

Stabilities of Flexible Electrochemical Capacitors Based on Polypyrrole/Carbon Fibers in Different Gel Electrolytes*

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Abstract Flexible electrochemical capacitors (ECs) are vitally important as the emerging flexible electronics. We have prepared polypyrrole doped with counter ion of Cl[−] on carbon fibers (PPy-Cl/CFs) *via* the simple electrochemical deposition method. The flexible ECs based on PPy-Cl/CFs electrodes have been assembled by using H₃PO₄/poly(vinyl alcohol) (PVA), H₂SO₄/PVA, LiClO₄/PVA, KCl/PVA and LiCl/PVA as gel electrolytes. The capacitive properties of ECs have been systematically evaluated with electrochemical methods. The results show that the cells with H₃PO₄/PVA electrolyte exhibit good cyclic stability (91.5% retention after 15000 cycles) although PPy-Cl/CFs has moderate specific capacitance in H₃PO₄/PVA (41.6 mF·cm^{−1} or 52.0 F·cm^{−3}). However, the ECs in other electrolytes have poor cyclic stability. Further electrochemical analysis reveals that the doping/dedoping processes of PPy-Cl/CFs are different in the five electrolytes, and X-ray photoelectron spectra demonstrate that the ratios of counter anions in PPy's oxidized states to those in reduced states are obviously different when PPy-Cl/CFs are kept in reduced or oxidized states in the five electrolytes. The results also illustrate why the capacitors using H₃PO₄/PVA as electrolyte exhibit good cyclic stability. Furthermore, a light emitting diode (LED) with a threshold voltage of 2.5 V can be lighted by three ECs connected in series.

Keywords Polypyrrole; Electrochemical capacitors; Stability; Gel electrolytes

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INTRODUCTION

The demand for small energy storage devices is dramatically increased with the rapid growth of portable electronics. Electrochemical capacitors (ECs), as the clean energy storage devices, have attracted significant attention over the last decades due to their benefits of high power density, long lifetime and fast charge/discharge rate^[1–6]. Typically, ECs materials can be classified into three categories: carbon materials (*e.g.* activated carbon, graphite, graphene and carbon nanotubes *etc.*), transition metal compounds and conducting polymers (*e.g.* polypyrrole (PPy), polyaniline, polythiophene and their derivatives). Among them, carbon materials are generally used in electrochemical double layer capacitors (EDLCs) owing to their excellent electrical, thermal

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conductivity, and large specific surface area. In such materials, the energy storage is based on the adsorption of ions at the interface of electrode and electrolyte^[7–11]. Transition metal oxides and conducting polymers are used in the pseudo-capacitors according to their rapid reversible redox reactions at the surface or in the bulk of electrode materials^[12]. Compared with carbon materials, pseudo-capacitor materials exhibit a relatively low rate-capability, but a high specific capacitance (C_s) because the energy is stored through a reversible faradaic redox reaction^[13–16].

Conventional ECs are heavy, rigid and bulky, which cannot fully meet the growing development and demand for small, flexible, thin and even roll-up portable electronic devices due to the presence of inactive components such as metal substrates, binders and conductive additives^[17, 18]. Therefore, it is essential to develop flexible and portable ECs with light weight^[19–21]. Recently, significant progress has been made in the development of flexible ECs by fabricating specially structured electrode materials. Among all the conducting polymers, PPy has attracted a wide range of interest for being used as flexible electrodes due to its good conductivity, facile synthesis, flexibility, versatility as well as light weight^[22–24]. Wang *et al.* have successfully deposited nanostructured MnO_2 (as the positive electrode) and PPy (as the negative electrode) on the Ni/graphene fiber substrates and fabricated a flexible solid-state asymmetric supercapacitor with high capacitive performance^[7]. Yuan *et al.*^[25] have fabricated the PPy/paper composites with the C_s of flexible electrodes up to $0.42 \text{ F}\cdot\text{cm}^{-2}$, and the energy density about $1 \text{ mW}\cdot\text{h}\cdot\text{cm}^{-3}$ at the power density of $0.27 \text{ W}\cdot\text{cm}^{-3}$.

In order to achieve better capacitive performance, the components of ECs, including electrodes, electrolytes, separators and current collectors need to be investigated in detail^[26]. For flexible ECs, it is especially important to choose the flexible current collectors with excellent flexibility and mechanical strength besides the materials with light weight and high energy density. Up to date, the wires of carbon materials, such as the wires of carbon nanotubes, fibers of reduced graphene oxide, activated carbon fibers and their composites have been used to design fiber-like ECs^[26, 27]. In view of these carbon-based materials, carbon fibers (CFs) are considered an ideal current collector for flexible capacitors because of their high mechanical strength, conductivity and good flexibility. However, the main drawback of PPy-based ECs' electrodes is the poor stability during cycling use. It is attributed to the mechanical degradation and electrochemical performance fading, which is from the continuous volume expansion and shrinkage during doping/dedoping process^[15, 28]. Therefore, it is still a vital challenge to improve the cyclic stability of conducting polymers. Most of the researchers aim to improve the cyclic stability through fabricating composite electrode materials. For example, Wu and Chen *et al.* designed an all-solid-state ECs based on the composites of PPy nanowires and reduced graphene oxide. The assembled ECs exhibited good cycling stability (88.1% capacitance retention after 5000 cycles)^[29]. We previously synthesized the composites of PPy and graphene oxide (GO) by co-electrochemical deposition method to improve the cyclic stability. Notably, the composites achieved 96.4% retention of the initial capacitance after 5000 cycles^[30].

On the other hand, electrolytes used in ECs also have an important influence on the stability. Unfortunately, most of the reported examples focus on the electrode materials although the selection of electrolyte is an alternative method to improve cyclic stability. It is proved that the nature of doping anions in PPy matrix has great influence on the structures and properties of PPy films. The ions of Cl^- , SO_4^{2-} , ClO_4^- , *p*-toluene sulfonate (*p*-TS) and dodecyl benzene sulfonate have been widely used as counter anions to control the properties of PPy films^[31, 32]. As reported, the ionic compensation mechanism is different during the redox process when PPy is synthesized from the deposition solution containing different anions (large-size or small-size). In addition to the study on the capacitive performances of PPy doped with *p*-TS^[33], recently, PPy doped with naphthalene sulfonate has also been electrochemically synthesized on the functionalized carbon cloth. It is found that the samples have good properties in LiCl electrolyte^[34].

The above mentioned reasons encourage us to investigate the capacitive performance of PPy doped with small-size anions in various electrolytes. In this work, PPy doped with Cl^- has been electrochemically deposited on the CFs and the ECs based on the composites have been assembled with various gel electrolytes such as $\text{H}_3\text{PO}_4/\text{PVA}$, $\text{H}_2\text{SO}_4/\text{PVA}$, $\text{LiClO}_4/\text{PVA}$, KCl/PVA and LiCl/PVA . The capacitive performance of the devices

has been systematically investigated, and the different cyclic stability of PPy doped with Cl^- in various electrolytes has been clarified.

