A low cost, wide temperature range, and high energy density flexible quasi-solid-state zinc-ion hybrid supercapacitors enabled by sustainable cathode and electrolyte design

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ABSTRACT

Zinc-ion hybrid supercapacitor (ZHSC), emerging as a promising energy storage device, bring together the benefits of the high power density of supercapacitors, the high energy density of batteries and the environmental and cost benefits of zinc-ion technology. However, the development of high energy density ZHSC working in a wide temperature range is still a challenge. The key to achieve this target is to develop the electrolyte with thermal stability and anti-freezing property which is compatible with the advanced cathode material. Herein, a natural biomass coconut shell derived activated carbon as cathode and cost-effective aqueous Zn(ClO$_4$)$_2$ as electrolyte are applied in aqueous ZHSC. The fabricated aqueous ZHSC exhibits an outstanding high energy density of 190.3 W h/kg at 89.8 W/kg. Furthermore, a robust flexible quasi-solid-state ZHSC device was constructed by using a cross-linked poly(vinyl alcohol)/montmorillonite/Zn(ClO$_4$)$_2$ gel electrolyte (PVA/MMT/Zn (ClO$_4$)$_2$), which shows superior electrochemical performance over a wide working temperature range. Experimental analysis and molecular dynamics simulations reveal that the Zn(ClO$_4$)$_2$ process faster ionic migration compared to other Zn-based salts and form more hydrogen bonds with H$_2$O, leading to a superior anti-freezing property. Our flexible device maintains the high energy storage capacities and excellent cycling stability over a wide temperature range from –50 to 80 ℃, suggesting its great potential applications for energy storage applications in harsh environmental conditions.

1. Introduction

With the gradually exhausting fossil fuels and worsening global warming, it is urgent to develop energy storage devices to store electricity produced from renewable clean energy efficiently [1,2]. As a new generation of energy storage devices, supercapacitor (SC) has gained enormous attention due to its high power density, high rate performance, and durability [3,4]. Thanks to these advantages, SC is being successfully applied in portable electronics and hybrid electric vehicles [5]. Nonetheless, the relatively low energy density compared to the battery is hindering its widespread application [6,7]. One practical strategy to improve on this is to fabricate a hybrid supercapacitor (HSC), which can have a high energy density (than capacitor) and high power density (than battery) with long cycle life. HSC represent an innovative candidate for next-generation superb energy storage [8–10]. Recently, the zinc-ion hybrid supercapacitor (ZHC) has received attention, because of its high working voltage, material abundance, high safety, and low manufacture cost [11–13]. Generally, ZHSC is assembled by using carbon materials as the cathode, metallic zinc as the anode, and a zinc salt-containing solution as the electrolyte (such as ZnSO$_4$ and Zn (CF$_3$SO$_2$)$_2$) [11,14]. The energy storage mechanism of ZHSC is electrolyte ion adsorption/desorption on the carbonaceous cathode, and
Zn/Zn\(^{2+}\) stripping/plating on the zinc metal anode [15]. Considering that typically an excess amount of Zn is used as anode in ZHSC, the energy storage is commonly limited by the capacity of carbon cathode to adsorb/desorb electrolyte ions. Consequently, both cathode and electrolyte materials are highly significant in constructing high performance ZHSC. So far, many attempts about carbon cathode materials of ZHSC have been reported, for instance, activated carbon [11,16,17], carbon nanotubes [9], graphene [18,19], and porous carbon [10,20], as summarized in Table S1. Despite these achievements, the energy density of ZHSC is still far from satisfactory. Furthermore, these carbon nanotubes and graphene always have disadvantages of complicated fabrication processes, high manufacture cost, and even environmental concerns. Therefore, it is highly desirable to exploit low-cost, eco-friendly and high-performance carbon materials. In this regard, the natural biomass-derived carbons such as coconut shell [21], rice husk [22], bamboo biochar [23], litchi shell [24], apricot shell [25], and peanut shell [26] have attracted much attention due to the large surface area, high porosity, cost-effectiveness, and environment friendly. Among them, coconut shell derived carbons exhibit favorable electrochemical properties such as high specific capacity, good cycle ability, and availability, which is widely used in electric double layer capacitor as electrode [27–29]. Besides, in economic terms, coconut shells are a natural fruit waste, and it has been frequently utilized as an adsorbent for water and gas purification due to its rich micropore molecular structure [30]. In this regard, activated carbon of coconut shell origin may be an ideal cathode material for constructing ZHSC.

