Electrochemical Zinc Ion Capacitors Enhanced by Redox Reactions of Porous Carbon Cathodes

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Aqueous electrochemical zinc ion capacitors (ZICs) are promising next-generation energy storage devices because of their high safety, inexpensive raw materials, and long cycle life. Herein, an aqueous ZIC with superior performance is fabricated by employing an oxygen-rich porous carbon cathode. Excellent capacitance and energy density are obtained thanks to the electric double-layer capacitance of porous carbon, and additional pseudocapacitances originating from the variation in oxidation states of oxygen functional groups and the reversible electrochemical hydrogen adsorption and desorption during each round-trip charge–discharge cycle. Moreover, the cycling stability of ZIC is effectively prolonged by suppressing zinc dendrite growth with a simple surface carbon coating strategy. The assembled ZIC delivers a high capacitance of 340.7 F g⁻¹, a high capacity of 179.8 mAh g⁻¹ in a wide voltage window of 0–1.9 V, a maximum energy density of 104.8 Wh kg⁻¹, and an ultrahigh power density of 48.8 kW kg⁻¹. Furthermore, the as-fabricated aqueous ZIC exhibits an ultralong cycle life of 30 000 cycles with a high capacity retention of 99.2%. This work provides a novel design strategy by incorporating reversible hydrogen and oxygen redox reactions to enhance the energy storage capability of aqueous ZICs toward practical energy storage applications.

1. Introduction

Renewable energy storage requires low-cost energy storage systems with high safety and long cycle life.^[1] Among various rechargeable batteries and supercapacitors, aqueous electrochemical energy

storage systems are preferred due to their high safety and low capital cost.^[2] However, commercial aqueous lead- and nickel-based rechargeable batteries possess low energy densities (≈ 45 Wh kg⁻¹ for Pb–acid batteries;^[3] ≈ 50 Wh kg⁻¹ for Ni–Cd batteries^[4]) and limited life spans, which increases the energy storage cost per unit energy output,^[5,6] thus limits their practical applications. Zinc metal is considered as an ideal anode for aqueous energy storage devices because of its high theoretical capacity (gravimetric, 820 mAh g⁻¹; volumetric, 5851 mAh cm⁻³), low potential (-0.76 V vs standard hydrogen electrode (SHE)), and high hydrogen evolution overpotential.^[7] Zinc-based rechargeable batteries and capacitors are expected to be low-cost, long-life energy storage devices since they utilize inexpensive zinc metal anode and aqueous electrolytes.^[8,9] However, most transition-metal oxide cathodes display limited cycle life due to dissolution and parasitic reactions, which deteriorates the cycle performance of zinc ion batteries.^[10]

Electrochemical zinc ion capacitors (ZICs) are hybrid supercapacitors con-

sisting of zinc anodes and porous carbon cathodes.^[11,12] On the one hand, theoretically, a porous carbon cathode has unlimited cycle life due to the adsorption/desorption charge storage mechanism without phase transition.^[13] On the other hand, the zinc anode shows Faradaic reactions with infinite theoretical capacitance compared with a porous carbon cathode, which exerts the maximum electric double-layer capacitance (EDLC) of porous carbon cathode.^[14] Nevertheless, in an aqueous ZIC system, commercial porous carbon has low capacity, energy density and power density (typical values are ≈ 55 mAh g⁻¹, 43.1 Wh kg⁻¹, and 12.0 kW kg⁻¹ for YP-50F, Kuraray Chemical, Japan)^[15] due to its EDLC dominated charge storage mechanism.^[16,17] Therefore, novel porous carbon cathodes are designed to boost the electrochemical performances of full-cell ZIC.^[18] Kang and co-workers reported a ZIC with activated carbon cathode and Zn anode in an aqueous ZnSO₄ electrolyte.^[19] The assembled ZIC delivered a capacity of 272.3 F g⁻¹ and a high power density of 14.9 kW kg⁻¹ with a corresponding energy density of 30 Wh kg⁻¹ in the operational voltage window of 0.2–1.8 V. Liu and co-workers employed a porous carbon cathode to assemble ZIC. The as-fabricated ZIC delivered a capacitance of 298.6 F g⁻¹, a maximum energy density of 82.36 Wh kg⁻¹, and a maximum power density of up to 3.76 kW kg⁻¹ in the operating voltage