EXPERIMENTAL

Materials and Reagents

Pyrrole is A.R. grade (Shanghai Chemical Reagent) and stored at lower than 5 °C. Potassium chloride, sodium chloride, lithium perchlorate, lithium chloride, sulfuric acid, phosphoric acid and PVA-124 are A.R. grade without further purification before use. CFs with an average diameter of 6.0 μm were purchased from Gansu Haoshi Carbon Fiber Co., Ltd.

Electrochemical Deposition of PPy-Cl on CFs

A bunch of CFs (~ 0.2 mm in diameter) was used as the working electrode to electrochemically deposit PPy in a three-electrode system, while a platinum foil and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. The electrolyte containing 1.0 $\text{mol}\cdot\text{L}^{-1}$ KCl and 0.1 $\text{mol}\cdot\text{L}^{-1}$ pyrrole was treated under ultrasonic condition for about 15 min to form a homogenous colloidal solution before use. During the preparation process, a constant current density of 0.5 $\text{mA}\cdot\text{cm}^{-1}$ was used to deposit PPy from 100 s to 1000 s and the obtained PPy-Cl/CFs samples were then washed by deionized water and dried under room temperature. In order to determine the counter ions in PPy after different cyclic voltammetry (CV) cycles, PPy-Cl/CFs composites were tested in various electrolytes at scan rate of 20 $\text{mV}\cdot\text{s}^{-1}$ for 5, 20 and 100 cycles and stopped at positive potential; to determine the counter ions of PPy-Cl/CFs under oxidative and reductive states, the sweep was stopped at positive potential to obtain the oxidative PPy while stopped at negative potential to obtain the reductive state of PPy. The obtained PPy samples were rinsed by deionized water and dried under vacuum at room temperature.

Preparation of Gel Electrolytes

The gel electrolytes of $\text{H}_3\text{PO}_4/\text{PVA}$, $\text{H}_2\text{SO}_4/\text{PVA}$, $\text{LiClO}_4/\text{PVA}$, KCl/PVA and LiCl/PVA were prepared by dissolving 1.0 g of PVA powder into 10.0 mL of H_3PO_4 , H_2SO_4 , LiClO_4 , KCl and LiCl solutions with the concentration of 1.0 $\text{mol}\cdot\text{L}^{-1}$ under vigorous stirring 85 °C, respectively. Then the solutions were cooled down to room temperature and kept for use.

Characterization and Electrochemical Measurements

The morphologies of the PPy-Cl/CFs samples were investigated by scanning electron microscope (SEM, JEOL 6701). An attenuated total reflection Fourier transform infrared spectrometer (Nicolet iS50R; USA) was used to collect ATR-FTIR spectra at 400–4000 cm^{-1} with a resolution of 2 cm^{-1} . The determination of relative content of the counter ions in PPy was carried out by X-ray photoelectron spectroscopy (XPS ESCAL-ab 220i-XL, VG Scientific, England) using a monochromic Al $K\alpha$ as source. The PPy-Cl/CFs electrodes were soaked with gel electrolytes for 2 min and then assembled by locating them on a PET film in parallel. Subsequently, the ECs were placed in a fume hood to evaporate water and allowed to become gel at room temperature. All the capacitive tests of the flexible ECs were performed with an electrochemical workstation (CHI 760E, Chenhua, Shanghai) by using CV in a potential range of -0.5 – 0.5 V from 10 $\text{mV}\cdot\text{s}^{-1}$ to 200 $\text{mV}\cdot\text{s}^{-1}$ (the scan rate of 100 $\text{mV}\cdot\text{s}^{-1}$ was performed in the cycling stability tests), galvanostatic charge/discharge (GCD) at current densities ranged from 0.1 $\text{mA}\cdot\text{cm}^{-1}$ to 1.6 $\text{mA}\cdot\text{cm}^{-1}$ and the electrochemical impedance spectra (EIS) were carried out by applying a sine wave with 5 mV amplitude over a frequency range of 100 kHz to 0.01 Hz.

The formulae used for calculating C_s (in length), C_v (in volume) and C_m (in mass) depending on CV and GCD curves, and the parameters of energy density and power density from the specific capacitance are described in the supporting information (SI).

RESULTS AND DISCUSSION

The deposition time is the key parameter for the preparation of PPy-Cl/CFs electrodes *via* galvanostatic method,

which needs to be optimized. The C_s of CFs can be ignored due to the very low capacitance as compared to PPy-Cl/CFs with relatively high content of PPy (Fig. S1 in SI). The relationship between deposition time and C_s of PPy-Cl/CFs is shown in Fig. S2 (in SI), which is obtained by measuring a three-electrode cell in $1.0 \text{ mol}\cdot\text{L}^{-1}$ KCl aqueous solution. At low scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$, the C_s values of PPy-Cl/CFs show almost a linear relationship with the deposition time, indicating that more active materials on the CFs is beneficial to the C_s . Nevertheless, the C_s values of PPy-Cl/CFs increase firstly and decrease later at higher scan rates with further prolongation of the deposition time. This phenomenon is ascribed to the following reasons: (1) at low scan rates, the active materials and the electrolyte can interact effectively, leading to the relatively large C_s values; (2) with the increase of scan rates, only part of the active materials can be utilized because the dense polymer matrix prohibits the diffusion of the electrolyte^[30]. In our case, we choose 900 s (the mass loading of PPy is $0.125 \text{ mg}\cdot\text{cm}^{-1}$) as the optimal deposition time due to the relatively large C_s and high rate-capability.

From the SEM images (Fig. 1), it is found that the pristine CFs consists of bundles of filaments (average diameter of about $6.0 \text{ }\mu\text{m}$) with many grooves on fiber's surface and exhibits relatively good orientation (Fig. 1a). After being deposited with PPy, the CFs are coated with PPy and the grooves on the surface disappear (Figs. 1b–1d). Furthermore, some large particles can be observed on PPy-Cl/CFs prepared with the deposition time of 1000 s. From the cross-sectional SEM images inserted in Figs. 1(b)–1(d), it can be found that PPy layers coated on the CFs surface are uniform, and the thicknesses of PPy layers are about 208, 358 and 584 nm for the samples of PPy-Cl/CFs prepared with the deposition time of 400, 900 and 1000 s, respectively. It is obvious that the dynamic process of ion diffusion in the polymer matrix is strongly affected by the thickness of PPy layer, which directly affects the rate-capability of the electrode materials.

