined by video optical contact angle measurements. As displayed in Fig. 2b, pristine electrolyte exhibits a poor wetting behavior on Li plate with a stable contact angle of 40° after 2 s. On the other hand, the electrolyte with zein has a much smaller contact angle of 23° on Li plate and the contact angle keeps a decreasing tendency after 2 s. The enhanced wetting behavior of the electrolyte with zein on Li plate is due to the abundant functional groups of protein. The functional groups can react with Li and modify the surface chemical compositions of Li metals and thus enhance the affinity with electrolyte. On a PP separator (Fig. S3a), the electrolytes with and without zein both reach a stable state in 0.7 s. However, the introduction of zein additive increases the stable contact angle of electrolyte on the separator because there are only non-polar functional groups in PP chains [54]. On the porous LiFePO₄ electrode sheet (Fig. S3b), the contact angle of the electrolytes with and without zein shows the same decreasing tendency and a close stable contact angle after 2 s [55]. The results demonstrate the effect of protein functional groups on the wetting behavior of electrolytes.

The electrochemical stability window of the electrolytes with and without zein was measured by linear sweep voltammetry (LSV) in Li|Fe coin cells. As shown in Fig. 2c, pristine electrolyte is stable within the voltage range of 2.5–5 V and decomposes after 5 V. After introducing zein, the electrolyte decomposes from 3.2 V to 6 V and shows a strong



Fig. 2. (a) ionic conductivity, (b) wetting behavior (on Li plates), (c) electrochemical window of the electrolytes with and without zein; (d) first-principles study of the role of EC, EMC, -(Ala-Glu-Leu)_n- and short peptides (Ala-Glu, Ala-Leu, Ala-Pro, Ala-Glu-Leu-Pro) composed of main amino acids of zein.

and 2nd scans (Fig. 2c).

2.2. Electrochemical performance

the formation of SEI at the first cycle. The peaks after 5 V result from the decomposition of solvent, Li salt and specific functional groups of zein molecules. At the second cycle, the electrolyte with zein exhibits a stable electrochemical window of 2.5–4.7 V. These results indicate that the functional groups (e.g., –COOH, –OH, –NH₂) of zein are reduced starting at ~3.2 V, but zein becomes stable after it is fully reduced as indicated by the result from the 2nd scan [56].

peak at the first cycle, indicating that a majority of zein participates in

To obtain the molecular insights into the SEI compositions with zein additive, we calculate the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of EC, EMC and protein molecules by first-principles calculation. To simplify the simulation, short peptide chains are designed based on several major amino acids of zein (Ala, Glu, Leu, Pro). The long peptide chain is designed as -(Ala-Glu-Leu)_n-. Molecular structures of the calculated molecules are shown in Fig. S4. The calculation results are listed in Table S2 and presented in Fig. 2d. During the charging/discharging processes, the short peptides (Ala-Glu, Ala-Leu, Ala-Pro, Ala-Glu-Leu-Pro) and long polypeptide of -(Ala-Glu-Leu)_n- with lower levels of the LUMO (-1.96, -1.62, -1.38, -1.49 and -1.51 eV) will be reduced earlier than EC (-0.52 eV) and EMC (-0.21 eV) on the surface of Li anode. These results show that zein additive can first participate in the formation of SEI on Li anode and then decrease the consumption of electrolyte solvents during cycling process [27]. Moreover, the above-mentioned peptides have higher HOMO than EC and EMC, which shows the potential to take part in the cathode electrolyte interface (CEI) formation [57]. The LUMO and HOMO results agree with the electrochemical window of zein in the 1st