Besides carbon cathode materials, the electrolyte also plays a pivotal role in the performance of the advanced ZHSC. Additionally, in some situations, energy storage devices need to be applied in harsh environmental conditions, especially in severe low and high temperature. Selecting the suitable electrolytes plays the critical role for designing ZHSC that can work in harsh environments. ZHSC with aqueous electrolytes has low cost, high safety, and environment friendly. Among them, coconut shell derived carbons exhibit favorable electrochemical properties such as high specific capacity, good cycle ability, and availability, which naturally suffers from severe ionic conduction capacity, thereby limit the low-temperature operation. Furthermore, Wang et al. reported the 1 M ZnClO\(_4\) aqueous electrolyte in a Zn-V_2O_5 battery, which exhibited high anodic stability and excellent electrochemical performance at room temperature [32]. However, we are surprised to discover that the low concentration ZnClO\(_4\) aqueous has superior anti-freezing property, which is completely different from traditional freeze-resistant design strategy of “water-in-salt” electrolyte [33,34] and cosolvents or additives [35,36], as compared in Fig. S1. The low concentration ZnClO\(_4\) aqueous electrolyte is highly desired electrolyte for ZHSC with the wide working temperature range and low manufacturing cost.

In this work, an aqueous ZHSC with excellent electrochemical performance was assembled by using a natural coconut shell derived activated carbon as the cathode, ZnClO\(_4\) as the electrolyte, and electrodeposited Zn as the anode. The aqueous ZHSC exhibits an outstanding high energy density of 190.3 W h/kg at 89.8 W/kg, which is the highest reported values for aqueous carbon-based ZHSC. Furthermore, a novel flexible quasi-solid-state ZHSC device was constructed based on cross-linked poly(vinyl alcohol)/montmorillonite/ZnClO\(_4\) gel electrolyte. This flexible quasi-solid-state ZHSC device delivers high energy storage capacities and great cycling stability over a wide temperature range from −50 to 80 °C, meaning that our flexible device opens a cost-effective and sustainable but efficient way for designing industrial zinc-ion hybrid supercapacitors and it has a promising application in harsh conditions for energy storage.

2. Experimental section

2.1. Chemical reagents

ZnSO\(_4\)·7H\(_2\)O (AR, > 99%), Zn(CrF\(_3\))\(_2\)·H\(_2\)O (AR, > 99%), Zn(ClO\(_4\))\(_2\) (AR, > 99%), MMT, and PVA (Mw = ~ 145,000) were purchased from Aladdin Chemical Reagent Co., Ltd. Activated carbon (SSA: ~ 1150 m\(^2\)/g), hydroxylate multi-walled CNTs (SSA: ~ 233 m\(^2\)/g) and rGO (~ 700 m\(^2\)/g) were purchased from China XFNANO Materials Tech Co., Ltd., and they were used for comparison.

2.2. Material preparation

2.2.1. Preparation of coconut shell activated carbon (CSAC)

The CSAC cathode slurry was prepared by following steps. First, 70 wt% of CSAC powder, 20 wt% of Super P, and 10 wt% of polytetrafluoroethylene (PTFE) were mixed and the mixture was dispersed in a certain of distilled water under magnetic stirring for 5 h. Then, the slurry was uniformly coated on the carbon cloth and dried at 80 °C for 8 h. The mass loading of active material was around 2 mg/cm\(^2\). The Zn anode was carried out by a constant current electrodeposition technique in an aqueous medium (0.4 M ZnSO\(_4\)·7H\(_2\)O + 0.9 M Na\(_2\)SO\(_4\) + 0.3 M H\(_2\)BO\(_3\)). An electrochemical cell with a carbon cloth was used as the working electrode and Pt plate as counter/reference electrode. The current density and time were ~ 40 mA/cm\(^2\) for 15 min at room temperature. The mass loading of zinc was ~ 8 mg/cm\(^2\) (The surface morphology of the as-prepared Zn is shown in Fig. S2).

2.2.2. Preparation of coconut shell activated carbon (CSAC) cathode and Zn anode

The cathode was constructed by a certain of distilled water under magnetic stirring for 5 h. Then, the slurry was uniformly coated on the carbon cloth and dried at 80 °C for 8 h. The mass loading of active material was around 2 mg/cm\(^2\). The Zn anode was carried out by a constant current electrodeposition technique in an aqueous medium (0.4 M ZnSO\(_4\)·7H\(_2\)O + 0.9 M Na\(_2\)SO\(_4\) + 0.3 M H\(_2\)BO\(_3\)). An electrochemical cell with a carbon cloth was used as the working electrode and Pt plate as counter/reference electrode. The current density and time were ~ 40 mA/cm\(^2\) for 15 min at room temperature. The mass loading of zinc was ~ 8 mg/cm\(^2\) (The surface morphology of the as-prepared Zn is shown in Fig. S2).