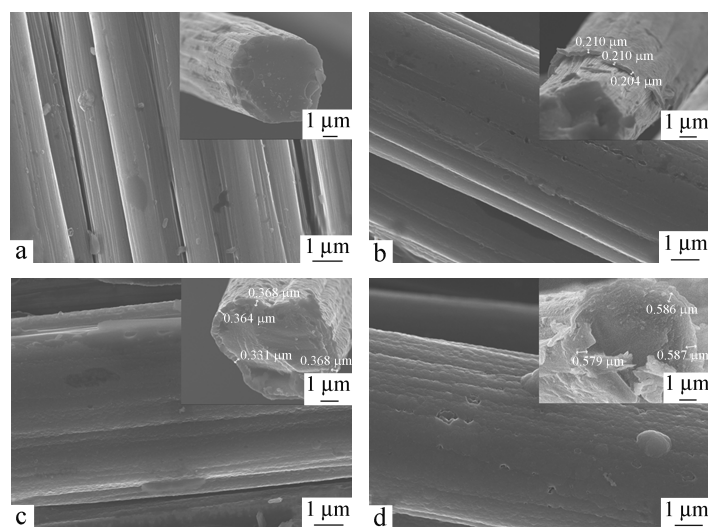


Fig. 1 SEM images of (a) CFs, PPy-Cl/CFs prepared with electrochemical deposition time of (b) 400 s, (c) 900 s and (d) 1000 s (The inserts are the cross sectional SEM images.)

On the other hand, compared with the ATR-FTIR spectrum of CFs, the characteristic peaks at 1577 and 1477 cm^{-1} for PPy/CFs (Fig. S3 in SI) are originated from the backbone stretching vibrations of $\text{C}=\text{C}$ and $\text{C}-\text{C}$ in PPy rings, the peaks at 1341 and 1219 cm^{-1} are attributed to the ring-stretching of PPy and $\text{C}-\text{N}$ stretching vibrations, and the peaks of 1052 , 973 and 942 cm^{-1} are due to the $\text{N}-\text{H}$ and $\text{C}-\text{H}$ in plane deformation and the ring deformation associated with the di-cation and radical cation, respectively^[35]. These additional peaks confirm the presence of PPy on CFs.

In order to evaluate the capacitive performance of PPy-Cl/CFs in various gel electrolytes, the ECs have been assembled and tested. From the CV curves (Fig. 2) recorded through a two-electrode test system, it is clear that the CV curves are nearly symmetrical rectangular shape, suggesting an almost ideal pseudo capacitive

response^[36]. Moreover, the current responses of the ECs exhibit obvious difference in various gel electrolytes. For instance, the flexible ECs by using LiClO_4 as gel electrolyte show relatively poor capacitive properties, while the ECs with $\text{H}_2\text{SO}_4/\text{PVA}$ and KCl/PVA as electrolyte display smaller deviation from the rectangle shape than those with $\text{H}_3\text{PO}_4/\text{PVA}$ - and LiCl/PVA -based electrolytes at the same scan rates. For ECs containing $\text{H}_2\text{SO}_4/\text{PVA}$ and KCl/PVA , the CV shapes at high scan rates are almost similar to those at low scan rates, indicating a high rate-capability and efficient ionic and electronic transport within the bulk materials^[37, 38]. From the plots of C_s (based on the equations in the SI) versus scan rates of the ECs in five gel electrolytes (Fig. 2F), the maximum C_s values of ECs assembled in $\text{H}_3\text{PO}_4/\text{PVA}$, $\text{H}_2\text{SO}_4/\text{PVA}$, $\text{LiClO}_4/\text{PVA}$, KCl/PVA and LiCl/PVA are about 28.7, 31.2, 19.3, 29.0 and 27.5 $\text{mF}\cdot\text{cm}^{-1}$ at scan rate of $10\text{ mV}\cdot\text{s}^{-1}$, respectively. The values of C_v and C_m are also calculated (Fig. S4 in SI). The maximum values of C_v reach to about 35.9, 38.9, 24.2, 36.3 and $34.4\text{ F}\cdot\text{cm}^{-3}$, and C_m achieved 229.9, 249.4, 154.7, 232.1 and $220.3\text{ F}\cdot\text{g}^{-1}$ at scan rate of $10\text{ mV}\cdot\text{s}^{-1}$ for the cells in $\text{H}_3\text{PO}_4/\text{PVA}$, $\text{H}_2\text{SO}_4/\text{PVA}$, $\text{LiClO}_4/\text{PVA}$, KCl/PVA and LiCl/PVA , respectively. The ECs fabricated with different gel electrolytes have similar specific capacitance except the ECs with $\text{LiClO}_4/\text{PVA}$.

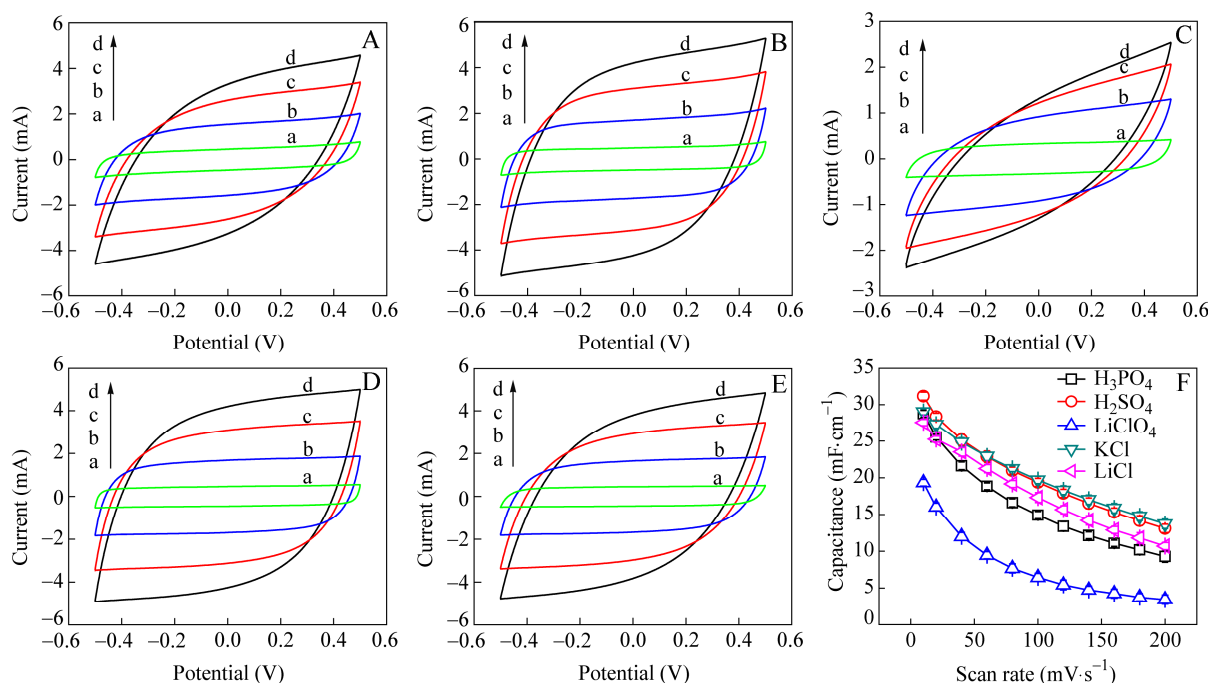


Fig. 2 The CV curves of ECs measured with two-electrode system by using (A) $\text{H}_3\text{PO}_4/\text{PVA}$, (B) $\text{H}_2\text{SO}_4/\text{PVA}$, (C) $\text{LiClO}_4/\text{PVA}$, (D) KCl/PVA and (E) LiCl/PVA as gel electrolytes; (F) The plots of C_s of electrodes versus scan rates (The scan rate of a, b, c and d are 10, 40, 80 and $120\text{ mV}\cdot\text{s}^{-1}$, respectively.)

