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Optimizing the sulfonic groups of a polymer to coat the zinc anode for dendrite suppression†

Yan Wang,^{‡a} Yuetao Wang,^{‡a} Chuanxi Chen,^a Xin Chen,^a Qinghe Zhao,^a Luyi Yang,^{id a} Lu Yao,^a Runzhi Qin,^{id *a} Hong Wu,^{id *b} Zhongyi Jiang^{id b} and Feng Pan^{id *a}

The zinc metal anodes in aqueous zinc-ion batteries suffer from low cycling performance caused by uncontrolled dendrite. We have designed sulfonated poly-ether-ether-ketone (SPEEK) polymers as a surface coating layer on the zinc anode for dendrite suppression, in which the sulfonic groups in polymers act as effective active sites for zinc-ion diffusion. In SPEEK, the un-sulfonated domain serves as the framework and the sulfonated domain serves as the functional part to re-distribute the zinc ions. By optimizing the degree of SPEEK sulfonation, the best zinc anode coating has been achieved to present a high reversibility of over 1600 hours in symmetric cells and improved performance in full cells.

The aqueous zinc-ion battery (AZIB), with its low price and high energy density, is a promising solution for large-scale energy storage applications and owns huge market value; thus, it has become a research hot spot and attracted enthusiasm.¹ The typical AZIB utilizes layer-structured crystals as the cathode for the insertion/extraction of zinc ions,^{2,3} and metallic zinc as the anode due to its intrinsic virtues, which include low redox potential (−0.762 V vs. the standard hydrogen electrode), high volumetric capacity (5585 mA h cm^{−3}), and low price. However, the anode is far from maturity and has become the choke point of the battery system. The main problem of the zinc anode is the unsatisfactory cycling lifetime caused by zinc dendrites. Uncontrolled zinc deposition leads to the arbitrary growth of selected clusters, which then become towering dendrites. These dendrites may pierce the separator and bridge the cathode, giving rise to fatal short-circuit failure in subsequent cycles.⁴

The key factor in dendrite control lies in the ordered deposition of zinc ions, *i.e.*, each zinc ion on the threshold of

reduction should be forced to diffuse to the adjacent place and become accreted, instead of accumulating at a more energetic site to form a possible dendritic seed.⁵ Focusing on this issue, researchers have proposed various approaches including electrolyte tuning,^{6,7} structure design,^{8,9} zincophilic site modification,^{10,11} and surface modification.¹² Recently, the strategy of surface modification has attracted intense attention. The organic polymers have been reported as protective coatings on zinc anodes that show a strong effect on the re-distribution of zinc ions and further the suppression of dendrites. Zhao *et al.* constructed a PA layer¹³ that elevates the nucleation barrier, thus raising the number of nucleation sites for zinc deposition. Cui *et al.* proposed a Nafion coating,¹⁴ which restricts water permeation *via* minimizing the diffusion channels in the polymer. Additionally, other polymers including PVB,¹⁵ PVP/PAM,¹⁶ cyanoacrylate,¹⁷ *etc.* have been found to be protective in terms of dendrite suppression. It is widely accepted that a non-conductive coating layer with small diffusion channels can suppress dendrite formation and prolong the cycling performance by uniformly inducing zinc ion flux and the electric field.¹⁸ However, some vagueness remains in the mechanism of the diffusion of the zinc ions through the thick polymer. The complicated structure and diverse functional groups in the polymers (−OH, C=O, N−H, C≡N, *etc.*) increase the difficulty of further study.

Herein, we utilize a simple polymer system, poly-ether-ether-ketone (PEEK), as a model to study the diffusion of zinc ions. The unmodified PEEK coating does not work. After sulfonation, however, the polymer (denoted as SPEEK) successfully accomplishes ion re-distribution and dendrite suppression. The SPEEK-coated zinc electrode can be cycled for over 1600 h with moderated polarization, indicating an enhanced reversibility of the zinc metal. The effect of the sulfonation degree is further studied to provide an optimization principle. A rechargeable zinc-ion battery based on the polymer coating is then constructed, and presents a stable lifespan of 200 cycles with an excellent capacity retention of 99.1%. This research not only provides an affordable alternative to high-performance organic

^a School of Advanced Materials, Peking University Shenzhen Graduate School, Shenzhen 518055, P. R. China. E-mail: bushihaoren@pku.edu.cn, panfeng@pku.edu.cn

^b School of Chemical Engineering and Technology, Tianjin University, Tianjin 30072, P. R. China. E-mail: wuhong@tju.edu.cn

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‡ Yan Wang and Yuetao Wang contribute equally in this work.