2.2.3. Preparation of poly(vinyl alcohol)/montmorillonite (PVA/MMT) hydrogel electrolyte

The preparation process of the PVA/MMT hydrogel electrolyte is similar to the previous report (37). The hydrogel electrolyte was prepared as follows: 90 mg PVA powder and 10 mg MMT powder were added into 10 mL H\(_2\)O. The mixture solution was conducted at 80 °C under constant stirring until forming a jelly-like solution. Then, the jelly-like solution was transferred to a mold and the PVA/MMT membrane was easily peeled off after the vacuum drying for 24 h. Finally, the PVA/MMT hydrogel electrolyte was obtained after immersing into 3 M ZnClO\(_4\) solution for 30 min.

2.3. Structural characterization and computational details

The molecular structure of the samples was measured by Raman spectrometer (Raman, LabRAM HR8000, Horiba Jobin Yvon S.A.S) and Fourier transform infrared spectrometer (FTIR, Bruker Vertex-70). The crystal phase of the samples was examined by X-ray diffraction (XRD, Bruker). The surface morphology of the samples was analyzed by field emission scanning electron microscopy (SEM, Zeiss Supra, Carl Zeiss) equipped with EDX analyzer. The morphological features of the samples were examined using transmission electron microscopy (TEM, JEM-3200FS, JEOL). The chemical composition of the products was analyzed using X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Kratos Analytical Ltd.). The freezing point of the electrolyte was examined by the differential scanning calorimetry (DSC, DSC1, Mettler Toledo). The dynamic reaction coordinate (DRC) simulation, one of the molecular dynamics (MD) methods, is employed to investigate the
properties of electrolyte aqueous in the study by MOPAC 2016 [38,39]. The simulation temperature is set to 300 K, and the simulation lasts for 20 ns, with a 1 fs interval and total 1000 steps. The 'half-life' for loss of kinetic energy is 50 fs. Additionally, VMD3 (Visual Molecular Dynamics) is applied to build the model and study the RDF (Radial Distribution Function). The electrolytes are surrounded by a [60 * 60 * 60] Å water box [40].

2.4. Assembly of ZHSC devices

Aqueous and quasi-solid-state ZHSC devices were fabricated for cell performance evaluation by stacking the CSAC cathode and the electro-deposited Zn anode, in which aqueous 3 M Zn(ClO$_4$)$_2$ solution was used for aqueous ZHSC and the PVA/MMT/Zn(ClO$_4$)$_2$ hydrogel electrolyte for quasi-solid-state ZHSC devices. For aqueous ZHSC, the Zn anode and CSAC cathode were separated by a 50 µm-thick fiberglass separator.

2.5. Electrochemical characterization

Cyclic voltammmogram (CV), linear sweep voltammetry (LSV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements were carried out on a commercial CHI660 electrochemical workstation (Shanghai CH Instrument Co., Ltd.). The EIS measurement was measured in the frequency range of 0.01–100 kHz with an amplitude of 5 mV. The ionic conductivities of the aqueous and hydrogel electrolytes were measured by using EIS method. The ion conductivity was calculated from the Nyquist plot using the following equations:

\[ \sigma = \frac{L}{R_s A} \]
where \( \sigma \) (S/cm) represents the ion conductivity; \( L \) (cm) is interval distance between the two stainless steel electrodes; \( A \) (cm\(^2\)) is electrode contact area; \( R_e \) (\( \Omega \)) is the electrolyte resistance, which was obtained from the intercept with the \( x \)-axis in Nyquist plots. All the electrochemical measurements were conducted under the constant applied temperature and humidity chamber at different temperatures (RHP-23, REALE). CV curves of Zn plating/stripping were measured using a three-electrode system consisting of stainless steel/Zn/Zn as working/counter/reference electrode.

3. Results and discussion

3.1. Structural study

The energy density improvement and low manufacturing cost of ZHSCs are the main challenge to realize the future large-scale commercial applications. As carbonaceous materials are used as the cathode in ZHSC, so the carbon material with high surface area, sustainability and low cost is extremely important for commercial applications. Coconut palm is grown in more than 93 countries and is very prolific [41]. Coconut shell, as a source used to produce activated carbon, has the double advantage of low manufacturing cost and sustainability. The optical and SEM image of the CSAC prepared in this work is illustrated in Fig. 1a. XRD and Raman were used to characterize the structure of as-prepared CSAC sample. As shown in Fig. 1b, the two broad diffraction peaks at 2\( \theta \) values of around 25° and 43° are indexed as the (002) and (100) planes of graphite structure [42]. Raman spectra of CSAC are depicted in Fig. 1c, where two characteristic peaks at around 1340 cm\(^{-1}\) and 1588 cm\(^{-1}\) are the typical D and G bands, respectively. The intensity ratio of \( I_D/I_G \) bands can reflect the graphitic degree of the carbon materials. It is found that the CSAC has a higher \( I_D/I_G \) value (1.02) than the reported graphene oxide [43,44], suggesting that it formed more defects in CSAC during the preparation process. The SEM (Fig. S3a) and TEM (Fig. 1d) images of the CSAC clearly see that the carbonaceous materials with porous structure, which can facilitate the adsorption/desorption of electrolyte ions onto/into the sample surface to enhance the energy storage performance. EDX and XPS further characterized the chemical composition and elemental distribution of the CSAC. EDX mapping analysis (Fig. S3b) exhibits a homogeneous distribution of the elements (C, O, and N) in the CSAC. The full XPS spectrum of the as-synthesized sample (Fig. S3c) indicates about 90.76% C, 7.91% O, and 1.33% N in CSAC. Nitrogen adsorption-desorption measurement was conducted to investigate the pore structures of as-prepared CSAC powder. As displayed in Fig. 1e, the BET specific surface area of CSAC is 1260 m\(^2\)/g with the pore volume of 1.8 cm\(^3\)/g, which is larger than many reported CSAC [21,27]. And the porosity is mostly concentrated around 1.03 nm, indicating a nano-sized porous structure of bulk CSAC. The larger specific surface area and nano-porous structure of CSAC can accelerate the kinetics of electrolyte ions and provides sufficient active sites for charge storage. All the above results prove the CSAC should be a promising cathode material for high energy density ZHSC.