Galvanostatic cycling performance of the electrolyte with zein was investigated using symmetric Li|Li cells at various current densities with a fixed plating/stripping capacity of 1 mAh cm⁻². As shown in Fig. 3a, the electrolyte with zein additive exhibits a longer cycling lifetime $(\sim 420 \text{ h})$ compared with pristine cell $(\sim 280 \text{ h})$ at the same cycling process. To further study the evolution of the polarization at different cycles and current densities, the voltage profiles of symmetric Li|Li cells at the 1st, 5th, 25th, and 105th cycles are enlarged in Fig. 3b. In the first cycle with the current density of 0.2 mA cm⁻², the cell with zein has a stable plating/stripping curve and low polarization (0.032-0.061 V), while pristine cell shows an unstable curve and a high polarization range of 0.045-0.227 V. After 5 cycles under the current density of 0.2 mA cm⁻², the polarizations of the cells with zein and without zein were decreased to \sim 0.044 V and \sim 0.055 V, respectively. Both samples have a relatively stable curve compared with the 1st cycle. At the 25th and 105th cycles with 0.5 and 1 mA cm⁻², respectively, the cell with zein shows obvious lower polarization compared to that of pristine cell. These results may be due to the composition change of the SEI on Li metal after introducing zein additive.

In order to investigate the evolution of the SEI on Li anode during cycling, the electrochemical impedance spectroscopy (EIS) of the symmetrical Li|Li cells without and with zein additive at various cycles were obtained and shown in Fig. 3c and d, respectively. At high-frequency



Fig. 3. (a) Galvanostatic cycling of symmetric Li|Li cells with and without zein at various current densities and a fixed plating/stripping capacity of 1 mAh cm⁻². (b) The blow-up of voltage profiles of Li|Li cells at the 1st, 5th, 25th, 105th cycles, respectively. Nyquist plots of Li|Li cells (c) without and (d) with zein after different cycling numbers.

range (Fig. S5), the intercept point at real axis represents the bulk resistance (R_b). The semicircle in the range between high and medium frequency is attributed to the resistance of SEI for Li metal (R_{SEI}). The small semicircle at low frequency is correspondent to the charge-transfer interfacial resistance (R_{CT}) [58]. As shown in Fig. 3c, the pristine cell has a decreasing R_{SEI} from fresh state (19.62 Ω) to the 5th cycle (15.32 Ω) and the 15th cycle (8.99 Ω), while keeps nearly unchanged between the 15th (8.99 Ω) and 25th (9.84 Ω) cycles (Table S3). This is because of the thick SEI formation at the initial state and reaction of SEI compositions during cycling. In contrast, the cell with zein (Fig. 3d) shows a high R_{SEI} at the initial state (44.8 $\Omega)$ and a lower R_{SEI} at the 5th, 15th and 25th cycles, which are 10.73 Ω , 6.82 Ω and 8.91 Ω , respectively. The high impedance at the initial state is possibly because of the high reactivity and affinity of zein molecules on Li metal compared to electrolyte molecules, therefore forming a thick layer that increases the resistance of the cell. During the cycling process, the absorbed zein molecules may disperse in electrolytes, and therefore, decrease the resistance of cells. This result demonstrates that zein takes part in the formation of SEI in the initial state and cycling process. Furthermore, the R_{ct} of the pristine cell decreases from 296.6 Ω (fresh cell) to 263.4 Ω (5th cycle) and 124.5 Ω (15th cycle), and then increases to 159.3 Ω at the 25th cycle. After introducing zein additive, the R_{ct} of the fresh cell increases to 482.1 Ω , which may be due to the affinity of zein functional groups with Li anode. At the 5th, 15th and 25th cycles, R_{ct} of the cell with zein are 77.7 Ω , 70.72 Ω and 74.29 Ω , respectively. The much lower R_{ct} of the cell with zein is due to the modification of SEI chemical compositions induced by zein additive.