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range of 0.2–1.8 V.^[20] In another work, Tang and co-workers reported a ZIC consisted of Zn anode and bioderived porous carbon cathode using 1 M $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ in acetonitrile (AN) as the electrolyte.^[11] The organic electrolyte enabled a wide operation voltage window of 0–1.8 V so that the ZIC showed a high capacitance of 170 F g^{-1} and a high energy density of 52.7 Wh kg^{-1} at a power density of 1.73 kW kg^{-1} . Despite these achievements, the energy densities of ZICs still need to be improved to compete with the rechargeable zinc ion batteries (ZIBs) while maintaining the long cycle life merit of ZICs. A promising approach to enhance the energy density is to utilize the Faradaic redox reactions occurring on the surface of porous carbon.^[21] Lu and co-workers used a nitrogen-doped porous carbon cathode to assemble ZIC. Nitrogen dopants significantly increased the energy storage capability of ZIC by decreasing the energy barrier for C–O–Zn bonding, thus effectively boosting the chemical adsorption of Zn ions at the cathode surface. The ZIC with N-doped porous carbon cathode displayed a high power density of 24.9 kW kg^{-1} at an energy density of 107.3 Wh kg^{-1} in the voltage range of 0–1.8 V.^[22] Besides, due to the relatively low working potential of zinc anode (-0.76 V vs SHE), the reversible hydrogen chemistry may be adopted in the charge storage of a porous carbon cathode.

In this work, a high-performance aqueous ZIC is fabricated by employing an oxygen-rich porous carbon (PC) as the cathode. The ZIC assembled with PC cathode delivers a high capacitance of 340.7 F g^{-1} , a high energy density of 104.8 Wh kg^{-1} , and a high power density of 48.8 kW kg^{-1} , which originates from the coupled charge storage mechanisms of EDLC and reversible hydrogen and oxygen redox reactions occurring at porous carbon cathode. Furthermore, the cycle life of ZIC is prolonged to 30 000 cycles by suppressing the zinc dendrite growth with a simple carbon coating strategy. Additionally, the as-fabricated ZIC also displays a low self-discharge rate. Based on these merits, the ZIC developed in this work is a promising electrochemical energy storage device for practical applications.

2. Results and Discussion

Porous carbon (PC) was used as a cathode in the construction of hybrid ZIC in this work. PCs were prepared from the direct pyrolysis of pyromellitic acid tetra-potassium salt (PMA4K) with acid etching (Figure 1a shows the schematic). The pyrolysis process of PMA4K was recorded and analyzed by thermogravimetric analysis coupled with mass spectroscopy (TGA-MS)

Figure 1. Physicochemical characterizations of PC samples. a) Schematic diagram illustrating the synthesis processes of PC; b) SEM and c,d) TEM images of PC800 with different magnifications; e) Raman spectra, f) N_2 adsorption and desorption isotherms, and g) XPS survey spectra of PC700, PC800, and PC900.

(Figure S1, Supporting Information), X-ray diffraction (XRD) (Figure S2, Supporting Information), and energy-dispersive X-ray spectroscopy (EDS) (Figure S3, Supporting Information). Prominent activation occurs at the pyrolysis temperature above 700 °C,^[23,24] so pyrolysis temperatures of 700, 800, and 900 °C were chosen to prepare PC. The obtained PC samples are denoted as PC700, PC800, and PC900, respectively. The PC800 sample shows a hierarchical framework composed of hollow nanocarbon spheres with diameters of ≈ 50 nm (scanning electron microscopy (SEM) image in Figure 1b) and wall thicknesses of ≈ 10 –20 nm (transmission electron microscopy (TEM) images in Figure 1c,d). Because the activation becomes extensive with increasing thermal treatment temperature, the PC800 formed a more porous structure than PC700. PC900 formed a hierarchical porous structure with obvious macropores because partial carbon spheres began to collapse at the temperature of 900 °C (Figure S4, Supporting Information). The broad (002) peaks in the X-ray diffraction (XRD) (Figure S5, Supporting Information) pattern indicate that the PC samples are amorphous, which is in line with the following Raman results. PC900 exhibits sharper (002) peaks than PC700 and PC800, which is consistent with the increased 2D Raman peak intensity of PC900 (a sign of stacked graphene layers) in the Raman spectra (Figure 1e). The D-band at ≈ 1351 cm^{-1} and G-band at ≈ 1588 cm^{-1} are attributed to the disordered sp^3 -hybridized carbon and ordered graphitic sp^2 -hybridized carbon. The ratios of D and G peaks (I_D/I_G) are used to compare the intrinsic structure of carbon materials. The I_D/I_G value decreases with increasing thermal treatment temperature (0.902 for PC 700, 0.833 for PC800, and 0.714 for PC900), indicating an increased graphitic crystalline structure. N_2 adsorption and desorption isotherms of PC samples belong to combined I/IV isotherms indicative of the coexistence of meso- and microporous structures (Figure 1f). The N_2 adsorption and desorption isotherms indicate that both the specific surface areas (SSA) and the pore volumes of PC increase with increasing thermal treatment temperature. PC700, PC800, and PC900 show SSAs of 773.3, 1094.7, and 1976.6 $\text{m}^2 \text{g}^{-1}$, and pore volumes of 0.67, 1.11, and 1.77 $\text{cm}^3 \text{g}^{-1}$, respectively (Table S1, Supporting Information). The pore size was also enlarged with increasing thermal treatment temperature (Figure S6, Supporting Information). More importantly, as the carbon–oxygen bond is less strong than the carbon–carbon bond,^[25] the oxygen content of PC (7.6 at% for PC700, 6.7 at% for PC800, and 3.2 at% for PC900) decreases with increasing thermal treatment temperature (Figure 1g). High-resolution O 1s XPS spectra also indicate that the relative ratios for carbonyl and hydroxyl groups of PC samples are comparable (Figure S7 and Table S2, Supporting Information).