3.2. Electrochemical performance of aqueous ZHSC device

To assess the performance of as-prepared CSAC for zinc-ion energy storage in realistic applications, an aqueous CSAC/Zn(ClO\(_4\))\(_2\) (aq.)/Zn device was manufactured, as illustrated in Fig. 2a. Due to the hybrid of battery-type Zn anode and EDLC-type CSAS cathode, the assembled ZHSC can store charges through reversible Zn\(^{2+}\) ions stripping/deposition onto the Zn anode and electrolyte anion adsorption/desorption onto CSAS cathode [10]. Thus, improved power and energy densities can be fulfilled in this device. The ionic conductivity of Zn(ClO\(_4\))\(_2\) electrolyte at different molar concentrations was first studied by calculating through EIS (Fig. S4a) and the values of ionic conductivity are represented in Fig. 2b. With raising the concentration, the ionic conductivity of Zn(ClO\(_4\))\(_2\) aqueous solution increases first and then decreases under room temperature. Notably, the 3 M Zn(ClO\(_4\))\(_2\) aqueous solution has the highest ionic conductivity (Fig. 2b). While the concentration increases to higher than 3 M, the ionic conductivity of the electrolyte decreases. It is probably due to the increase of viscosity with raising the concentration [45,46]. The high viscosity will slow down the transport of ions in electrolyte and decrease the ionic conductivity [47,48]. Thus, the 3 M Zn(ClO\(_4\))\(_2\) with the optimal ionic conductivity was selected as the electrolyte for fabricating aqueous ZHSC in this work. Meanwhile, the electrochemical stability window of electrolytes was also verified by applying LSV measurement. As shown in Fig. S4b, the Zn(ClO\(_4\))\(_2\) electrolyte has a high electrochemical stability window of 2.5 V, which is capable to perform almost all aqueous ZHSC devices. To confirm the practical electrochemical stability window of the assembled aqueous ZHSC, the CV measurements were performed with various potential ranges (Fig. S4c). In detail, the CV curve within 0–1.8 V has negligible distortion, while an apparent polarization phenomenon is observed with extending the window voltage to 1.9 V. Consequently, the suitable potential window of ZHSC was 0–1.8 V. In addition, to highlight the performance of ZHSC, other carbon-based cathodes (commercial AC, rGO, and CNT) were also applied in ZHSC for comparison.

The energy density improvement and low manufacturing cost of ZHSC can store charges through reversible Zn\(^{2+}\)/(aq.)//Zn anode and electrolyte anion adsorption/desorption onto the Zn anode and electrolyte at different molar concentrations was first studied by calculating through EIS (Fig. S4a) and the values of ionic conductivity are represented in Eqs. (1) and (2), the values of \( k_1 \) and \( k_2 \) can be obtained from the curve plotting the relationship curves of \( i(V) \) vs. \( V^1/2 \) and \( V^2 \), and thus the charge storage contributions of diffusion/capacitive can be assessed. Thus, the overall capacitance \( Q \) can be separated into the capacitance charge storage \( Q_{cap} \) derivate process and bulk charge storage \( Q_{bulk} \), which depends upon a diffusion-controlled process as shown in the following Eq. (3).

\[
Q_{cap} = \frac{Q}{\tau} \quad \text{and} \quad Q_{bulk} = \frac{Q}{\tau}
\]