Subsequently, the GCD curves of ECs are compared by using the five different electrolytes (Fig. 3) under various current densities (from $0.1\text{ mA}\cdot\text{cm}^{-1}$ to $1.6\text{ mA}\cdot\text{cm}^{-1}$). All the GCD curves exhibit perfectly linear and symmetric triangular shapes, indicating significant capacitive characteristic. The iR drop caused by the overall internal resistance of the devices^[39, 40] is relatively low. The discharging time of ECs and iR drop become longer and smaller with the decrease of current densities. It can be explained that the ions diffused from the electrolyte have access to all available space at low current densities, leading to a complete doping/dedoping reaction. However, the influence on the matrix is opposite when the current densities increase. Overall, the plots of C_s calculated from GCD display the similar trend with those from CV curves. The highest C_s of electrode based on $\text{H}_3\text{PO}_4/\text{PVA}$ can be determined to be about $41.6\text{ mF}\cdot\text{cm}^{-1}$, $52.1\text{ F}\cdot\text{cm}^{-3}$ or $333.3\text{ F}\cdot\text{g}^{-1}$ (Fig. S5 in SI) at current density of $0.1\text{ mA}\cdot\text{cm}^{-1}$ (Fig. 3F), but the C_s values decrease more promptly than those in $\text{H}_2\text{SO}_4/\text{PVA}$ and KCl/PVA with the increase of current densities.

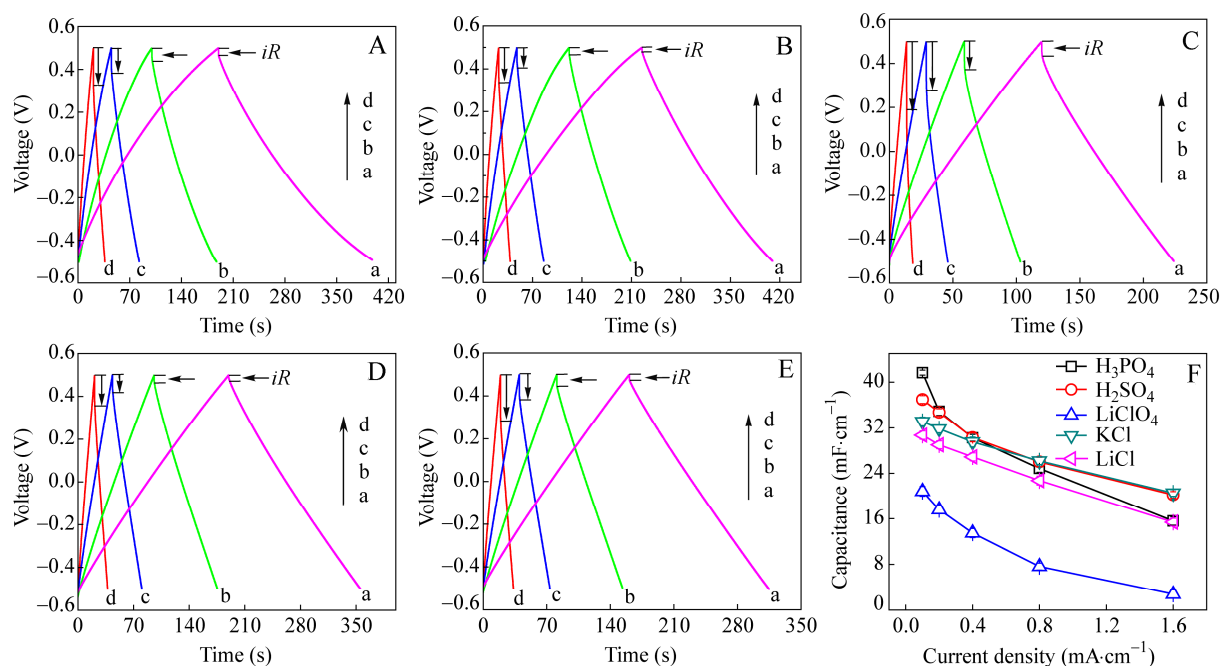


Fig. 3 GCD curves of ECs assembled from PPy-Cl/CFs by using (A) H₃PO₄/PVA, (B) H₂SO₄/PVA, (C) LiClO₄/PVA, (D) KCl/PVA and (E) LiCl/PVA as gel electrolytes at various current densities; (F) The plots of C_s versus the current densities (The current density for a, b, c and d are 0.1, 0.2, 0.4 and 0.8 mA·cm⁻², respectively.)

Energy and power density are two meaningful parameters to characterize the performance of energy storage devices. It can be found from Fig. 4 that the flexible ECs with H₃PO₄/PVA gel electrolyte exhibit an energy density of 3.51 mWh·cm⁻³ at a power density of 0.06 W·cm⁻³, while it maintains 0.91 mWh·cm⁻³ at power density of 0.67 W·cm⁻³. The ECs based on H₂SO₄/PVA and KCl/PVA show similar energy densities with that based on H₃PO₄/PVA; however, larger power density is observed, which can reach to 0.74 and 0.77 W·cm⁻³, respectively. The energy densities obtained in our case is competitive with those reported flexible ECs, including PPy/paper supercapacitors (1.0 mWh·cm⁻³)^[25], CuO@AuPd@MnO₂ (0.55 mWh·cm⁻³)^[41] and solid-state asymmetric capacitors fabricated by three-dimensional graphene/MnO₂ and graphene/polypyrrole (1.23 mWh·cm⁻³)^[7], flexible PPy-nanocellulose fiber (3.1 mWh·cm⁻³)^[19] and MnO₂/carbon nanoparticles (0.06 mWh·cm⁻³)^[42].

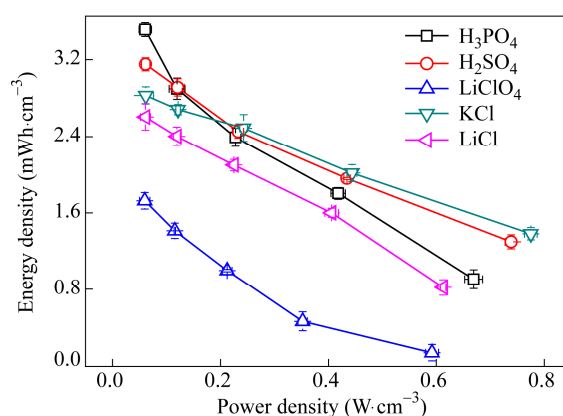


Fig. 4 Ragone plots of the energy densities versus power densities calculated according to the discharged curves of ECs by using H₃PO₄/PVA, H₂SO₄/PVA, LiClO₄/PVA, KCl/PVA and LiCl/PVA as gel electrolytes