Three kinds of zinc-ion containing electrolytes, 1 mol L^{-1} ZnSO_4 , 1 mol L^{-1} $\text{Zn}(\text{ClO}_4)_2$, and 3 mol L^{-1} $\text{Zn}(\text{ClO}_4)_2$ aqueous solutions, were chosen for electrochemical stability investigations. The electrolyte stabilities were investigated with linear voltammetry scan (LSV) technique in a three-electrode configuration composed of a stainless-steel working electrode, a zinc counter electrode, and a zinc reference electrode. Within the voltage range of 0–2.4 V versus Zn/Zn^{2+} , 1 mol L^{-1} $\text{Zn}(\text{ClO}_4)_2$ electrolyte shows comparable hydrogen evolution reaction (HER) overpotential and higher oxygen evolution reaction (OER) overpotential with that of 1 mol L^{-1} ZnSO_4 electrolyte

(Figure S8, Supporting Information). The 3 mol L^{-1} $\text{Zn}(\text{ClO}_4)_2$ electrolyte exhibits much higher HER and OER overpotentials than its counterpart of 1 mol L^{-1} $\text{Zn}(\text{ClO}_4)_2$. The high overpotential of HER and OER of the 3 mol L^{-1} $\text{Zn}(\text{ClO}_4)_2$ could reduce parasitic reactions in the ZIC.^[26] Furthermore, we tested the cyclic voltammetry (CV) curves of PC800 in 3 mol L^{-1} $\text{Zn}(\text{ClO}_4)_2$ and 1 mol L^{-1} ZnSO_4 . PC800 shows higher gravimetric capacitance (225.5 F g^{-1}) in 3 mol L^{-1} $\text{Zn}(\text{ClO}_4)_2$ electrolyte than that in 1 mol L^{-1} ZnSO_4 electrolyte (165.2 F g^{-1}) at a scan rate of 1 mV s^{-1} in the potential range from 0 to 1.9 V versus Zn/Zn^{2+} (Figure S9, Supporting Information). Given the high specific capacitance of porous carbon and wide voltage window, 3 mol L^{-1} $\text{Zn}(\text{ClO}_4)_2$ was selected as the electrolyte in this work.