As shown in Fig. S6, the capacitive contribution (the shaded area) is calculated to be almost 83% of the total charge stored at 20 mV/s for CSAC/Zn(ClO\(_4\))\(_2\) (aq.)/Zn. Moreover, in Fig. 2e, the capacitance contributions are 70%, 71%, 83%, 84%, 87%, and 89% from 5 to 50 mV/s, indicating the capacitive contribution is dominant during the charge storage even at a low scan rate, which proves that it has high kinetics and high rate performance in CSAC/Zn(ClO\(_4\))\(_2\) (aq.)/Zn. As presented in Fig. 2f, CSAC/Zn(ClO\(_4\))\(_2\) (aq.)/Zn delivers excellent rate properties of 423.5–178.8 F/g at current densities from 0.1 to 20 A/g, much higher than that of AC/Zn(ClO\(_4\))\(_2\) (aq.)/Zn (364.4–147.2 F/g), rGO/Zn(ClO\(_4\))\(_2\) (aq.)/Zn (109.0–53.5 F/g) and CNT/Zn(ClO\(_4\))\(_2\) (aq.)/Zn (26.3–18.5 F/g) under the same measurements. The compelling capacitance and rate performance of our CSAC/Zn(ClO\(_4\))\(_2\) (aq.)/Zn are superior to many recently reported work on carbon-based ZHSC, as
Fig. 2. Electrochemical performance of aqueous ZHSC device. (a) Schematic illustration of the CSAC//Zn(ClO$_4$)$_2$ (aq.)/Zn device. (b) Ionic conductivities of the zinc perchlorate electrolyte at different molar concentration. (c) CV curves of ZHSC devices with different carbon cathode at 10 mV/s. (d) CV curves of the ZHSC device with CSAC cathode at different scan rates. (e) The capacitive and diffusion contribution ratios to the total capacity of ZHSC at different scan rates. (f) Specific capacitance values of ZHSC devices with different carbon cathode at various current densities. (g) Ragone plots of CSAC//Zn(ClO$_4$)$_2$ (aq.)/Zn device in comparison to other ZHSC at 25°C. (A color version of this figure can be viewed online).
superior electrochemical properties of this device can be ascribed to the superior capacitance, good rate capability, and high energy density. The density 24.5 kW/kg, for now, which is highest energy densities value in aqueous ZHSC was achieved. It should be noted, however, that Zn

3.3. Electrochemical properties of quasi-solid-state ZHSC devices

As described, the satisfactory electrochemical performance of aqueous ZHSC was achieved. It should be noted, however, that Zn(ClO₄)₂ belongs to the class of Lewis acids [54]. Although aqueous electrolyte can provide high ionic conductivity, 3 M Zn(ClO₄)₂ aqueous solution displays strong acidity, which may cause the risk of leakage and safety in practical application, especially for the application of flexible wearable electronics. Preparation of gel electrolyte can effectively solve this problem. Based on this consideration, a quasi-solid-state CSAC/PVA/MMT/Zn(ClO₄)₂ (gel)/Zn device was further manufactured, where CSAC, PVA/MMT/Zn(ClO₄)₂, and Zn respectively served as cathode, separator/electrolyte, and anode (Fig. 3a). Fig. S7a shows the GCD curves of the quasi-solid-state ZHSC device at various current densities. The specific capacitance of the quasi-solid-state ZHSC is 206 F/g at 0.5 A/g and the specific capacitance retention can still retain 70% at 20 A/g (Fig. S7b), suggesting its excellent rate capability. The operating temperature range is also a critical parameter for flexible energy storage devices, especially for the device needs to work in harsh environments. Thus, thermal performance is also one of the critical elements for the energy storage device. First, the thermal behavior of PVA/MMT/Zn(ClO₄)₂ gel electrolyte was analyzed. The result in Fig. S8a reveals that the endothermic peak is hard to be observed at the low temperature range, which suggests that the crystallization is strongly suppressed. It has a sharp exothermic peak at around 95 °C due to water vaporization. In Fig. S8b, the peak at 84 °C represents the glass transition temperature of PVA [55]. The results reveal the PVA/MMT/Zn(ClO₄)₂ gel possesses a larger working temperature window (−60 to 80 °C). Depended on the thermal performance, the electrochemical measurements have carried out under a series of working temperatures. Fig. 3b shows the specific capacitance variation with changing working temperatures of the quasi-solid-state ZHSC. The specific capacitance of the device increases almost linearly with the temperature. The ZHSC displays around 303 F/g at 80 °C, which is about 195% capacitance retention compared to that at 25 °C. Furthermore, the ZHSC still has approximate 110 F/g at −20 °C, which is almost 54% capacity retention compared to that at 25 °C. More significantly, from 25 to −50 °C, the ZHSC can still maintain a high capacitance retention of 26.5%. It is worth to note that this is achieved without any anti-freezing agent. EIS measurement was employed to further explore the electrochemical behavior of the ZHSC with varying working temperatures, and the Nyquist plots are shown in Fig. 3c. All the nearly vertical lines in the low-frequency region also suggest the ZHSC have the ideal capacitive behavior at different working temperature, proving the above dominant capacitive contribution during the charging-discharging process. Moreover, it is clear to see that the equivalent serial internal resistance (Rₛ), charge-transfer resistance (Rₜ), and Warburg impedance (Zₘₚ) vary significantly with the change of the test temperature. The inset in Fig. 3c is the equivalent circuit model, and the relative parameters are summarized in Table 1. With decreasing the ambient temperature from 80 to –30 °C, the Rₛ, Rₜ, and Zₘₚ show an increasing tendency. It is highlighted that the electrochemical performance has a strong effect on the electrolyte. With the decrease of working temperature, the mobility of Zn(ClO₄)₂ in PVA/MMT decreases, which leads to the decrease of ionic conductivity. The reduced ionic conductivity caused the increase of Rₜ. The kinetics of active materials for Zn²⁺ ions de/intercalation and electrolyte ion adsorption/desorption decrease significantly with reducing temperature, which will result in an increased Rₑ.