Figure 5(A) displays the complex plots of our ECs. EIS is a powerful tool to show the electronic/ionic conductivity of the cells' components during the charging and discharging progress^[43]. As the interception with x -axis and inconspicuous arcs in the high frequency region represent the internal resistance, the small value indicates a good conductivity and a low internal resistance for the ECs^[44]. It is found that the ECs based on $\text{H}_3\text{PO}_4/\text{PVA}$, $\text{H}_2\text{SO}_4/\text{PVA}$, KCl/PVA and LiCl/PVA as gel electrolytes have smaller internal resistance than that with $\text{LiClO}_4/\text{PVA}$ as the electrolyte. In the region of low frequency, the vertical shape indicates the capacitive process and the ionic diffusion. It is clear that the ECs based on $\text{LiClO}_4/\text{PVA}$ have inferior capacitive properties than those of $\text{H}_3\text{PO}_4/\text{PVA}$ -, $\text{H}_2\text{SO}_4/\text{PVA}$ -, KCl/PVA - and LiCl/PVA -based ECs, and the ECs with $\text{H}_3\text{PO}_4/\text{PVA}$ only exhibit moderate capacitive performance through careful observation. According to the results from CV, GCD and EIS, the ECs with the gel electrolytes of $\text{H}_2\text{SO}_4/\text{PVA}$ and KCl/PVA show better capacitive performance.

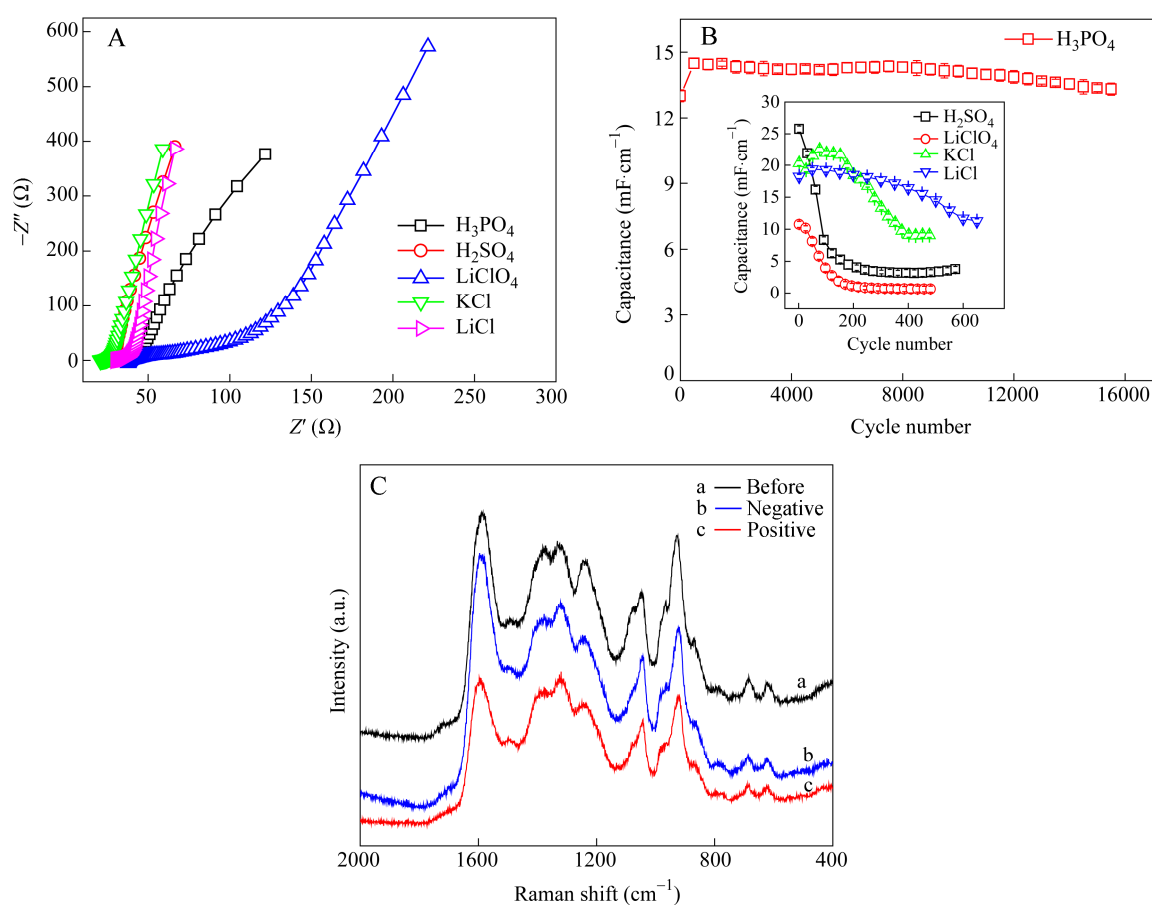


Fig. 5 (A) The complex plots of EIS for ECs assembled from PPy-Cl/CFs by using $\text{H}_3\text{PO}_4/\text{PVA}$, $\text{H}_2\text{SO}_4/\text{PVA}$, $\text{LiClO}_4/\text{PVA}$, KCl/PVA and LiCl/PVA as gel electrolytes in two-electrode test; (B) The cyclic stability of ECs with $\text{H}_3\text{PO}_4/\text{PVA}$ as gel electrolyte under successive scan at rate of $100 \text{ mV}\cdot\text{s}^{-1}$ (The inserted figure shows the cyclic stability of ECs based on $\text{H}_2\text{SO}_4/\text{PVA}$, $\text{LiClO}_4/\text{PVA}$, KCl/PVA and LiCl/PVA gel electrolytes under successive CV scan at $100 \text{ mV}\cdot\text{s}^{-1}$); (C) The Raman spectra of the ECs with $\text{H}_3\text{PO}_4/\text{PVA}$ as gel electrolyte (a) before and after the cycling test with (b) negative electrode and (c) positive electrode

Cycling stability is a very important parameter besides the energy density and power density^[45], which is the main obstacle for practical utilization of conducting polymer-based ECs. From Fig. 5(B), it is interesting to find that the ECs by using $\text{H}_3\text{PO}_4/\text{PVA}$ as the gel electrolyte have excellent cycling stability although its energy