To evaluate the electrochemical behaviors of PC electrodes in 3 mol L^{-1} $\text{Zn}(\text{ClO}_4)_2$ electrolyte, a hybrid ZIC was constructed with PC800 as the cathode, zinc metal foil as the anode, wood pulp/polyester nonwoven fabrics (Sontara MicroPure AP) as the separator, and 3 mol L^{-1} $\text{Zn}(\text{ClO}_4)_2$ aqueous solution as the electrolyte. The CV curves of PC800 were recorded at a scan rate of 20 mV s^{-1} . When PC800 is cycled within the potential range of 0.5 to 1.5 V, the CV curve of PC800 presents a typical rectangular shape indicating an EDLC behavior.^[27] When the negative cutoff potential gradually decreases from 0.5 to 0 V, a cathodic peak appears close to 0 V, and a corresponding hump anodic peak appears around 1.26 V. These peaks could be ascribed to the redox reactions.^[27] Although the thermodynamic potential of HER (E_{HER}) in 3 mol L^{-1} $\text{Zn}(\text{ClO}_4)_2$ aqueous electrolyte is calculated to be 0.55 V versus Zn/Zn^{2+} (Figure 2a; Section S1.5 in the Supporting Information),^[5,28] no significant hydrogen evolution and potential hysteresis was observed for PC800 discharged to 0 V. Hence, the cathodic peak may be associated with reduction reaction contributed by electrochemical hydrogen adsorption on the surface of PC800, while the hump peak at 1.26 V is ascribed to the oxidizing reaction of hydrogen atoms which are electrochemically desorbed from the surface of PC800 in the charge process. The above reversible electrochemical hydrogen adsorption and desorption are similar to the electrochemical hydrogen storage processes.^[29] By setting the negative cutoff potential at 0 V and gradually increasing the positive cutoff potential to 2 V, a significant anodic OER peak appears with a reduction peak around 1.1 V shown up. Although the thermodynamic potential of OER (E_{OER}) for 3 mol L^{-1} $\text{Zn}(\text{ClO}_4)_2$ is 1.78 V versus Zn/Zn^{2+} (Section S1.5 in the Supporting Information), oxygen evolution on PC800 is significantly prohibited until 2.0 V due to slow OER kinetics. The small anodic peak around 2.0 V and the cathodic peak around 1.1 V could be ascribed to the reversible oxidation and reduction of surface carbon atoms or oxygen functional groups. By further increasing the cutoff potential beyond 2 V, the current response rises significantly due to the contribution of OER and the oxidation of PC800, which is confirmed by the swelling of coin cell. Meanwhile, the oxidation of carbon electrode leads to serious carbon consumption that can result in the failure of ZIC. Thus, the operational voltage window of ZIC in this work was set as 0–1.9 V based on the considerations of long-term cycle stability and high Coulombic efficiency.

Furthermore, to verify the capacitance contributions of two redox reactions, we calculated the potential-dependent capacitances^[30] of PC800 (Figure 2b). Due to the potential-dependent

Figure 2. Electrochemical behavior investigations of PC800 cathode. a) CV curves obtained using different potential windows at a scan rate of 20 mV s⁻¹ and b) corresponding specific capacitances, c) GCD curves at a current density of 0.1 A g⁻¹, d) CV curves at different scan rates, e) logarithm relationship between the scan rates and the peak current densities at the cathodic peaks of 0.85–0.54 V (b_R) and anodic peaks of 0.98–1.36 V (b_O), and f) capacitive contribution calculated at a scan rate of 2 mV s⁻¹.

redox reactions, the capacitances of PC800 cathode increase efficiently when the working potential range is expanded to specific potentials. Specifically, when the cutoff potentials were negatively expanded from 0.5 to 0 V, and positively expanded from 1.5 to 1.9 V, the specific capacitances of PC800 increased significantly. The increase of specific capacitance results from the pseudocapacitances of reversible hydrogen redox reactions at low potential range (≈ 0.2 –0 V) and reversible oxygen reactions at a high potential range (≈ 1.7 –1.9 V). Coupled with the reversible hydrogen and oxygen redox reactions, the specific capacitance of PC800 within 0–1.9 V is 133.0 F g⁻¹ which is 33% higher than the specific capacitance of 99.5 F g⁻¹ tested within 0.5–1.5 V at a scan rate of 20 mV s⁻¹ (Figure 2b). The galvanostatic charge–discharge (GCD) curves of PC800 also show the variation in specific capacitances at different potential windows (Figure 2c). When decreasing the negative cutoff potential, the slope of GCD curve becomes smaller, indicative of the increasing of specific capacitance. With increasing the positive cutoff potential, the slope of GCD curve tends to slacken, demonstrating the increase of specific capacitance. The specific capacitances of PC800 cathode calculated by GCD within 0–1.9 V are higher than that within 0.5–1.5 V at various current densities (Figure S10, Supporting Information). The rate capacitances of PC800 within 0–1.9 V are worse than those within 0.5–1.5 V, reflecting the nature of redox reaction-induced pseudocapacitance. Furthermore, we utilized CV analysis to study the electrode kinetics of PC800. The CV curves of PC800 electrodes were tested at scan rates from 1 to 300 mV s⁻¹, implying a charge–discharge rate from 31.7 min to 6.3 s (Figure 2d). The logarithms relationship between peak currents and