Ragone plots of quasi-solid-state ZHSC devices are derived to assess the ZHSC device’s output in terms of energy and power density. Remarkably, our quasi-solid-state ZHSC device delivers an outstanding energy density of 49.1 Wh/kg and an excellent power density of 6.5 kW/kg under −20 °C (Fig. 3d), which is significantly superior to previous reported carbon-based hybrid devices with anti-freezing property [35,56–62]. On the other side, the quasi-solid-state ZHSC device also delivers a superior energy density of 138.6 Wh/kg and an excellent power density of 18 kW/kg under 60 °C (Fig. 3e), which is also significantly superior to other advanced supercapacitor with high temperature application [63–67]. Additionally, the cycling stability of the quasi-solid-state ZHSC device was evaluated by the charge-discharge process at 5 A/g. As shown in Fig. 3f, over 10,000 cycles, the specific capacitance retentions of ZHSC are 99% at 25 °C and 98% at −20 °C, respectively. The results uncover that the quasi-solid-state ZHSC device is stable to charge/discharge under a room temperature and even ultra-low temperature. Meanwhile, at the high temperature 60 °C, the specific capacitance can retention 80% after 5500 cycles. The capacitance retention decreases with the cycles, which mainly resulting from the water evaporated caused ion diffusion of the hydrogel electrolyte to decrease little by little (see Supporting information Figs. S9–S11 for details) [68]. It is worth noting that when the operating temperature of the quasi-solid-state ZHSC is further increased, the capacitance fading rate of the ZHSC is also increased. As shown in Fig. S12, although the quasi-solid-state ZHSC can work, the cycle stability is poor under 80 °C. In addition, it is found that it can work well again after resting at room temperature for 2 h, which may relate to the PVA become glassy state again at room temperature.

For the flexible quasi-solid-state ZHSC devices, besides the flexible CSAC cathode and zinc anode, the flexibility of the PVA/MMT gel decides whether it can be used as power supply for wearable electronic devices. Optical images of PVA/MMT hydrogel and flexible ZHSC device are shown in Fig. 4a. The PVA/MMT hydrogel shows good flexibility with very thin and bendable. Because of the flexibility of the PVA/MMT hydrogel and electrodes, the assembled solid state ZHSC also demonstrates excellent flexibility. To perform an evaluation of the mechanical property in its operational condition, the quasi-solid-state ZHSC device was bend at different angles (from 0° to 120°) and the corresponding GCD curves were measured in Fig. 4b. It depicts that the electrochemical performance can almost remain with varying bending angles, meaning the admirable mechanical flexibility of the quasi-solid-state ZHS device. To verify its practical application, the assembled flexible device was used to light an electric desktop clock after being charged to 1.8 V, indicating its considerable potential in renewable energy storage.

3.4. Mechanism research of ZHSC device achieving superior electrochemical performance

As mentioned above, the CSAC/Zn(ClO₄)₂ (aq.)/Zn device achieved enhanced capacitance, good rate performance, and outstanding energy density, which can surpass many other carbon-based zinc-ion hybrid devices. One of the reasons for the enhanced electrochemical performance of CSAC/Zn(ClO₄)₂ (aq.)/Zn could be ascribed to the CSAC cathode. The CSAC cathode could exhibit fast dynamics during the charging-discharging process. It exposes more electroactive sites for energy storage, which was attributed to its high specific surface area and nano-porous structure. In addition, compared with other carbon-based ZHSC devices, zinc perchlorate salt is used as an electrolyte for the first time in ZHSC. Therefore, the second reason may be ascribed to the use of zinc perchlorate as electrolyte. To verify our thoughts, we tested the CV and GCD measurements in ZHSC devices with different zinc salts (ZnSO₄, Zn