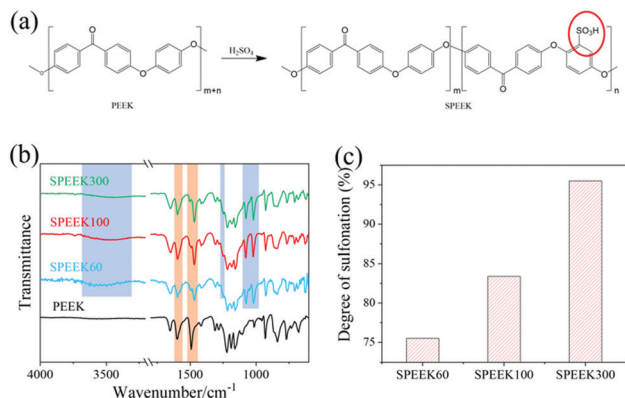


Fig. 1 (a) The synthesis reaction of SPEEK. (b) FTIR spectra of PEEK and SPEEK materials. (c) The degrees of sulfonation in different SPEEK samples.

coatings for surface modification of the zinc anode, but also deepens the understanding of coating design.

We constructed models of PEEK and SPEEK to illustrate the optimization mechanism of the organic polymers. PEEK is a widely used engineering plastic with excellent mechanical strength and ultrahigh electrochemical inertness. The ether groups and the carbonyl groups present very weak polarity (Fig. 1a); thus, the zinc ions with strong polarity are hardly able to diffuse through the PEEK coating. This can be observed in the galvanostatic performance of symmetric cell with a PEEK-coated zinc electrode; the lifetime of the cell is only 18 hours (h, Fig. S1, ESI[†]).

The SPEEK was synthesized from commercial PEEK *via* a sulfonating reaction in different reaction times (Fig. 1a). The products of sulfonation for 60, 100, and 300 minutes are denoted as SPEEK60, SPEEK100, and SPEEK300, respectively. The FTIR results show the successful introduction of sulfonic groups (Fig. 1b), which is characterized by the asymmetrical stretching vibration (1080 cm^{-1} , 1020 cm^{-1}) and symmetrical stretching vibration of $\text{O}=\text{S}=\text{O}$ (1255 cm^{-1}), as well as the peaks of the stretching vibration of $-\text{OH}$ in the sulfonic groups (3460 cm^{-1}).¹⁹ The original structure of PEEK is not influenced, as can be observed from the aromatic $\text{C}-\text{C}$ bond (1489 cm^{-1}) and the backbone carbonyl group (1651 cm^{-1}). ^1H NMR was conducted to determine the degree of sulfonation (DS) in SPEEK (Fig. S2, ESI[†]), which reflects the average number of sulfonic groups in the repeating unit of the structure. The chemical shift of the ortho H (Fig. S2b, ESI[†]) moves ~ 0.25 ppm in the low-field direction due to the strong electron-withdrawing effect of the sulfonic group. Thus, the DS can be calculated from the ratio of the peak area of this shifted hydrogen nucleus to the sum of the peak areas of the other hydrogen nuclei.¹⁵ The DS values of SPEEK60, SPEEK100, and SPEEK300 are 75.5%, 83.4%, and 95.5%, respectively (Fig. 1c). The low DS values of SPEEK60 and SPEEK100 indicate the presence of significant un-sulfonated domains in the material.

The obtained SPEEK materials were dissolved in DMF and cast on a zinc plate to prepare the Zn@SPEEK anodes. After drying, the SPEEK solidified as a dense and translucent yellow coating layer (Fig. S3, ESI[†]). Fig. S4 (ESI[†]) shows the cross-section of a typical