scan rates was calculated as b value (Section S1.5 in the Supporting Information).^[31,32] The b value of 0.5 corresponds to a diffusion-controlled redox reaction, while the b value of 1.0 is related to a capacitive surface dominated reactions (Faradaic or charge adsorption). The b values for the reduction and oxidation peaks of PC800 were calculated to be 0.903 and 0.896, respectively, indicating the fast capacitive dominated reactions (Figure 2e) with a certain degree of diffusion-controlled redox reactions. The Dunn method^[33] (Section S1.5 in the Supporting Information) was further applied to calculate the potential-dependent capacitive and diffusion-controlled contributions of PC800. The capacitive and diffusion contributions of PC800 at 2 mV s⁻¹ are 73.3% and 26.7%, respectively (Figure 2f). When the scan rate increases from 2 to 100 mV s⁻¹, the diffusion-controlled contribution of PC800 decreases from 26.7% to 16.8% (Figure S11, Supporting Information). Furthermore, Figure 2f also demonstrates that diffusion-controlled reactions occur in the high and low potential ranges, which indicates that the charge storage mechanisms in these ranges are Faradaic, and is in line with our previous electrochemical study.

The charge–discharge processes of PC800 were further investigated by SEM, X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) to probe the chemical transformation details (Figure 3). SEM images indicate that the morphology of PC800 cathode does not change during the charge process from 0.76 to 1.90 V (Figure 3b). We further used XPS to study the oxidation state change of O element. O 1s XPS spectra indicate that the carbonyl (C=O, located at 531.7 eV)^[14,34] of PC800 electrode increases from 16.9 to 44.3 at% during the charge process from 0.76 to 1.9 V. When PC800 is discharged to 0.76 V, the

Figure 3. Study of charge storage mechanism of PC800 cathode. a) Typical GCD curves showing different charge–discharge states with their b) corresponding SEM images, c) high-resolution O 1s XPS spectra, and d) XRD pattern of PC800.

carbonyl (C=O) decreases back to 17.5% (Figure 3c). Obviously, partial hydroxyl groups (C–OH located at 533.4 eV)^[14,34] of PC 800 electrode take part in oxidizing reaction into carbonyl groups (C=O) during the charge process and are reduced back to hydroxyl groups (C–OH) during the discharge process (Equations (1) and (2)).^[35] On the other hand, SEM images suggest that some flocculent particles are generated on the cathode after PC800 is discharged from 0.76 to 0 V, and then disappear during the charge process from 0 to 1.9 V (Figure 3b). XRD analysis demonstrates that the flocculent particles are alkaline salts of Zn₄ClO₄(OH)₇ and Zn(OH)₂ (Figure 3d). EDS elemental analysis further verifies that the flocculent particles consist of C, Zn, Cl, and O elements (Figure S12, Supporting Information). Thus, electrochemical hydrogen adsorption and desorption (Equations (3) and (4)) lead to a dynamic local alkaline environment that is responsible for the formation and dissolution of alkaline salts (Equationa (5)–(8)). Based on the above mechanism, hydrogen adsorption is estimated to occur during the discharge process from 0.25 to 0 V, while hydrogen desorption is estimated to occur during the charge process from 0 to 1.8 V, which is indicated by the deposition and dissolution of alkaline zinc salts shown in the in situ XRD technique

(Figure S13, Supporting Information). In summary, besides EDLC, we observed two sources of pseudocapacitances (reversible hydrogen and oxygen redox reactions) both of which contribute to the specific capacitance of PC800 cathode

