Solid-state polymeric coating as regulating deposition layer for dendrite-free and stable rechargeable aqueous Zn metal anode

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Abstract. The growth of dendrites and self-corrosion issues of Zn anodes in aqueous energy storage systems cause poor stability and cycling life. Hence, poly-quinol-phenylenediamine (PQA) is synthesized and constructed as the surface protective layer of bare Zn by blade coating, promoting the even dispersion of the electric field, inducing the uniform nucleation and growth of Zn. Consequently, PQA coated Zn (PQA@Zn) electrode demonstrates the improved cycling life of 450 h at 1 mA cm^{-2} and 220 h even at 5 mA cm^{-2} with the symmetric cells, superior rate capability and relatively lower overpotential at different current densities, far more than bare Zn foil. The surface morphology after cycles indicates that PQA coating restrains dendrites by leading to the deposition of Zn dendrites and decreasing the side effects by capturing the Zn^{2+}. In brief, the PQA@Zn anode exhibited remarkable improvement in service life, cycling stability and rate capability, providing more possibilities for advanced energy systems.

Keywords: Dendrites, Zn-ion energy storage, poly-quinol-phenylenediamine, anode.

1. Introduction

Aqueous rechargeable energy storage devices have drawn extensive notice due to their rapid ion diffusion kinetics, environmentally friendly, and highly safe features, which are expected to be the promising renewable energy to satisfy the demand for intelligent and flexible electronics [1]. Among various options, aqueous Zn-ion energy storage systems (batteries and supercapacitors) are referred to as one of the competitive alternatives because of the remarkable theoretical property of 820 mAh g^{-1} and 5855 mAh cm^{-3} (Zn/Zn^{2+}), the low redox potential of −0.76 V (*vs* standard hydrogen electrode), low cost and good compatibility [2]. However, despite recent advances in cathode exploration, Zn metal anode suffer from the issue of dendrite growth and side effects during the nonuniform zinc stripping/plating procedure, which leads to corrosion, failure of the electrode material and even a short circuit, further resulting in the energy storage devices with limited cycle life and impedes their further development. Therefore, the exploration of electrochemically stable Zn anode is one of the most significant factors in developing dendrite-free Zn-ion energy devices for long life and stabilization.

Zn dendrites growth is intensely influenced by the Zn^{2+} ion dispersion between electrode and electrolyte. The anomalous concentration gradient of Zn^{2+} on an anode surface can lead to the uneven electric field contribution in the plating/stripping course, which promotes the formation and proliferation of dendrites. Therefore, controlling the uniform dispersion of Zn^{2+} and electric field, regulating homogeneous electrodeposition and crystal plane orientation of Zn are the dominant solutions to obtain the electrochemically stable Zn anode. To address the issues, several efforts have been carried out, such as Zn anode modification, electrolyte and membrane modification, etc [2]. Nonetheless, despite eventual efforts that have gained great progress, currently, limited scalability approaches are high-cost and complex in operation, which is hard to follow low cost and intrinsic safety natures. The solid-state polymeric coating is confirmed as a promising candidate for modified Zn anode to achieve the solid-state protective layer for coordinating the migration and uniform nucleation of Zn^{2+}. This protects highly active Zn from rapid direct contact with bulk electrolyte resulting in rapid dendrite growth, which is equivalent to the in situ protection mechanism of solid electrolyte interface film on anodes.

Inspired by these, we propose the poly-quinol-phenylenediamine (PQA) coating as polymeric interphase on a bare Zn surface to improve the aqueous Zn cyclic stability. The PQA coated Zn (PQA@Zn) electrode with the unique protective layer, prevents the severe reaction between Zn and water, provides the appropriate channels and reaction kinetics for Zn^{2+}, and induces the deposition of Zn between bare Zn and PQA interlayer, enabling the improvement of stability and cycle life. Therefore, dendrite-free and stable PQA@Zn anode displayed the longer Zn/Zn^{2+} cycling performances and stable overpotential than bare Zn in symmetrical cells, which achieved 450 h life at 1 mA cm^{-2} with low voltage hysteresis and 220 h even at 5 mA cm^{-2}. Moreover, the PQA@Zn anode reveals the more stable plating/stripping behaviors at various current densities, which shows the excellent rate capability. Therefore, the PQA@Zn anode with PQA protective coating is regarded as the potential candidate for ultra-stable and long-lived Zn-ion rechargeable devices.

2. Experimental section

2.1. Materials

P-Benzoquinone, p-Phenylenediamine, ethanol absolute and N-methylpyrrolidone were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All the chemicals were analytical reagents and directly used. Polyvinylidene fluoride (PVDF, HSV900) was obtained from Arkema Kynar, superconductive carbon blacks (BP 2000) were obtained from Cabot Corporation, and the high purity Zn foil was purchased from Qinghe county bo dun cemented carbide Co., Ltd.