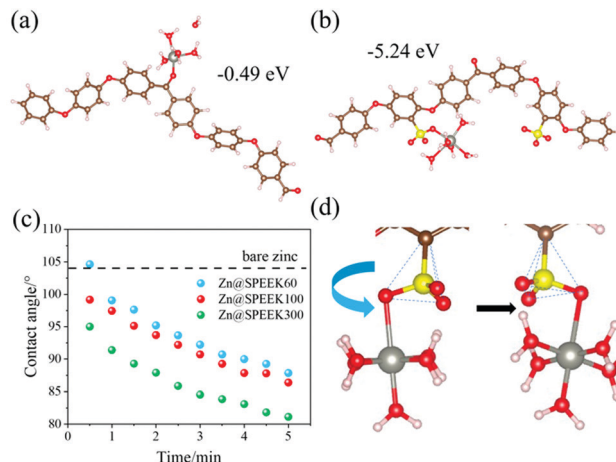


Fig. 2 Calculation model of the (a) Zn/un-sulfonated domain and (b) Zn/sulfonated domain. (c) Contact angle results of SPEEK. (d) A schematic diagram of the paddle-wheel effect of the sulfonic group.

SPEEK100 coating, which has a thickness of $\sim 7\text{ }\mu\text{m}$. The elements C, S, and O are uniformly distributed in the layer, indicating an even remodelling of SPEEK accompanied by volatilization of the solvent. The SPEEK layer has great adhesion to the zinc surface due to the existence of carbonyl groups.¹⁶ As clearly demonstrated by Fig. S5 (ESI[†]), the Zn@SPEEK anode retains its integrity after a bending and twisting experiment.

The mechanism of the interaction between zinc ions and SPEEK materials was investigated using DFT calculations. Models of the coordination complex of a zinc ion ($[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$)²⁰ attached to an un-sulfonated domain or sulfonated domain were constructed. In the un-sulfonated domain, the zinc-ion complex re-coordinated *via* the carbonyl group (Fig. 2a). The bonding energy of this process is only 0.49 eV , indicating a weak interaction. In the sulfonated domain, the sulfonic groups tend to ionize and release the proton, and were thus negatively charged. Consequently, the zinc-ion complex interacts with the $-\text{SO}_3^-$ group with a very high bonding energy of -5.24 eV due to the strong electrostatic interaction (Fig. 2b). These results indicate that the sulfonic groups have high zinc affinity, and the abilities of the other functional groups in SPEEK to coordinate with the zinc ions are not comparable; thus, the zinc ions are mainly transformed by the sulfonic groups. The strong bonding between the zinc ions and sulfonic groups was examined by contact angle. As shown in Fig. S6 (ESI[†]), the coating membrane with a higher DS exhibits a lower contact angle, which demonstrates better wettability at the interface of SPEEK and the electrolyte. Impressively, the contact angle at the SPEEK coating decreases with time (Fig. 2c), showing robust evidence of the continuous permeation of zinc ions/electrolyte *via* the sulfonic groups. However, very high wettability is not always favourable for zinc protection in a battery system. Other practical issues, such as volume expansion, is discussed below.

The diffusion path of the zinc ions in SPEEK can also be facilitated by the additional sulfonic groups. The blank template of the PEEK molecules acts as steric hindrance for the diffusion of zinc ions due to the relatively large monomers in

the spatial configuration. In SPEEK, however, the paddle-wheel effect of the $-C-SO_3^-$ structure leads to easier diffusion of zinc ions.²¹ Specifically, since the $-C-SO_3^-$ of the sulfonic group could form a tetrahedral structure, the O atoms around one S atom could rotate around the axis of the C-S bond without consuming much energy (Fig. 2d).²² Therefore, the diffusion path of the zinc ions is shortened, and the mobility of the zinc ions is strongly enhanced by the coupled rotational motion of the sulfonic groups. The EIS results prove that the charge transfer of the zinc electrode is not hindered by the insulated coating layer (Fig. S7, ESI†).

The galvanostatic cycling performance of symmetric zinc cells was tested to confirm the diffusion-promoting effect of the sulfonic groups. As mentioned above, seeking appropriate functional groups is vital for the design of surface modification. Therefore, the poor performance of the PEEK coating (Fig. S1, ESI†) is related to a mechanism in which the zincophobic groups, such as the phenyl groups, the ether groups, and the carbonyl groups, hinder the distribution of the zinc hydration ions. In comparison, the SPEEK-coated zinc electrodes present improved cycling stability (Fig. 3a). Zn@SPEEK60 presents enhanced cycling stability for 803 h until failure, which indicates the strong effect of the sulfonic groups on the zinc-ion redistribution, even with a low DS. At the same time, the facilitated diffusion channels formed by the sulfonic groups also guarantee low polarization. The SPEEK100 coating with a higher DS of 83.4% can further prolong the cycling lifetime to over 1600 h, showing high practical value. Correspondingly, in the SEM images, large dendrite clusters, which are the origin of