The morphology of cycled Li after various cycles in the Li|Li cells with and without zein additive was obtained to investigate the stripping/plating process of Li anodes (Fig. S6 and Fig. 4). The current density and specific areal capacity at various cycles were kept consistent with the cell in Fig. 3a. The Li anodes were carefully rinsed by dimethoxymethane (DME) for three times to remove LiPF₆, and then dried in glovebox. The digital images of the Li anodes disassembled from cycled cells are shown in Fig. S6. For the stripped and plated Li anodes in the pristine cell after 15 cycles, a rough deposition of Li ion can be clearly found in Fig. S6a and Fig. S6c. After further cycling at a higher current density of 0.5 mAh cm⁻² to 25 cycles, an uneven surface with severe corrosion is observed on the stripped (Fig. S6e) and plated Li anodes in the pristine cell (Fig. S6g). In sharp contrast, for the cells with zein, a flat surface without any corrosion pit is found on the stripped and plated Li anodes after 15 and 25 cycles (Fig S6b, d, f, h). We further employed the scanning electron microscope (SEM) and optical digital microscope to characterize the surface of cycled Li anodes. At the 15th cycle, the cracked surface and large pits can be found in the SEM and optical microscope images of stripped and plated Li anode (Fig. 4a, c, e, and g) in the pristine cell, while the Li anodes in the cell with zein have a more homogenous stripped and plated morphology (Fig. 4b, d, f and h) after 15 cycles. At the 25th cycle, more pits derived from the corrosion of liquid electrolyte are observed on the stripped Li anode of pristine cell (Fig. 4i). Exposed Li with a shiny light can be found in the optical microscope image (Fig. 4m). In contrast, the stripped Li anode in the cell with zein shows a more stable interface with smaller pits (Fig. 4j). The corresponding blurred optical image (Fig. 4n) demonstrates the



Fig. 4. Scanning electron microscope (SEM) and optical images of the stripped and plated Li plates of the cells with and without zein after 15 and 25 cycles.

existence of a zein-derived film on the surface of Li anode. For the plated Li anode at the 25th cycle, it can be seen that the pristine electrolyte exhibits an inhomogeneous deposition of Li ion (Fig. 4k), and the small Li dendrites with flower shape and exposed Li are observed in the optical image (Fig. 4o). Compared to pristine electrolyte, the electrolyte with zein generates a more homogenous surface and fewer Li dendrites (Fig. 4i, p). A longer cycling of 55 cycles for both electrolytes was further investigated by optical digital microscope as shown in Fig. S7. The electrolyte with zein exhibits an even surface without exposed Li metal (Fig. S7a, b), while the pristine electrolyte generates a rough surface with large pits and exposed Li area (Fig. S7c, d), indicating that zein additive protects the Li metal from the corrosion of liquid electrolyte.

To further explore the protective mechanism of zein additive, the evolution of the functional groups on the surface of Li anodes in the Li Li cells with and without zein was studied by ATR-FTIR (Fig. 5a). The fresh Li, stripped and plated Li anodes were marked as fresh, stripped-5th and plated-5th, respectively. The top half and bottom half part of Fig. 5a show the curves of the Li anode with and without zein, respectively. The fresh cells were stand in airbox for 10 h, and all the Li anodes disassembled from fresh or cycled Li|Li cells were rinsed by DME for three times and dried in glovebox. The peak at ~ 1777 cm⁻¹, which is attributed to the C=O stretching in EC and EMC, exists in the fresh Li, stripped Li and plated Li anodes after 5 cycles in pristine cells. This peak is also observed in the fresh Li with zein, and then disappears after 5 cycles in the stripped Li and plated Li with zein. In contrast, the C=O (δ -lactam) stretching (\sim 1650 cm⁻¹) that is related to zein (Fig. S8) can be found in the Li anodes with zein while not exists in the Li anodes of pristine cell. These results indicate that in the pristine cell, EC and EMC participate in the formation of SEI during cycling process. However, in the cell with zein, the O–H bonding in COOH (1407 cm^{-1}) can be observed in the stripped-5th Li and fresh Li with zein, while comparatively weaker in plated-5th Li with zein and all the Li anodes of pristine cells. This may be because of that on the stripped Li, zein reacts with exposed Li metal and forms the SEI layer with different chemical compositions. The C-N stretching (1321 cm⁻¹) can only be found in the Li anodes with zein, and the C-O stretching in C-OH (1082 cm⁻¹) does not exist in the stripped-5th and plated-5th Li with zein, further demonstrates the main participation of zein in the formation of SEI during cycling process.