2.2. The synthesis of PQA and PQA@Zn

Typically, 1 g p-Benzoquinone and 0.35 g p-Phenylenediamine were respectively dissolved in 50 mL ethanol, then mixed the above two solutions with continuous stirring for 10 min and reacted for 24 h. Subsequently, collecting the product via a vacuum filtration process after being washed a few times with water and ethanol. Finally, the black powder of PQA was obtained after being dried at 50 ºC for 12 h.

The PQA@Zn composite materials were prepared by a blade coating method. Firstly, PQA, superconductive carbon blacks and PVDF were mixed with N-methylpyrrolidone by grinding according to the mass ratio of 8:1:1. Then the mixture was coated on the bare Zn (100 mm × 100 mm, the thickness of 0.08 mm) surface via a blade coater for 200 μm followed dried at 50 ºC for 12 h to obtain the PQA coated Zn foil which was labeled as PQA@Zn.

2.3. Materials and electrochemical characterization

The scanning electron microscope (SEM, JEOL JSM-7600F) measured the surface morphology of the samples. Fourier transform infrared (FTIR, Perkin Elmer Frontier) spectroscopy tested the functional groups of the PQA. X-ray diffraction (XRD, NEW SmartLab) was used to test the crystal structures from the sample and electrodes.

The symmetrical coin-type cells (CR2032) assembled were composited of two PQA@Zn or bare Zn foil at ambient temperature, 2 M $ZnSO_4$ used as the electrolyte, glass fiber served as the separator. To study the cycling stability, galvanostatic charging-discharging (GCD) cycles were measured under the current densities of 0.5−5 mA cm^{-2} and capacities of 0.5−5 mAh cm^{-2} on a NEWARE battery testing system. Electrochemical impedance spectroscopy (EIS) was used to evaluate the internal impedance and ions diffusion characteristics.

3. Results and discussion

The synthesis of PQA was displayed in Figure 1a. Typically, owing to the p-Benzoquinone and p-Phenylenediamine spontaneously reacting under oxidation conditions in ambient temperature, p-Benzoquinone is used as an oxidant and that is reduced as monosubstituted hydroquinone, monosubstituted benzoquinone and disubstituted benzoquinone, the PQA is then synthesized by

continuous substitution and addition reactions with a solution polymerization. As shown in Figure 1b, digital and SEM images of bare Zn foil are shown on the smooth and flat surface, then as-prepared PQA powder is served as a unique protective layer, which overlayed on the surface by a blade coating approach. Finally, the PQA@Zn is obtained after removing the redundant solvent. The digital photo of PQA@Zn indicates the black PQA coating is attached to the Zn surface successfully, while the SEM image further manifests that the PQA particles are uniformly distributed on bare Zn.



Figure 1. (a) The synthesis of PQA materials. (b) The preparation diagram of PQA@Zn composite materials.

As shown in Figure 2a, FTIR spectra of PQA@Zn reveal the diffraction peak of phenol O−H stretch that is found at about 3213 cm^{-1}, the peaks around 1632, 1570, 1512, 1484 cm^{-1} belongs to the aromatic C=C bending characteristic. The peaks displayed around 1348 and 1280 cm^{-1} represent the aromatic C−N bending, and the aromatic C−H bending peak is demonstrated at 830 cm^{-1}. Furthermore, XRD patterns of the samples are observed in Figure 2b. The bare Zn shows the strong peaks located at 36.3º, 39.0º, 43.2º, 54.3º, 70.1º and 77.0º, which proves that the bare Zn is composed of a pure Zn phase (PDF # 87-0713). Moreover, PQA@Zn preserved the peaks of PQA and bare Zn proving the presence of the PQA on the Zn surface. The above results are consistent with those obtained in previous studies [3].