Figure 4. Comparison study for the electrochemical performances of PC700, PC800, and PC900 cathodes. a) CV curves recorded at a scan rate of 1 mV s⁻¹, b) GCD curves of PC800, c) the dependent galvanostatic specific capacities and d) capacitances of PC samples at current densities from 0.1 A g⁻¹ to 20 A g⁻¹, e) the variation trends for gravimetric specific capacitances, atomic oxygen contents, and areal specific capacitances (normalized by the SSAs) with thermal treatment temperatures of PC samples, f) Ragone curve of PC800 compared with the maximum power density values of zinc ion energy storage devices (ZICs (♦): Zn//1 M Zn(CF₃SO₃)₂/bioderived porous carbon,^[11] Zn//3M Zn(CF₃SO₃)₂/graphene derived porous carbon,^[13] Zn//1 M ZnSO₄/layered B/N codoped porous carbon,^[15] Zn//2 M ZnSO₄/activated carbon (AC),^[19] Zn//1 M ZnSO₄/porous carbon,^[20] Zn//1 M ZnSO₄/hierarchical porous carbon (HPC),^[22] Zn//2 M ZnSO₄/AC,^[37] Zn//2 M ZnSO₄/HPC,^[38] Zn//1 M ZnSO₄/hollow carbon spheres,^[39] Zn//2 M ZnSO₄/AC,^[40] Zn//2 M ZnSO₄/AC,^[41] Zn//2 M ZnSO₄/graphene oxide film,^[42] Zn//1 M ZnSO₄/porous carbon nanoflake,^[43] ZIBs (△): Zn//ZnCl₂//PANI/carbon fiber,^[12] Zn//2 M ZnSO₄/PTO,^[44] Zn//20 × 10⁻³ M ZnSO₄/CuHCF,^[45] Zn//2 M ZnSO₄/MnO₂,^[46] Zn//20 × 10⁻³ M ZnSO₄/CuZnHCF,^[47] Zn//2 M ZnSO₄/MXene-rGO₂,^[48] and M denotes mol L⁻¹) reported in recent years.

Moreover, the electrochemical performances of PC700, PC800, and PC900 were comparatively studied to correlate their structural characteristics and surface chemistry with their capacitive performances (Figure 4). All the CV curves of PC samples show cathodic and anodic peaks at 0.85 and 1.08 V, respectively (Figure 4a). According to the charge storage mechanism of EDLC, high SSA leads to high capacitance. However, PC700 cathode with lower SSA shows a higher current than PC800 and PC900 cathodes in the CV test, which indicates that the capacitance of PC700 is higher than that of PC800 and PC900 cathodes. The high capacitance of PC700 cathode can be attributed to its high pseudocapacitance contribution. The high pseudocapacitance contribution in PC700 originates from its high content of oxygen functional groups which result from the relatively low thermal treatment temperature. On the contrary, PC900 was prepared at a higher temperature, which results in its relatively low content of oxygen functional groups. The low oxygen content of PC900 contributes to a limited pseudocapacitance. Therefore, PC900 cathode with high SSA and low oxygen content only delivers a limited specific capacitance. GCD curves show decreasing slopes at the end of charge and discharge curves under various current densities (Figure 4b), which is a sign that the capacitances increase

at high and low potential ranges.^[27] This phenomenon demonstrates that hydrogen and oxygen pseudocapacitances are involved in the charge–discharge process. Rate capabilities of PC samples are compared with the capacities calculated by GCD curves at current densities of 0.1–20 A g⁻¹ (Figure 4c). The specific capacities (Section S1.5, Supporting Information) of PC700, PC800, and PC900 are 191.5, 179.8, and 145.7 mAh g⁻¹ at a current density of 0.1 A g⁻¹ and 58.2, 78.4, and 63.1 mAh g⁻¹ at 20 A g⁻¹, respectively. Compared with PC800 and PC900 cathodes, the PC700 cathode shows higher specific capacities at current densities below 0.5 A g⁻¹, but lower specific capacities at current densities above 10 A g⁻¹. The poor rate capability of PC700 cathode results from the low contribution of EDLC type capacitance due to its low SSA and the high contribution of pseudocapacitance related to the high oxygen content. PC800 and PC900 cathodes exhibit good rate capabilities owing to their high SSAs and mesoporous volumes. PC800 cathode shows a higher capacity than the PC900 cathode at each current density, which results from its relatively high oxygen content. High oxygen content is responsible for high pseudocapacitance and good wettability of the carbon electrode.^[36] PC700, PC800, and PC900 exhibited contact angles of 28.7°, 34.7°, and 67.4° at 0.02 s after the

contact between water droplets and the surfaces of PC cathodes (Figure S14, Supporting Information). Because of the relatively poor wettability of PC900, partial micropores of PC900 are inaccessible to the electrolyte. Thus, PC900 with relatively higher SSA shows relatively lower specific capacitance than that of PC700 and PC800. Under the GCD current density of 0.1 A g^{-1} , PC700, PC800 and PC900 deliver gravimetric specific capacitances (Section S1.5, Supporting Information) of 362.8, 340.7, and 276.1 F g^{-1} (Figure 4d), and areal specific capacitances (normalized by SSAs; Section S1.5, Supporting Information) of 46.9, 31.1, and $14.0 \mu\text{F cm}^{-2}$, respectively (Figure 4e). Compared with PC900, PC700, and PC800 show much higher areal specific capacitances due to their better wettability and higher oxygen contents which contribute more to hydrogen and oxygen redox reactions. Significantly, with relatively high SSA, good wettability, and high oxygen content, PC800 can be operated at current densities ranging from 0.1 to 60 A g^{-1} (Figure S15a,b, Supporting Information). At the current density of 60 A g^{-1} , the ZIC with PC800 cathode can be charged and discharged within 3 s. Meanwhile, high Coulombic efficiencies of ZIC with PC800 cathode are achieved