The chemical compositions on the surface of Li anodes after 25 cycles were studied by the X-ray photoelectron spectroscopy (XPS) technique. Fig. 5b, c show XPS spectra of C1s for Li anode in the cells without and with zein, respectively. The peaks of C 1 s can be assigned to C-C/C-H (284.6 eV), C-O (285.5 eV), C=O (286.6 eV), RCO₂Li (289 eV) and Li₂CO₃ (290.1 eV). It is noticed that the Li anode with zein has a higher peak of C-C/C-H and smaller peaks of C-O and C=O compared to pristine cell, which indicates that the major SEI chemical compositions of Li anode in the cell with zein are derived from the zein additive. For the F1s spectra (Fig. 5d, e), the peaks at 685.1 cm⁻¹ and 687.4 cm⁻¹ are related to LiF and Li_xPF_y, respectively[59]. The peaks of P2p (Fig. 5f, g) are attributed to Li_xPF_y (136.9 cm⁻¹) and Li_xPO_yF_z (134 cm⁻¹). The atomic ratios of C, F and P in various bindings or chemicals were calculated and presented in Fig. 5h. The relatively increase of peak intensity of LixPFv in both F1s and P2p spectra of the Li anode with zein may be because of the PF₆⁻ trapping ability of the SEI after introduced zein additive.

To demonstrate the above supposition of anion trapping in the zeinderived SEI, considering the water absorption and decomposition of LiPF_6 in air [60],

$$\text{LiPF}_{6}(s) + \text{H}_{2}\text{O} \rightarrow \text{LiF}(s) \downarrow + 2\text{HF}(g) \uparrow + \text{POF}_{3}(s) \downarrow$$
(1)



Fig. 5. (a) FTIR spectra of the surface of stripped and plated Li anodes with and without zein additive at the uncycled state (fresh) and 5th cycles. X-ray photoelectron spectroscopy (XPS) curves of (b, c) C1s, (d, e) F1s, (f, g) P2p and (h) atomic ratio of C, F, P of the plated Li anodes in the cells without and with zein after 25 cycles.

Chemical Engineering Journal 437 (2022) 135283

the Li anodes dipped with the electrolyte with and without zein was fully dried at 50 °C in glovebox and carefully rinsed by dimethoxyethane (DME) for three times, thereafter fully dried in glovebox and then put in air to observe the physical change of Li anode surface. The pure Li without treating was applied as a reference sample. As shown in Fig. S9, at the initial state, all the Li anodes have a shiny surface. After 1 min, the surface coating of Li with zein transforms to liquid state, while the Li with pristine electrolyte and pure Li are still dry. After 10 min, numerous bubbles can be found in Li with zein, and the surface is less oxidized than the sample with pristine electrolyte and pure Li. This phenomenon is the result of the formation of HF (gas) during the hydrolysis of LiPF₆. When standing in air for 12 h, three Li plates are fully oxidized. The chemical compounds on the surface of those fully oxidized Li plates were characterized by FTIR and shown in Fig. S10. A strong peak of the P-F bonding (832 cm^{-1}) [61] in POF₃ can be found on the Li metal with zein. In a sharp contrast, this peak is extremely weaker in pristine Li metal and does not exist in pure Li metal, which indicates the high ratio of PF_6^- on the Li metal with zein, demonstrating the anion trapping ability of the zein-derived SEI.

In brief, the improved cycling performance of symmetrical Li cells benefits from zein additive and the working mechanism of zein are presented in Fig. 6. In the pristine cell (Fig. 6a), EC and EMC first form an inorganic rich SEI composed of LiF, Li₂CO₃, ROCO₂Li, Li_xPF_y, R-O-CO-O-R, etc. [62]. The wave-like surface of Li anodes causes uneven Li ion deposition during plating, inducing the formation of Li dendrites. In