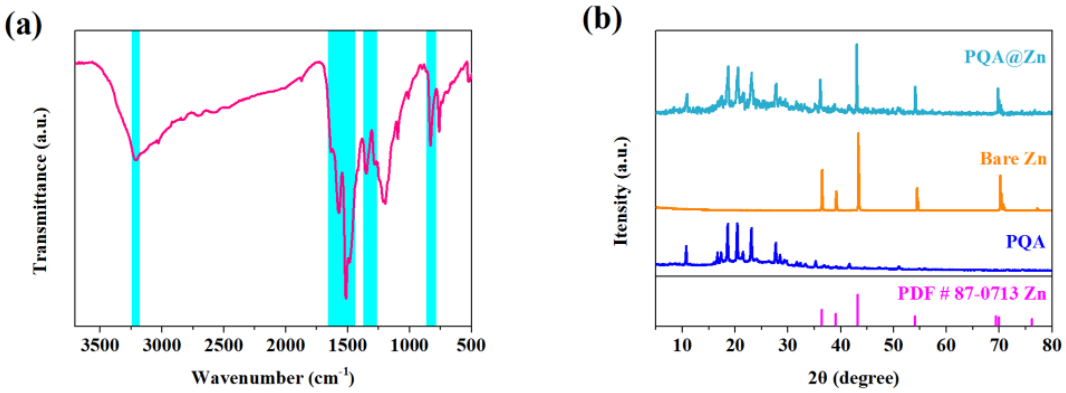


Figure 2. (a) FTIR spectra of PQA@Zn. (b) XRD patterns of PQA, bare Zn and PQA@Zn.

Here, the service life and stability are evaluated by assembling Zn//Zn and PQA@Zn//PQA@Zn symmetric devices with the continuous plating/stripping process. When applied the capacity of 1 mAh cm^{-2} at 1 mA cm^{-2}, bare Zn exhibits large voltage oscillation after only 16 h and finally results in device failure, which might be attributed to the dendrite-induced failure. In comparison, the PQA@Zn electrode displays superior stability and long cycle life of 450 h when compared with bare Zn (Figure 3a). In the first cycle, the voltage hysteresis of PQA@Zn (133.5 mV) is higher than bare Zn (78.3 mV), which is concerned with the diffusion procedure of electrolyte between the PQA and bare Zn,

resulting in a slightly increased hysteresis [4]. After 12 h of plating/stripping, the PQA@Zn displays stable voltage responses and low hysteresis (97.3 mV), manifesting the PQA coating exhibits outstanding conductivity and the charge redistribution ability. The obvious enhancement effect is observed from the high capacity of 5 mAh cm^{-2} at 5 mA cm^{-2} (stable for 220 h) in Figure 3b, demonstrating the uniform plating/stripping and remarkable inhibition for the dendrite growth. Figure 3c confirms the predominant rate capability and cyclability, while the PQA@Zn electrode exhibits favorable stability and relatively lower overpotential even at 5 mA cm^{-2}. Moreover, EIS measurements (Figure 3d) fitting the R_s and R_{ct} of bare Zn are 1.52 Ω and 405.8 Ω, while the PQA@Zn is 1.58 Ω and 419.5 Ω, respectively. The nuanced difference indicates that the introduction of the PQA protective layer on Zn has nonexistent effects on the internal impedance and ions transfer characteristic.