summarized in Table S2. The results show that our device possesses superior capacitance, good rate capability, and high energy density. The superior electrochemical properties of this device can be ascribed to the high ionic conductivity of Zn(ClO₄)₂ electrolyte and the CSAC cathode with a larger specific surface area and nano-porous structure. To evaluate the performance of the ZHSC device in terms of energy and power density, the Ragone plot is shown in Fig. 2g. The CSAC/Zn(ClO₄)₂ (aq.)/Zn device can offer an ultra-high energy density of 190.3 Wh/kg at 89.8 W/kg and it still can retain 80.5 W h/kg at an ultra-high power density 24.5 kW/kg, for now, which is highest energy densities value in previously reported aqueous ZHSC work [10,11,18,20,51–53].
Fig. 3. Electrochemical properties of quasi-solid-state ZHSC device. (a) Schematics of quasi-solid-state CSAC//PVA/MMT/Zn(ClO$_4$)$_2$ (gel)//Zn. (b) Specific capacitance at different temperature with a current density of 0.5 A/g. (c) Nyquist plots at different temperature. (d, e) Ragone plot of the quasi-solid-state ZHSC device in comparison to other SCs at 60 °C and -20 °C. (f) Cycling performance of the quasi-solid-state ZHSC device at 5 A/g under different temperatures.
Table 1

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(CF$_3$SO$_2$)$_2$), but using the same cathode and anode. In Fig. S13, the larger CV integral area and longer discharge time demonstrate that the device with Zn(ClO$_4$)$_2$ electrolyte can obtain more excellent electrochemical performance. Therefore, the enhanced electrochemical performance should be related to the stripping/plating reaction rate of Zn anode and the ion diffusion rate of electrolyte. The deposition/dissolution efficiency of Zn anode in three electrolytes was investigated via using a CV test. Fig. S14a-c show the comparison of the 2nd and 20th CV curves in three electrolytes, which reflects the electrochemical stripping/plating process of Zn. The details are displayed in Table S3, where $I_{pc}$ is the Zn dissolution peak current corresponding to the 2nd to the 20th cycles, respectively. The purpose of Fig. S14d is to depict the average of the CV measurement data recorded over the potential range from −0.25 to +0.5 V during 19 cycles (from the 2nd cycle to the 20th cycle) in three electrolytes. It discovers that $I_{pc}$ in the curve of Zn(ClO$_4$)$_2$ is much higher than those in the curves of the ZnSO$_4$ and Zn(CF$_3$SO$_2$)$_2$ electrolytes. It indicates that using Zn(ClO$_4$)$_2$ electrolyte can effectively improve the reaction rate of Zn anodic dissolution. Furthermore, as shown in Fig. S14a-c and Table S3, using Zn(ClO$_4$)$_2$ electrolyte provides the lowest peak current differences between the 2nd and 20th cycles, meaning its highly reversible electrochemical stripping/plating process of Zn. These inspired results manifest that the existence of ClO$_4^-$ could lead to faster dynamics during the electrochemical process, which could attribute to its high ionic conductivity.

To make a deep comprehension on the ionic conductivity of the different zinc salts electrolyte, molecular dynamics (MD) simulations were performed (Figs. 5a, S15a and b). The diffusion coefficients of different Zn-based salts were analyzed by the radial distribution functions (RDF) (Fig. 5b). For the Zn(CF$_3$SO$_2$)$_2$ electrolyte, the main peak position is near 1.45 Å, which indicates Zn(CF$_3$SO$_2$)$_2$ has a low diffusion coefficient. For the Zn(ClO$_4$)$_2$ and ZnSO$_4$ electrolyte, they have similar radial distribution with average diffusion distribution, which should in principle leads to higher diffusion coefficient than that of the Zn (CF$_3$SO$_2$)$_2$. As for ZnSO$_4$ electrolyte, the number of SO$_4^{2-}$ anions is less than half of ClO$_4^-$ under the same concentration. Therefore, the diffusion of Zn(ClO$_4$)$_2$ should be more significant than that of ZnSO$_4$ and Zn(CF$_3$SO$_2$)$_2$ electrolyte. Therefore, the higher diffusion coefficient of Zn(ClO$_4$)$_2$ result in a faster ion diffusion rate in aqueous solution, which can accelerate the electrochemical reaction.