the stripping process, the large volume shrinkage of Li anode leads to the cracking of SEI and the formation of both dead Li particles and exposed fresh Li. The exposed Li directly contacts with electrolytes, causing continuous side reactions between Li and electrolytes. The large Li consumption leads to the corrosion of Li anode and large pits on Li anode. In the cell with zein additive, zein with a lower LUMO compared with EC and EMC, preferentially takes part in the formation of SEI on the surface of Li anode, generating an organic-rich SEI layer with abundant polar functional groups that can trap anion and exhibit interaction with Li ion. These polar functional groups and trapped anions can form a homogenous electric field, therefore inducing an even Li ion deposition on Li anode [63,64]. In addition, during the cycling process, the SEI crack caused by the large volume change of Li anode can be repaired by zein additive promptly, therefore effectively preventing the corrosion of Li anode from the liquid electrolyte.

We further test the electrochemical performance of the electrolyte with zein in Li|LiFePO₄ full cells. Fig. S11 shows the Nyquist plots of fresh Li|LiFeO₄ cells with and without zein. The measured cells were standstill for 10 h after assembling. It can be seen that the electrolyte with zein generates a smaller semicircle comparing with pristine electrolyte, demonstrating the low resistance of the cell with zein. Correspondently, the R_{SEI} (14.25 Ω) and R_{ct} (22.87 Ω) of the cell with zein are both lower than the pristine cell, which are 22.87 and 131.40 Ω , respectively (Table S4). This result demonstrates that zein effectively decreases the charge-transfer reaction resistance of SEI by modifying the



Fig. 6. Schematic of the effect of zein additive on the plating and stripping process of Li ion on Li anodes.

SEI composition. Compared to the fresh Li|Li cells (Fig. 3c, d), the lower resistance of electrolyte with zein in Li|LiFeO₄ cells is because part of zein molecules are trapped in the cathode components and therefore decreases the concentration of zein on the surface of Li metal. Hence, a thin zein-derived SEI is formed on Li metal in the initial state.

The charge/discharge profiles of the cells without and with zein in the 1st cycle are shown in Fig. 7a. The cell with zein has a higher initial discharge capacity (168.3 mAh g⁻¹) compared with pristine cell (143.9 mAh g⁻¹) at the current density of 0.1 C. This result is possibly due to the different chemical compositions of zein-derived CEI, which leads to the quick electrolyte infiltration on the surface of active materials, inducing a high utilization of active materials in the first cycle [65–67]. However, the cell with zein has a lower initial coulombic efficiency (91.7 %) than pristine cell (94.6 %), which demonstrates the significant participation of zein in the formation of SEI for Li anode in the first cycle. In the 20th cycle (Fig. 7b), the discharge capacity of cells without and with zein decreases to 115.4 and 141.3 mAh g⁻¹ at 1 C, respectively. Moreover, that is close to 100 % at the 20th cycle, while that of pristine cell is 99.3 %, indicating that the zein-derived SEI effectively protects Li anode from the side reactions with liquid electrolyte.

The polarization of cells is closely related to the cycling performance of Li anode. Large polarization of cells will lead to the rapid formation of Li dendrites. Therefore, the polarization of Li|LiFePO₄ full cells at various cycles with various current densities was collected from the charge/discharge profiles (Fig. S12 and Fig. S13). As presented in Fig. 7c, in the 1st cycle at the current density of 0.1C, the polarization of the cell with zein (0.07 V) is lower than pristine cell (0.08 V). This phenomenon demonstrates that zein-derived SEI has a higher ionic conductivity of Li ion, which may be induced by the rich polar functional groups of zein. At the 10th (0.5 C), 20th (1 C), 100th (1 C), 200th (2 C) cycles, the polarization of the cell with zein increases to 0.09, 0.11, 0.11 and 0.18 V, respectively, in sharp contrast to the much higher polarization of 0.10, 0.15, 0.13 and 0.19 V for the pristine cell. This result indicates the long-term effectiveness of the zein protective function for Li anode. Specifically, the largest polarization difference of two cells at the 20th cycle and the small polarization directed at the 100th cycle may be due to the cyclic zein consumption during the repairing process for Li anodes.