the short-circuit hazard, can be observed on the bare zinc anode (Fig. 3b), while the zinc deposition is uniform underneath the SPEEK60 (Fig. S8, ESI†) and SPEEK100 (Fig. 3c). The zinc surface protected by SPEEK100 is highly ordered after 100 cycles (Fig. S9, ESI†). Therefore, SPEEK100 is the most protective in our experiments. Note that the peak intensity ratio in the XRD patterns of the electrodes (Fig. S10, ESI†) between $(002)_{Zn}$ and $(101)_{Zn}$ decreases from 0.368 to 0.300 after 100 cycles. This distinct crystallographic re-orientation may result from the inhibition effect of the polymer.

When further increasing the DS, however, the SPEEK300 coating presents inferior performance. The reason for this lies in the strong hydrophilicity of the sulfonic groups in SPEEK300. As shown in the optical image (Fig. S11, ESI†), the SPEEK300 membrane suffers severe swelling in the electrolyte, leading to peeling; thus, it loses its protective effect after a certain number of cycles. Correspondingly, the SEM image presents some local bumpy morphology after 10 cycles, indicating dendrite formation after the deadhesion of the coating layer (Fig. S12, ESI†). A conclusion can be drawn that the optimization of the coating requires some amount of un-sulfonated domains as the framework, and sulfonated domains as the functional part to interact and re-distribute the zinc ions. Although some other polymers have been studied as coating materials (Table S1, ESI†), the framework and the functional part are rarely expounded.

The polarization of the dissolution/deposition process is also important to the zinc anode. Lower polarization promotes the kinetics of the electrochemical process and decreased energy consumption. Zn@SPEEK60, Zn@SPEEK100, and Zn@SPEEK300 present a polarization of 39, 36, and 67 mV at the 10th cycle. As expected above, the polarization in the SPEEK60 and SPEEK100 coatings is lower than that of bare zinc (67 mV), which can attributed to the successful introduction of the sulfonic groups. The functional groups strengthen the zinc-ion transport capability and create easier diffusion paths that even have higher tortuosity. The polarization of Zn@SPEEK300 is not reduced because of the stripping of the membrane, which is illustrated in Fig. S11 (ESI†).

In short, the DS can be artificially controlled in the SPEEK system, which is different from the existing literature.^{13–17} For the first time, our results reveal the underlying issue in surface modification design, *i.e.*, the type and the density of functional groups should be precisely controlled for optimization. A scheme is proposed to illustrate the effect of the SPEEK coating. On the bare zinc anode, the uneven diffusion of zinc ions leads to dendrite formation (Fig. 3d).⁵ When the SPEEK coating is applied (Fig. 3e), however, the abundant sulfonic groups can be coordinated with zinc ions, and provide a facilitated pathway for diffusion. The uniform distribution of the zinc ions benefits the dendrite suppression and cycling performance of the zinc anode.

The zinc anodes with and without SPEEK coatings were further applied in full cells to test the effect of the sulfonic groups. $Zn_xV_2O_5 \cdot nH_2O$ (ZnVO) was synthesized as the cathode material according to the literature.²³ Due to its high stability