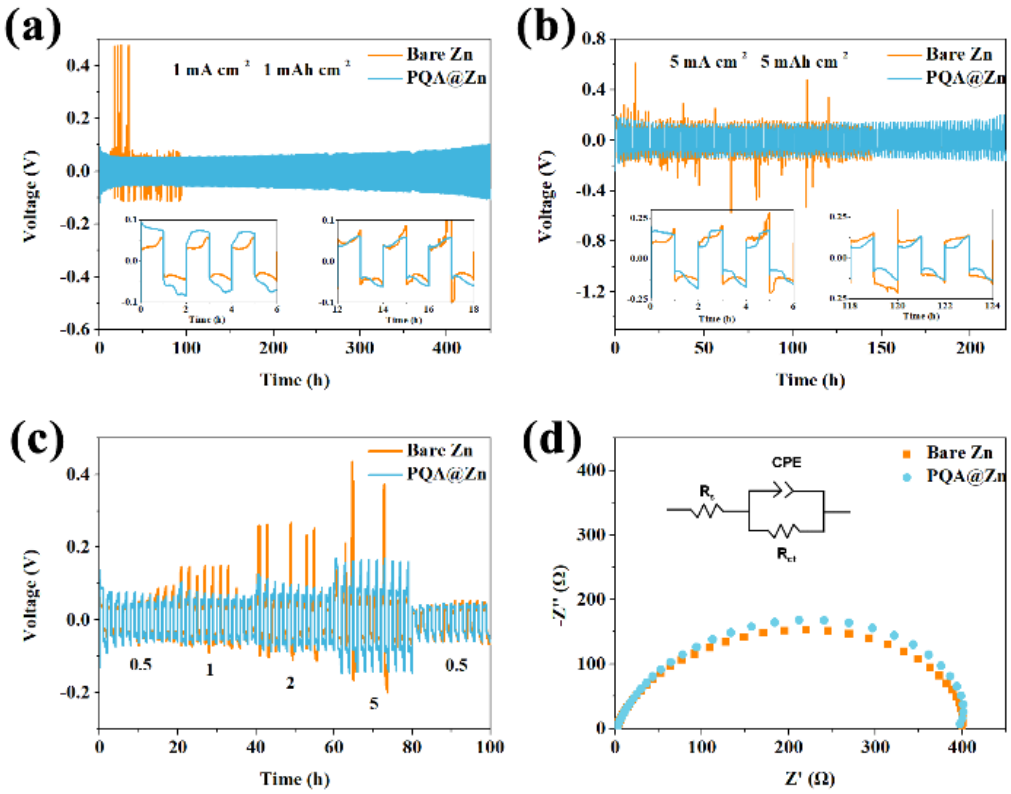


Figure 3. Cyclability of Zn//Zn and PQA@Zn//PQA@Zn symmetrical devices. Current-voltage profiles for (a) 1 mAh cm^{-2} at 1 mA cm^{-2}, (b) 5 mAh cm^{-2} at 5 mA cm^{-2}. (c) Rate capability at 0.5 ~ 5 mA cm^{-2}. (d) EIS measurements of different electrodes.

The formation of the Zn dendrites from Zn and PQA@Zn can illustrate in Figure 4. Generally, the surface morphologies of bare Zn are heterogeneously changed in the plating/stripping procedure, causing uneven nucleation and growth (Figure 4a), and further deposited on the sharp ends after repeated cycling, leading to the failure of the device. Therefore, the PQA coating played a positive role in controlled dendrites' growth (Figure 4). Firstly, the PQA prevents the Zn metal from violently reacting with water, restricts the irregular growth of dendrite, and reduces the short circuit risks. Secondly, PQA polymer chains provide abundant ion transfer and diffusion channels, which can availably redistribute Zn^{2+} flux near the interphase (Figure 4a), achieving an overstable Zn plating/stripping procedure. Thirdly, owing to the intense affinity between PQA and Zn^{2+}, the PQA@Zn electrode can capture/dissociate the Zn^{2+} during the discharge/charge state and adjust the Zn^{2+} deposition sites (Figure 4b), which results from a homogeneous electric field and nucleation of Zn^{2+} between PQA and Zn layers, enables a uniform and flat deposition of dendrite [3]. Finally, the PQA@Zn electrode displayed long service life and superior electrochemical stability.

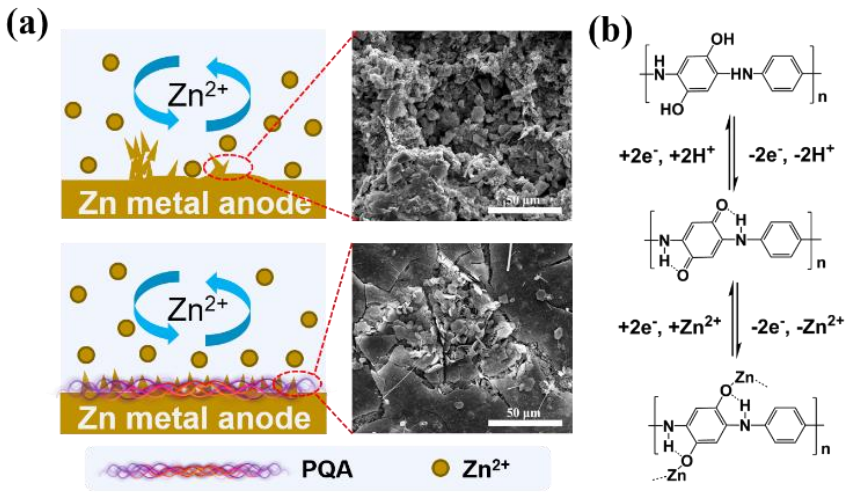


Figure 4. (a) Dendrites growth illustration of bare Zn and PQA@Zn anodes. (b) The proposed redox mechanism of PQA@Zn.

4. Conclusions

In summary, the PQA@Zn with ultra-stable cycling performances is prepared via a blade coating method that used PQA as a protective layer. As a result, due to the PQA layer presenting the barrier effect, suitable ion transport channels and intense affinity with Zn^{2+}, the PQA@Zn electrode displayed the superior stability and long cycle life of 450 h with 1 mAh cm^{-2} at 1 mA cm^{-2}, even stable for 220 h with 5 mAh cm^{-2} at 5 mA cm^{-2}. Moreover, the PQA@Zn electrode exhibits favorable rate capability and relatively lower overpotential at various current densities, which further demonstrates an excellent utilization potentiality in the field of Zn-ion energy storage.

Acknowledgments

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