and power densities are not outstanding. The ECs using $\text{H}_3\text{PO}_4/\text{PVA}$ as electrolyte show light decrease of C_s and retain about 91.7% of initial capacitance after 15000 cycles. However, from the inserted figure, it is surprised to find that the C_s values of ECs with $\text{H}_2\text{SO}_4/\text{PVA}$, $\text{LiClO}_4/\text{PVA}$ and KCl/PVA as gel electrolytes dramatically decrease after 200 cycles, but the ECs using LiCl/PVA as gel electrolyte remain 61.8% of capacitance after 650 cycles. The Raman spectra (Fig. 5C) have been recorded before and after long-term life test to find the change of the chemical structures of PPy. The as-prepared PPy-Cl/CFs show a strong band around 1580 cm^{-1} which represents the $\text{C}=\text{C}$ backbone stretching. The double peaks at approximately 1050 and 1080 cm^{-1} are ascribed to the $\text{C}-\text{H}$ in plane deformations, while the other double peaks at about 1320 and 1370 cm^{-1} are due to the ring-stretching mode of PPy. The bands at about 930 and 970 cm^{-1} are attributed to the ring deformation associated with dication (bipolaron) and radical cation (polaron), respectively. The bands at 1080 and 1370 cm^{-1} which are originated from the $\text{C}-\text{H}$ in-plane and the ring stretching may depict the oxidized species of PPy^[46]. It is found from Fig. 5(C) that the whole profiles of PPy's Raman spectra after cyclic test are quite similar to that in initial state although the peak intensities at 1080 and 1370 cm^{-1} become weak. The chemical structure of PPy is almost completely retained after the repetitive charging/discharging. Therefore, the $\text{H}_3\text{PO}_4/\text{PVA}$ -based ECs not only have a relatively good C_s value but also possess an excellent stability, which is better than those reported for solid-state supercapacitors, such as 88.1% for PPy nanowires and reduced graphene oxide after 5000 cycles^[29], 90.6% for PPy nanofiber/graphene film after 1000 cycles^[47], 83.6% for PPy electrodes after 2000 cycles^[48]. It can be concluded that $\text{H}_3\text{PO}_4/\text{PVA}$ is the appropriate electrolyte for PPy-Cl/CFs electrodes when considering the energy density, power density and stability.

We have further explored the reasons why the same material exhibits distinct stability in different electrolyte. From the fifth cycle of CV curves of PPy-Cl/CFs in different electrolytes (Fig. 6A), it can be seen that PPy-Cl/CFs show broad cathodic and anodic peaks, and the CV curves can be divided into two types according to their characteristic. One type shows obvious anodic peak while the other shows obvious cathodic peak. The CV curves of PPy-Cl/CFs in KCl , LiCl and LiClO_4 electrolytes have very similar features, such as only with the obvious anodic peak. In KCl and LiCl aqueous solutions, large current response is observed due to the same anion between solution and PPy's matrix, while in LiClO_4 electrolyte, small current response and an anodic peak (0.16 V) can be observed, which demonstrate that PPy-Cl/CFs have less activity in LiClO_4 due to the large size of ClO_4^- . The CV curves of PPy-Cl/CFs in H_3PO_4 and H_2SO_4 aqueous solutions exhibit obvious cathodic peaks located at about -0.28 and -0.21 V . Furthermore, the CV curve of PPy-Cl/CFs in H_3PO_4 also shows an anodic peak at about 0.17 V while in H_2SO_4 solution no obvious peak is observed. According to the characteristics of CV curves, we may deduce that the initial doped anions can be replaced by the anions in LiClO_4 , H_2SO_4 or H_3PO_4 during CV process. Furthermore, according to the successive CV curves of PPy-Cl/CFs in H_3PO_4 aqueous solution shown in Fig. 6(B), it is clearly that the CV changes in the proceeding of CV process until it reaches a steady state similar to that in Fig. 6(A). In order to confirm the deduction obtained from Figs. 6(A) and 6(B), the XPS spectra of PPy/CFs samples have been recorded after they have been tested in different electrolytes by 0, 5, 20 and 100 CV cycles and the typical spectra are shown in Fig. S6 (in SI). As expected, the relative contents of Cl in PPy matrixes decrease after the CV test in different electrolytes, and the relative contents of P, S and Cl in ClO_4^- increase (Fig. 6C). Furthermore, the atomic ratios of P/Cl, S/Cl and ClO_4^-/Cl increase to almost a constant after 20 CV cycles in the appropriate electrolytes, but the sample tested in LiCl electrolyte has a constant ratio due to the same anion between PPy matrix and electrolyte (Fig. 6D). These results prove that the doped anions in PPy matrix have been replaced by the anions in the testing electrolytes.

From the CV curves shown in Fig. 6, we can see that the doped anions in PPy-Cl/CFs have been substituted in different solutions of electrolytes. However, it is interesting that PPy-Cl/CFs in $\text{H}_3\text{PO}_4/\text{PVA}$ exhibit good stability. XPS is a useful tool to reveal the components of materials and valence of elements^[49], which is used to detect the anions content in PPy at oxidized and reduced states in different electrolytes. From Fig. 7, it can be seen clearly that the contents of counter anions in all the samples at oxidized state are higher than those in

reduced state. According to the integrate area of the peaks corresponding to P, S and Cl, the ratios of phosphate, sulfate, ClO_4^- and Cl^- in PPy's oxidized state to their reduced state are calculated to be about 4.11, 2.06, 2.27 and 1.37, respectively. Furthermore, we find that the XPS peak of Cl for PPy-Cl/CFs can be divided into Cl^- , PPy-Cl^- and C-Cl forms, and the formation of PPy-Cl^- and C-Cl species is unfavorable to the cyclic stability of PPy^[50]. ClO_4^- has larger size than Cl^- , which leads to the small C_s and poor cyclic stability due to the structure damage during repetitive charging and discharging cycles. It is strange that SO_4^{2-} can be found in both the oxidative and reductive PPy matrix. Therefore, H^+ ions may diffuse into PPy matrix to compensate the charge and increase the acidity in PPy matrix, resulting in high acidity to weaken the activity and damage the structure^[51]. However, H_3PO_4 is a moderate acid compared with H_2SO_4 , and only less content exist in reduced PPy matrix, which causes less H^+ accumulate in the PPy matrix and less structural damage. That may be the reason why the ECs of PPy-Cl/CFs in $\text{H}_3\text{PO}_4/\text{PVA}$ have excellent cyclic stability.