The voltage drop after the charge stop can reflect the Li-ion distribution and internal resistance at the state of charge (SOC) of 100 % [68]. As shown in Fig. S14, in the settling time of beginning 10 s after charge stop of the 1st cycle at 0.1 C, the cell with zein has a smaller instant voltage dropping (0.041 V) compared with pristine cell (0.143 V), indicating the low resistance of the zein-derived SEI layer. Moreover, in the settling time between 10 and 70 s, the voltage of cell with zein decreases to 3.502 V, while pristine cell keeps nearly steady around 3.450 V. This may be because of the participation of zein in the initial SEI



Fig. 7. Electrochemical performances of the electrolytes with and without zein additive in Li|LiFePO₄ cells. Charge/discharge profiles of cells (a) without and (b) with zein at the 1st, 20th cycles, respectively. (c) Polarization of cells at various cycles and different currents. (d) Rate performances at various current densities. (e) Long term-cycling performance.

formation, which guides the Li ion distribution on the Li anode. After long cycles at various currents (Fig. S15), in contrast with pristine cell, the cell with zein still shows a lower instant voltage drop after 10 s, while their settling voltages after 70 s are both close to \sim 3.45 V.

The rate performance and long cycling performance of the Li| LiFePO₄ full cells are presented in Fig. 7d and e, respectively. The electrolyte with zein exhibits excellent rate performance with higher discharge capacities of around 168, 161, 150, 142, 141 and 105 mAh g⁻¹ at 0.1, 0.2, 0.5, 0.8, 1 and 2 C, respectively, in comparison to the pristine electrolyte with much lower capacities of around 146, 147, 133, 124, 114 and 84 mAh g⁻¹ (Fig. 7d). Meanwhile, the cell with zein shows superior long-cycling performance with high discharge capacities of 130.1 mAh g⁻¹ after 200 cycles at 1 C and 83.8 mAh g⁻¹ after further 400 cycles at 2 C, while the pristine cell only has capacities of 105.9 and 53.3 mAh g⁻¹, respectively, under the same cycling process. The capacity retention of both cells was calculated and shown in Fig. S16. After 220 cycles and 600 cycles, the cell with zein has much higher capacity retention (79.8 % and 46.6 %) compared with the pristine cell (69.8% and 36.4 %).

3. Conclusions

In summary, abundant natural protein, zein, is explored as a novel additive of carbonate-ester electrolyte for the first time to effectively increase the stability of Li anode and deliver long-cycling LMBs. Zein is drastically denatured by the carbonate-ester electrolyte to open up the compact molecular structure. The exposed various functional groups from zein actively participate in the SEI formation, playing an important role in immobilizing anions to regulate uniform Li⁺ deposition. The cracked SEI layer can be effectively repaired by the preferential zein-Li reaction, preventing the corrosion of Li from the electrolyte. As a result, the growth of Li dendrites and Li-electrolyte parasite reactions are intensively suppressed. With the zein modified carbonate-ester electrolyte, a symmetrical Li cell shows an excellent long-term cycling performance of over 350 h (vs. < 200 h for pristine cell) at 1 mA/cm² with capacity of 1 mAh cm⁻². Moreover, the electrochemical performance of the Li|LiFePO₄ full cell is also improved, which yields a higher capacity of 130.1 mAh g $^{-1}$ and more stable capacity retention of ~ 80 % after 200 cycles at 1 C. This study suggests that the natural protein, zein, can be an effective additive for the most commercial carbonate-ester electrolytes to effectively advance the performance of LMBs, and provide a new insight on the mechanisms of the electrochemical performance enhancement.

CRediT authorship contribution statement

Chenxu Wang: Writing – original draft, Writing – review & editing, Investigation, Conceptualization, Formal analysis. Xuewei Fu: Formal analysis, Writing – review & editing, Supervision. Chunhua Ying: . Jin Liu: Supervision, Funding acquisition. Wei-Hong Zhong: Writing – review & editing, Supervision, Funding acquisition.

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

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