基于聚吡咯修饰的碳泡沫可压缩电极材料

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摘 要 在该研究中，通过高温碳化和原位聚合法制备了基于市售三聚氰胺泡沫和吡咯单体的聚吡咯/碳化三聚氰胺泡沫(Polypyrrole/Carbonized Melamine Foam，PPy/CMF)的可压缩超级电容器电极材料。通过三电极体系在 1 mol/L 高氯酸钠电解液中研究了可压缩 PPy/CMF 电极材料的电化学性质。结果显示，可压缩电极材料的体积电容在 2 mA/cm^3 时可达到 3 168 mF/cm^3，1 000 次充放电循环后可保持原始电容的 86.88%。此外，该材料的循环伏安曲线和恒流充放电曲线在不同压缩下无显著变化，表明 PPy/CMF 是具有高压缩稳定性的可压缩电极，适合于超级电容器。以上结果表明，PPy/CMF 可作为可压缩超级电容器的潜在电极材料。

关键词 三聚氰胺泡沫；聚吡咯；可压缩电极；原位聚合
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Compressible Electrode Material Based on Polypyrrole Decorated Carbonized Melamine Foam

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Abstract In this research, a compressible electrode of polypyrrole/carbonized melamine foam (PPy/CMF) based on commercial melamine foam and pyrrole monomer was fabricated by high temperature carbonization and *in-situ* polymerization. The electrochemical property of compressible PPy/CMF electrode material was investigated by three-electrode system in 1 mol/L sodium perchlorate electrolyte. The volumetric capacitance

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of compressible electrode material can achieve 3 168 mF/cm^3 at 2 mA/cm^3 and preserve 86.88% of initial capacitance after 1 000 charge and discharge cycles. Furthermore, cyclic voltammetry and galvanostatic charge-discharge curves of compressible electrode material did not change significantly under different compressions, indicating that PPy/CMF is an appropriate compressible electrode with high compressive stability for supercapacitor. These results demonstrate that PPy/CMF is an excellent candidate for compressible supercapacitor.

Keywords melamine foam; polypyrrole; compressible electrode; *in-situ* polymerization

1 Introduction

In recent years, wearable electronic devices have attracted increasing attention. Flexible and compressible energy conversion and storage device (supercapacitor and battery) need to be developed for wearable electronic device. Among these devices, supercapacitor is a significant class of energy conversion and storage device due to its long service life[1], high power density[2], fast charge and discharge rate[3] and relatively low cost. However, low energy density is a major issue to limit application of supercapacitor[4]. Usually, the capacitance performance of electric double layer capacitors (EDLCs) is affected by conductivity, specific surface area and pore volume of electrode material. Therefore, these factor need to be enhanced for improving capacitance performance[5]. In order to obtain the excellent compressible supercapacitor, we need to prepare a compressible electrode with good electrochemical performance. There are some works about compressible supercapacitor have been published. Xiao et al.[6] fabricated the compressible material based on melamine foam (MF) for supercapacitor, they adopted the high temperature carbonization to acquirea self-standing and hydrophilic nitrogen (N)-doped (NCF) electrode for compressible supercapacitor, which exhibits an area capacitance of 332 mF/cm^2 (52 F/g) at 1 mA/cm^2. NCF electrode can keep its original electrochemical performance even after 1 000 cycles under different compressions. These results illustrate that NCF is an exceptional electrode for compressible supercapacitor. Furthermore, they adopted smart etching and catalytic process using $KMnO_4$ solution to fabricate high temperature carbonized elastic electrode based on MF, and electrode material exhibits improved electrochemical performance[7]. After that, they fabricated a new electrode material for compressible supercapacitor[8]. There are many efforts have been made by other groups based on carbon foam[9-11].

Melamine foam is a cheap and elastic material, which is composed of 3D porous structure with large specific surface and volumetric density. Because of its special 3D internet structure, MF has high elasticity. However, the non-conductive property of MF has placed an obstacle to its development in compressible supercapacitors. Conductive MF is the key material to prepare compressible supercapacitor. Therefore, how to make MF conductive is a problem that needs to be solved in preparing MF-

based compressible electrode materials. The elastic property of MF has no significant decline even after high-temperature carbonization according to reports in the literature, indicating that MF is an exceptional matrix for compressible electrode with high stability and electrochemical property[12].

As an excellent conductivity polymer, pyrrole has been applied in many areas, which contains battery, biology, ion detection, supercapacitor and antistatic material and photovoltaic chemical cell, etc. Moreover, polypyrrole (PPy) is an outstanding electrode for supercapacitor due to its large theoretical capacitance, good conductivity and wide potential window[13]. Many works about PPy electrode have been performed by researchers[13-16]. Furthermore, there are many works about special structure of PPy are applied in electrode for high performance supercapacitor[17-20]. Therefore, PPy is an excellent electrode for supercapacitor.