at a wide range of current densities. The Coulombic efficiencies of ZIC with PC800 cathode increase with increasing current densities (Figure S15c, Supporting Information). The Coulombic efficiencies of ZIC at 0.1, 0.2, 0.5, and 1 A g^{-1} are 95.2%, 98.2%, 98.7%, and 99.6%, respectively, indicating the high reversibility of ZIC. The high Coulombic efficiencies of ZIC with PC800 cathode also demonstrate the high reversibility of oxygen and hydrogen redox processes. ZIC with PC800 cathode delivers a high gravimetric specific capacitance of 340.7 F g^{-1} , corresponding to a high energy density (Section S1.5, Supporting Information) of 104.8 Wh kg^{-1} at a power density of 58 W kg^{-1} (Section S1.5, Supporting Information). The ZIC can still deliver a gravimetric specific capacitance of 112.2 F g^{-1} even at a high current density of 60 A g^{-1} , demonstrating its superior rate capability. Notably, an ultrahigh power density of 48.8 kW kg^{-1} with a correspondingly high energy density of 40.4 Wh kg^{-1} can be achieved at a current density of 60 A g^{-1} , which is the highest value among the ZICs^[11,13,15,19,20,22,37–43] and ZIBs^[12,44–48] reported recently. Considering ZIC with PC800 cathode can deliver twice the energy density and six times the power density of the ZIC with

Figure 5. Study for cycling performance of (Zn/PC)//PC ZIC. a) Cycling stability of the (Zn/PC)//PC ZIC and the Zn//PC ZICs at a current density of 20 A g^{-1} , and corresponding GCD curves at the b) 1st, c) 4092nd and d) 30 000th cycles. SEM images of the separator of Zn//PC ZIC penetrated by Zn dendrite after 4092 cycles: e) side and f) top views, g) SEM image for the PC coated on the Zn anode of (Zn/PC)//PC ZIC after 30 000 cycles.

commercial YP-50F cathode (50.2 Wh kg^{-1} and 7.4 kW kg^{-1}),^[49] we believe our ZIC with PC800 cathode is a promising device for practical energy storage applications.

Although zinc anode is an ideal anode for aqueous energy storage devices in terms of capacity and working potential, zinc anode faces failure due to its dendrite formation related short circuit. To improve the stability of ZIC, we coated PC800 on the surface of zinc anode to suppress the growth of zinc dendrite. This strategy enables a ZIC with the configuration of (Zn/PC)//PC. This carbon coating strategy is more simple compared with complex artificial solid electrolyte interphase decoration methods^[50] and is more environmental-friendly compared with some toxic electrolyte additives.^[51] Carbon coating is also practical and can be scaled up in manufacturing environment. The mesoporous structure of PC800 could alleviate the growth of

zinc dendrite by decreasing the local current density.^[52,53] To demonstrate the effectiveness of our carbon coating strategy, a Zn//PC full cell consists of PC800 cathode and bare Zn anode was tested for comparison. In the GCD cycling test, the Zn//PC ZIC only run 4092 cycles and then short-circuited, while the (Zn/PC)//PC exhibited an ultralong cycle life of 30 000 cycles with a high capacity retention of 99.2% at a current density of 20 A g^{-1} (Figure 5a). The 1st GCD curves of Zn//PC and (Zn/PC)//PC ZICs are similar in shape (Figure 5b). However, the Zn//PC ZIC cannot be charged at the 4902nd cycle because of short-circuiting (Figure 5c), while the (Zn/PC)//PC ZIC exhibits similar GCD curves at the 1st cycle and 30 000th cycle indicating little capacity fading (Figure 5d). The Zn//PC ZIC failed due to the penetration of Zn dendrite through the separator (Figure S16, Supporting Information). Because