Furthermore, the flexible quasi-solid-state ZHSC device also displays excellent electrochemical performance under a wide temperature range from −50 to 80 °C. The constructed PVA/MMT/Zn(ClO$_4$)$_2$ gel electrolyte plays a key role for wide working temperature flexible ZHSC due to its thermally stable and anti-freezing capability. As shown in Fig. S16, the PVA/MMT membrane is the porous structure, which can form ion transport paths in the hydrogel electrolyte system and further enhancing its ionic conductivity under electrochemical processes. Moreover, MMT materials can promote the thermal stability and facilitate ionic conductivity of the hydrogel electrolyte, which is confirmed by TGA technique and electrochemical measurements (see Supporting Information Figs. S17 and S18 for details). Our experimental results are also similar to reported results by previous literature [37,69,70]. Therefore, the hydrogel has high ion transport efficiency and thermal stability. Usually, the hydrogel electrolytes without any anti-freezing agent freeze easily under subzero temperatures, resulting in deteriorated ionic conductivity. Surprisingly, the Zn(ClO$_4$)$_2$ aqueous electrolyte is found to have superior anti-freezing performance (Fig. S19) and excellent ionic conductivity (Fig. S20) even at −50 °C. It is worth mentioning that the Zn (ClO$_4$)$_2$ has excellent anti-freezing properties, which can be achieved under the low concentration zinc-based salt and without any anti-freezing agent. This is a cost-effective new way of making freeze-resistant electrolyte. In order to understand the mechanisms behind these phenomena, mechanism analysis was also conducted. The anti-freezing performance of Zn(ClO$_4$)$_2$ aqueous electrolyte should be related to the interaction of solute Zn(ClO$_4$)$_2$ with solvent water molecules to block the formation of the ordered hydrogen bond network among water molecules. The condition of hydrogen bonds between the Zn(ClO$_4$)$_2$ electrolyte and water molecules is investigated by analyzing the above simulation results (Fig. 5c), and we also compared with ZnSO$_4$ and Zn(CF$_3$SO$_2$)$_2$ electrolyte under the same condition (Fig. S15c, d). It is found that many hydrogen bonds are formed between solute zinc-based salts and solvent water molecules. Further observation found that most hydrogen bonds are formed between the hydrogen atoms of water molecules and the anions of the zinc-based salts. As for ZnSO$_4$ and Zn(CF$_3$SO$_2$)$_2$ aqueous electrolyte, the new hydrogen bonds were observed between hydrogen atoms of water molecules and the oxygen atom of SO$_4^{2-}$ and CF$_3$SO$_3^-$. Interestingly, for Zn(ClO$_4$)$_2$ aqueous electrolyte, the new hydrogen bonds were not only observed between hydrogen atoms of water molecules and the oxygen atom of ClO$_4^-$, but...
also between hydrogen atoms of water molecules and chlorine atom of ClO$_4^-$, which leads to more hydrogen bonds in Zn(ClO$_4$)$_2$ than in Zn(CF$_3$SO$_3$)$_2$ and ZnSO$_4$. The formation of new hydrogen bonds in aqueous Zn(ClO$_4$)$_2$ solution was also confirmed by FTIR. Usually, the absorption band of H-O-H bending vibration of liquid water is at 1640 cm$^{-1}$ \cite{71}. However, the FTIR spectrum in Fig. S21 indicates a slight red shift in the bending vibration of H$_2$O at around 1630 cm$^{-1}$ as the Zn(ClO$_4$)$_2$ concentration increases, implying hydrogen bond between Zn(ClO$_4$)$_2$ and H$_2$O. As shown in Fig. 5d, the ratio of the number of hydrogen bond for the Zn(ClO$_4$)$_2$, Zn(CF$_3$SO$_3$)$_2$ and ZnSO$_4$ is about 9:3:4. A large number of hydrogen bonds between solute Zn(ClO$_4$)$_2$ and solvent water molecules can effectively prevent the formation of an ordered hydrogen bond network among water molecules, thus reducing the freezing point of the aqueous electrolyte.

4. Conclusions

In this work, an advanced ZHSC with superior capacitance and anti-freezing performances has been successfully assembled. The pores coconut shell derived activated carbon accelerates the kinetics of electrolyte ions and provides sufficient active sites for charge storage. The high ionic conductivity of Zn(ClO$_4$)$_2$ promotes fast dynamics during the electrochemical process and improve the capacitance performance, with excellent anti-freezing performance. When tested in aqueous electrolyte, the ZHSC device shows an ultra-high specific capacitance of 423.5 F/g and an outstanding high energy density of 190.3 W h/kg at 89.8 W/kg. Besides, an anti-freezing and thermally stable PVA/MMT/Zn(ClO$_4$)$_2$ hydrogel electrolyte are used to prepare flexible quasi-solid-state ZHSC. The manufactured flexible device displays high energy density without compromising power density and excellent cycling stability under a wide temperature range, from –50 to 80 °C, which discloses the excellent anti-freezing property. Our ZHSC device could bridge the energy density gap between battery and supercapacitor for energy storage. It is worth mentioning that the CSAC has high surface area and low cost, and the low concentration Zn(ClO$_4$)$_2$ has excellent anti-freezing property without any anti-freezing agent, which has the potential realizing mass production for commercial applications for high-performance ZHSC. This work presented here also presents an encouraging pathway via sustainable cathode and electrolyte design pathway towards high energy density flexible energy storage devices with excellent flexibility as well as wide operating temperature range.

CRediT authorship contribution statement

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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