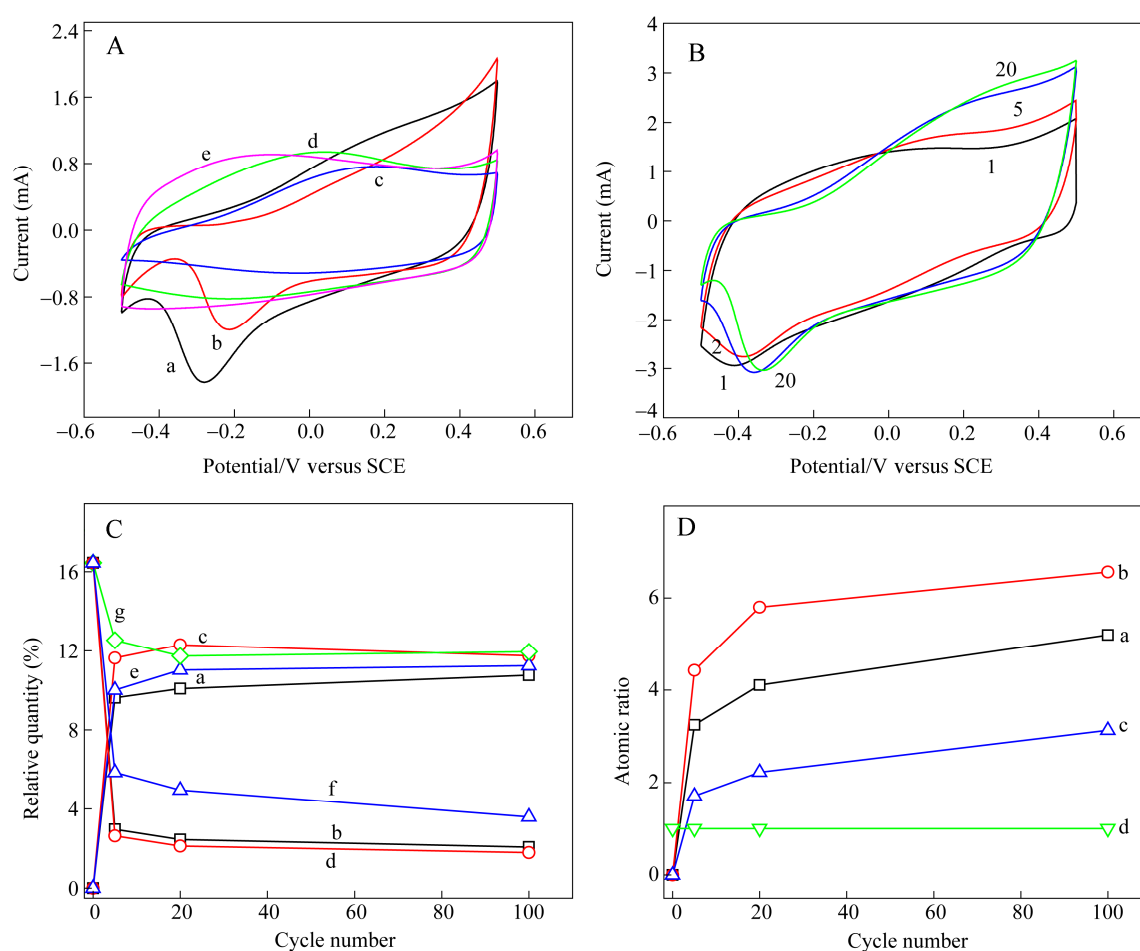


Fig. 6 (A) The fifth cycle CV behaviors of PPy-Cl/CFs in (a) H_3PO_4 , (b) H_2SO_4 , (c) LiClO_4 , (d) KCl and (e) LiCl electrolytes at $10 \text{ mV} \cdot \text{s}^{-1}$; (B) The successive CV of PPy-Cl/CFs in $1.0 \text{ mol} \cdot \text{L}^{-1} \text{H}_3\text{PO}_4$ aqueous solution at a potential scan rate of $20 \text{ mV} \cdot \text{s}^{-1}$ by using a three-electrode configuration; (C) The plots of relative contents of Cl (b in H_3PO_4 electrolyte, d in H_2SO_4 electrolyte, f in LiClO_4 electrolyte and g in LiCl electrolyte), (a) P, (c) S and (e) Cl in ClO_4^- doped in PPy in different electrolytes versus cyclic number with N as the standard; (D) The plots of relative atomic ratios of (a) P/Cl in H_3PO_4 electrolyte, (b) S/Cl in H_2SO_4 electrolyte, (c) ClO_4^-/Cl in LiClO_4 electrolyte and (d) Cl/Cl in LiCl electrolyte calculated from the data in (C) versus the cyclic number at the scan rate of $20 \text{ mV} \cdot \text{s}^{-1}$

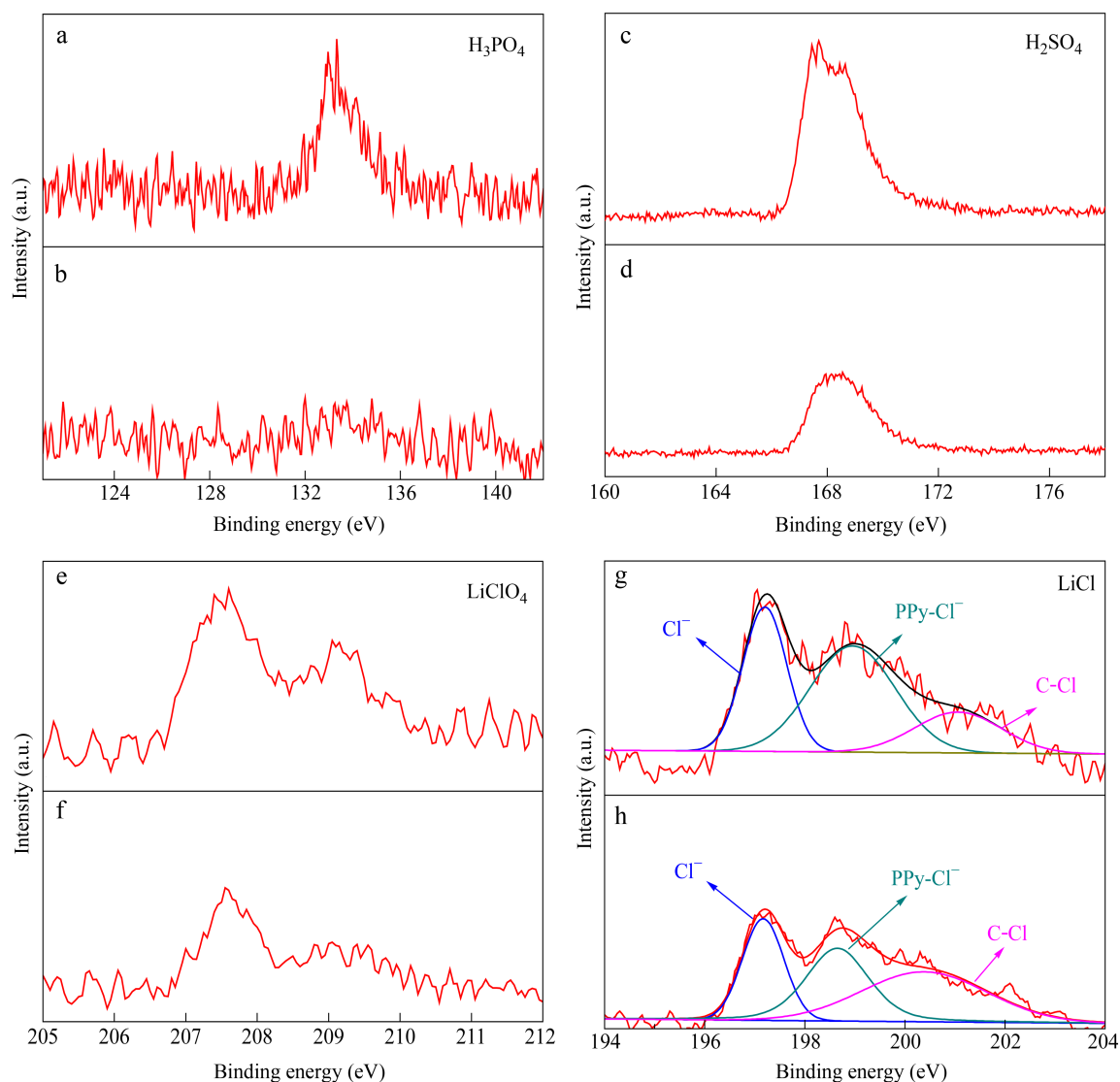


Fig. 7 High resolution XPS of (a and b) P2p, (c and d) S2p, (e and f) Cl2p and (g and h) Cl2p for PPY-Cl/CFs in H_3PO_4 , H_2SO_4 , LiClO_4 and LiCl aqueous solution tested after successive CV and kept (a, c, e and g) oxidized states and (b, d, f and h) reduced states