Figure 6. Electrochemical performance of the (Zn/PC)//PC ZIC pouch cell. a) Schematic illustration showing the charge storage mechanism during charge and discharge processes, b) digital photograph showing that a “KAUST” LED display powered by three (Zn/PC)//PC ZIC pouch cells in series, c) GCD cycle performance of a (Zn/PC)//PC ZIC pouch cell and insets show the charge and discharge curves of the first and the last five cycles, and d) self-discharge test of the (Zn/PC)//PC ZIC pouch cell.

of the inhomogeneous Zn plating and stripping during the charge and discharge processes, sharp Zn dendrite formed gradually and punctured the separator of Zn//PC ZIC at the 4092nd cycle (Figure 5e,f). On the contrary, PC800 could provide multiple active sites for homogeneous Zn deposition. The anode of (Zn/PC)//PC ZIC shows evenly distributed carrot-shaped zinc particles rather than zinc dendrite on the surface of PC800 (Figure 5g; Figure S16a–c, Supporting Information). Furthermore, electrochemical impedance spectra (EIS) of (Zn/PC)//PC ZIC were performed to compare the stability of (Zn/PC)//PC ZIC before and after cycling test (Figure S17, Supporting Information). The EIS of (Zn/PC)//PC ZIC is quite stable over 30 000 charge and discharge cycles, which is in line with the high cycling stability of (Zn/PC)//PC ZIC. Therefore, (Zn/PC)//PC ZIC exhibits superior cycle stability among the ZICs that reported in recent years (Table S3, Supporting Information). The high capacity retention of (Zn/PC)//PC ZIC is attributed to both the highly reversible PC cathode and the (Zn/PC) anode.

As a new energy storage mechanism of porous carbon cathode in an aqueous ZIC system, the hydrogen and oxygen redox reactions could be used to design ZICs with high energy storage capability and excellent cycling stability. Schematic shown in **Figure 6a** illustrates our design of ZIC with high capacity by coupled highly reversible hydrogen and oxygen redox reactions. The high capacity of PC cathode is achieved by combining multiple charge storage mechanisms of EDLC, reversible hydrogen and oxygen redox reactions. With the PC800 layer coating on the zinc anode, zinc can plate and strip reversibly from PC800, which enables the high cycling stability of ZIC. Given the fact that the HER and OER parasitic reactions cannot be avoided entirely, in situ gas chromatography may be applied to quantify the irreversibility in further research.

Furthermore, the viability of (Zn/PC)//PC ZIC is demonstrated by the pouch cells. Three pouch cells connected in series were used to light a red LED display (Figure 6b). Each pouch cell can deliver a capacity of ≈ 1.87 mAh at a discharge current of 32 mA. Moreover, the pouch cell shows a capacity decrement as low as 0.0072% per cycle within the 600 GCD cycles (Figure 6c). Notably, the low self-discharge rate of this pouch cell is also impressive. Before self-discharge test, the pouch cell was charged to 1.9 V for 1.830 h. After rested at open circuit for 10 days (240 h) (Figure 6d), the pouch cell was discharged to 0 V at the same current density of charge process for 1.706 h. Thus, the self-discharge rate is calculated to be 0.028% per hour (Section S1.5, Supporting Information). The low self-discharge rate of (Zn/PC)//PC pouch cell is competitive to the lead–acid batteries,^[54,55] and much lower than the nickel-based batteries,^[56,57] the zinc ion supercapacitors,^[15,58] and the carbon-based supercapacitors.^[59,60] The high cycling stability and low self-discharge rate of pouch cell certify that (Zn/PC)//PC ZIC is a promising energy storage device for practical applications.

3. Conclusion

In summary, we have developed a novel strategy to boost the capacitance and energy density of aqueous zinc ion capacitors by coupled highly reversible hydrogen and oxygen redox reactions on the porous carbon cathodes. Moreover, the cycling

stability of ZIC is improved by suppressing Zn dendrite with a simple carbon coating strategy. The as-fabricated ZIC shows a high capacitance of 340.7 F g^{-1} and a high power density of 48.8 kW kg^{-1} with a correspondingly high energy density of 40.4 Wh kg^{-1} . Notably, the ZIC exhibits an ultralong cycle life of 30 000 cycles with high capacity retention of 99.2% and low self-discharge rate. All these features suggest that our ZIC is an excellent energy storage device for low-cost, safe, and long cycle life practical applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

aqueous electrolyte, high power, porous carbon, pseudocapacitance, zinc ion capacitor

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