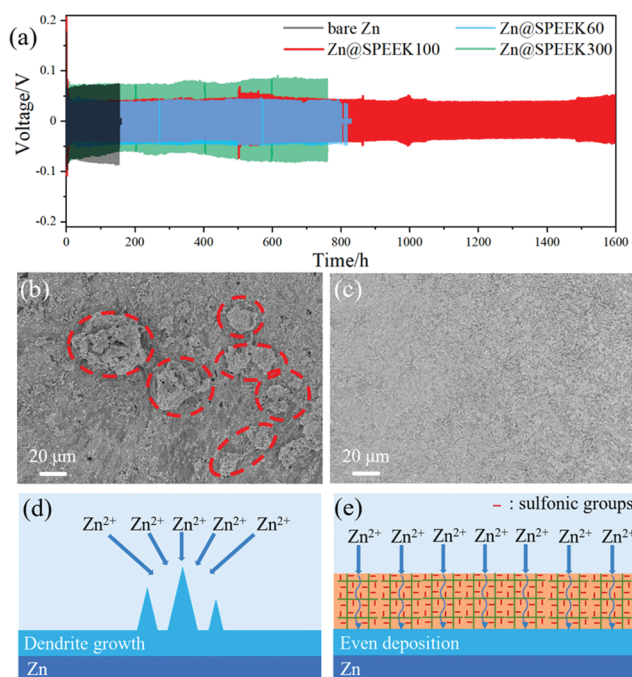


Fig. 3 (a) The cycling performances of bare zinc and Zn@SPEEK. SEM images of (b) bare zinc and (c) Zn@SPEEK100 after 10 cycles. (d) A schematic diagram of dendrite formation in bare zinc. (e) A schematic diagram of the even deposition in Zn@SPEEK100.

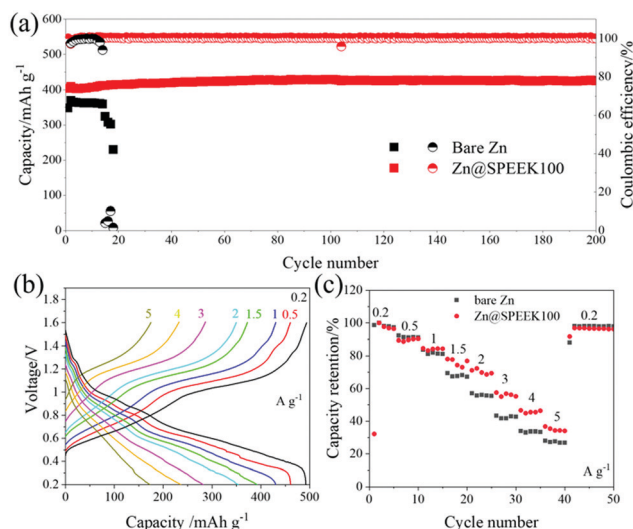


Fig. 4 (a) The cycling performances of bare zinc and Zn@SPEEK100. (b) The voltage profiles of Zn@SPEEK100 at different rates. (c) The rate performances of bare zinc and Zn@SPEEK100.

and reversibility, the ZnVO cathode itself would not be the bottleneck of the full cell;⁶ thus, the anode side determines the performance. The CV profiles of the bare zinc and Zn@SPEEK100 are similar, indicating that the mechanism of the redox reactions of the ZnVO cathode were unchanged (Fig. S13, ESI†). Fig. 4a presents the cycling performance of the full cell. Enabled by the ZnVO cathode, the cell with the bare zinc anode has a capacity of 363 mA h g⁻¹ (0.5 A g⁻¹). It was operated for only 18 cycles before a sudden capacity drop, which is attributed to dendrite generation and subsequent short-circuit of the cell. In comparison, the cell with a coated anode presents a high initial capacity of 403 mA h g⁻¹ (0.5 A g⁻¹), which remains almost undegraded in the following 200 cycles (99.1% @ 200th cycle). The results elucidate the beneficial impact of the SPEEK100 coating on the zinc anode and subsequently, on the capacity release of the full cell system. Fig. 4b shows the rate performance of the full cell. The voltage profiles for Zn@SPEEK100 are similar at various rates, indicating that this DS is sufficient for various current conditions. The cell shows higher capacity retention at a high rate of 5 A g⁻¹ compared to the bare zinc anode (Fig. 4c).

In conclusion, we designed a SPEEK coating by introducing the sulfonic groups into the common polymer. The hydrophobic and zincophobic functional groups in the un-sulfonated domain hinder the diffusion of zinc ions. In the sulfonated domain, the zincophilic groups can interact with zinc ions and enhance the transport of zinc ions due to the paddle-wheel effect. The SPEEK coating with a high DS shows a strong effect on the uniform re-distribution of zinc ions, and the dendrite suppression. As a result, the cycling performance of the coated zinc anode is greatly improved to over 1600 h, which is 10.7 times longer than that of the bare zinc anode. The DS greatly influences the integrity and the protective effect of the polymer coating, and the optimized coating is SPEEK100. The

adaptability of the SPEEK coating was further verified in Zn/ZnVO full cells, which exhibited stable cycling performance. Our work on the SPEEK coating not only reveals the mechanism of zinc-ion diffusion powered by specific functional groups, but also provides an optimization principle for coating design.

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Conflicts of interest

There are no conflicts to declare.

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