Flexibilities for ECs are essential when they are used to power portable electronic devices and smart garments^[52]. The obtained ECs with $\text{H}_3\text{PO}_4/\text{PVA}$ are further subjected to mechanical bending tests. Figs. 8(a) and 8(b) show the negligible electrochemical performance change under different bending angles (0° , 60° , 90° and 145°), demonstrating the superior mechanical flexibility of the ECs. In order to determine the cyclic flexibility, CV curves of the cell have been recorded after the device endures 100 and 500 bending cycles (90° , Fig. S7 in SI). Almost the same CV curves reveal that the devices exhibit good repeated bending performance. To meet the needs for practical applications in both energy and power, the studies on the ECs connected in series and parallel have been carried out. As shown in Figs. 8(c) and 8(d), the CV curves of the three capacitors connected in parallel and series have been measured at scan rate of $20 \text{ mV}\cdot\text{s}^{-1}$. The results show that the three ECs in series can expand the voltage three times, and those in parallel have about three times of area in CV curve as compared to a single cell. Furthermore, a light emitting diode with green emission (threshold voltage of 2.5 V)

can be powered for about three minutes when the three cells in series are charged full at current density of $0.4 \text{ mA} \cdot \text{cm}^{-1}$ (inserted figure in Fig. 8c), demonstrating the potential application of the $\text{H}_3\text{PO}_4/\text{PVA}$ -based ECs.

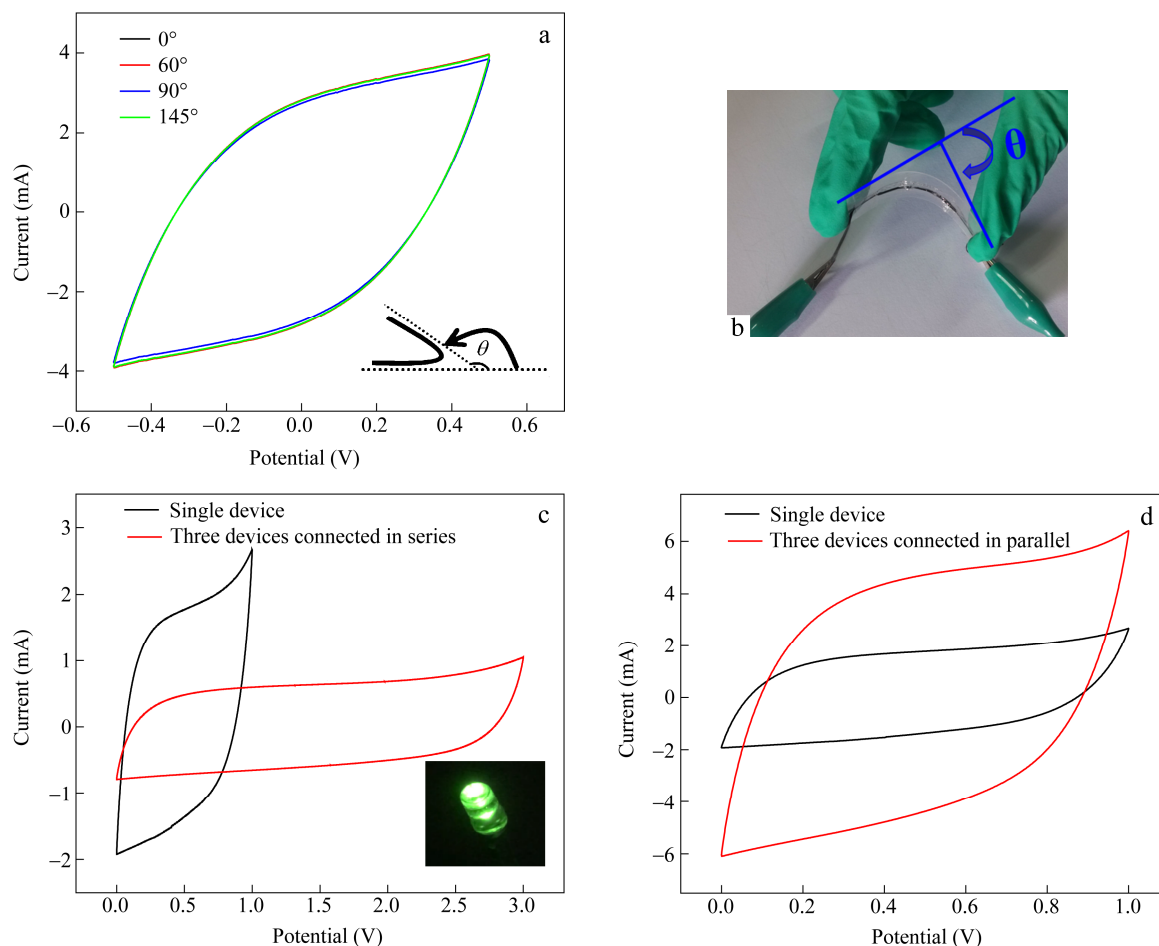


Fig. 8 (a) CV curves of the flexible ECs based on $\text{H}_3\text{PO}_4/\text{PVA}$ under different bending angles at scan rate of $100 \text{ mV} \cdot \text{s}^{-1}$; (b) Digital photograph of a flexible ECs based on $\text{H}_3\text{PO}_4/\text{PVA}$ under bending state; CV curves of three ECs based on $\text{H}_3\text{PO}_4/\text{PVA}$ (c) in series and (d) in parallel at $40 \text{ mV} \cdot \text{s}^{-1}$. Inserted figure in (c) is the optical image of a green LED turned on by the three ECs based on $\text{H}_3\text{PO}_4/\text{PVA}$ connected in series.

CONCLUSIONS

We have demonstrated that the electrodes of PPy-Cl/CFs in various electrolytes possess different capacitive properties. The ECs with $\text{H}_3\text{PO}_4/\text{PVA}$ as gel electrolyte exhibit a relatively high C_s and excellent cycling stability. However, the ECs in other gel electrolytes show very poor stability although the initial C_s values are relatively high as compared with that in $\text{H}_3\text{PO}_4/\text{PVA}$. The specific energy density of ECs in $\text{H}_3\text{PO}_4/\text{PVA}$ gel electrolyte is about $3.51 \text{ mWh} \cdot \text{cm}^{-3}$ at power density of $0.06 \text{ W} \cdot \text{cm}^{-3}$. Therefore, it can be concluded that an appropriate electrolyte can improve the EC's capacitance and cycling stability dramatically. The XPS data reveal that the content of counter anions in the reductive PPy matrix may be directly related to the PPy ECs' cycling stability.

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