Inspired by work of Xiao et al.[6], conductive melamine foam-based compressible material was prepared by high temperature carbonization. Using high-temperature carbonized MF as substrate to deposit PPy via *in-situ* polymerization for enhancing its electrochemical performance. The obtained composite electrode with advantages of PPy and MF is an exceptional candidate for compressible supercapacitor. Composite electrode exhibits compressibility and volume specific capacitance from MF and PPy. The electrochemical property of polypyrrole/carbonized melamine foam (PPy/CMF) was tested, PPy/CMF electrode exhibits a volume capacitance of 3.168 F/cm^3 at 2 mA/cm^3 and outstanding cyclic stability, which displays a volume capacitance retention of 86.88% even after 1 000 galvanostatic charge-discharge (GCD) cycles. Furthermore, PPy/CMF electrode illustrates high electrochemical stability under various compressions. All of these results indicate that PPy/CMF electrode is an exceptional electrode for elastic supercapacitor.

2 Experiment Section

2.1 Reagents and materials

The MF was supplied by Outlook Company (Chengdu), pyrrole was purchased from Aladdin Industrial Co., Ltd., ferric chloride ($FeCl_3$), sodium dodecyl benzene sulfonate (SDBS) and ethanol were acquired from Sinopharm Chemical Reagent Co., Ltd.

2.2 Preparation of carbonized melamine foam

The MF is subjected to heat under the protection of a high purity inert gas to volatilize all or most of the non-carbon components such as hydrogen, oxygen, nitrogen, sulfur, etc. in the compound, resulting in a compressible material having high carbon content. In a typical process, MF was cut into appropriate size and repeatedly washed with deionized (DI) water and ethanol to remove surface impurities. Then, the MF was dried at 60 ℃ for 12 h. After that, the obtained MF was annealed in a tubular furnace with a nitrogen atmosphere for 2 h (annealing temperatures: 850 ℃, heating rate: 5 ℃/min) to prepare carbonized melamine foam (CMF) elastic electrode. The obtained CMF was repeatedly washed with DI water and ethanol[6].

2.3 Preparation of polypyrrole/carbonized melamine foam

The polypyrrole material was grown on the surface of the CMF fiber prepared above by *in-situ* polymerization. In a general process for PPy,

0.069 7 g sodium dodecyl benzene sulfonate (SDBS) was sonicated in 10 mL DI water for 5 min, and then CMF was immersed into SDBS dispersion. Simultaneously, 2 mmol (140 μL) pyrrole was distributed in 10 mL DI water (ultrasound dispersion for 5 min). Next, the pyrrole dispersion was slowly poured into beaker containing CMF. After ultrasonic dispersion 5 min, mixed solution was allowed to place at room temperature for 30 min. An aqueous solution containing 2 mmol $FeCl_3$ was slowly dropped into above mentioned mixed solution, and the beaker was placed in a refrigerator at 0 ℃. After reacting 12 h, the obtained PPy/CMF was repeatedly rinsed with ethanol DI water and dried at 60 ℃ for 12 h.

2.4 Material characterization and electrochemical performance

The morphologies of MF, CMF and PPy/CMF were performed by the field emission scanning electron microscopy (FESEM, Nova Nano SEM 450). The fourier transform infrared spectroscopy (FTIR) was used to test the polymer bonds in elastic electrode for indicating the presence of PPy.

The electrochemical property of PPy/CMF elastic electrode was measured by three-electrode system in 1 mol/L $NaClO_4$ electrolyte. The cyclic voltammetry (CV) curve of PPy/CMF was measured with potential range of −0.5-0.5 V and scan rate range of 5-100 mV/s. The GCD curve of PPy/CMF was performed with potential window of −0.5-0.5 V and current density from 2 to 50 mA/cm^3. Next, the electrochemical performances of PPy/CMF electrode material under different compressions were measured in the same condition besides the compression fixture. After all, the electrochemical impedance spectroscopy (EIS) was investigated with 5 mV from 50 mHz to 50 kHz.

3 Results and Discussions

Figs. 1(a)-(c) depict the optical photographs of the PPy/CMF electrode material for purpose of proving the high compressibility of electrode material. It can be seen that the electrode material can recover the initial volume after the compression load is removed. Figs. 1(d)-(f) present SEM images of MF, CMF and PPy/CMF at different magnifications. As depicted in Fig. 1(d), MF is composed of 3D interconnected fibers with smooth surface (as shown in upper-left corner of Fig. 1(d)). After carbonized at 850 ℃, CMF remains original 3D interconnected structure of MF. However, the skeleton of 3D interconnected structure emerged the distortions phenomenon, and CMF fibers surface occurred wrinkles and volume contraction. Then, we utilized the CMF as substrate to attach PPy on its surface via *in-situ* polymerization. Fig. 1(f) displays surface topography of PPy/CMF at different magnifications. The introduction of PPy has no effect on 3D interconnected structure of CMF (as shown in Fig. 1(f)), and PPy particle is uniformly coated on CMF surface (as shown in upper-left corner of Fig. 1(f)) to form a conductive pathway, indicating that 3D interconnected structure ensures conductive pathway of electrode material. Furthermore, these 3D interconnected structures facilitate the transmission of charges and ions, which can further improve the capacity of supercapacitors, demonstrating that PPy/CMF is an excellent candidate for compressible electrode. Figs. 1(h)-(k) present the elemental mapping images of PPy/CMF in the area of (g). It can be seen that the elements carbon(C), nitrogen

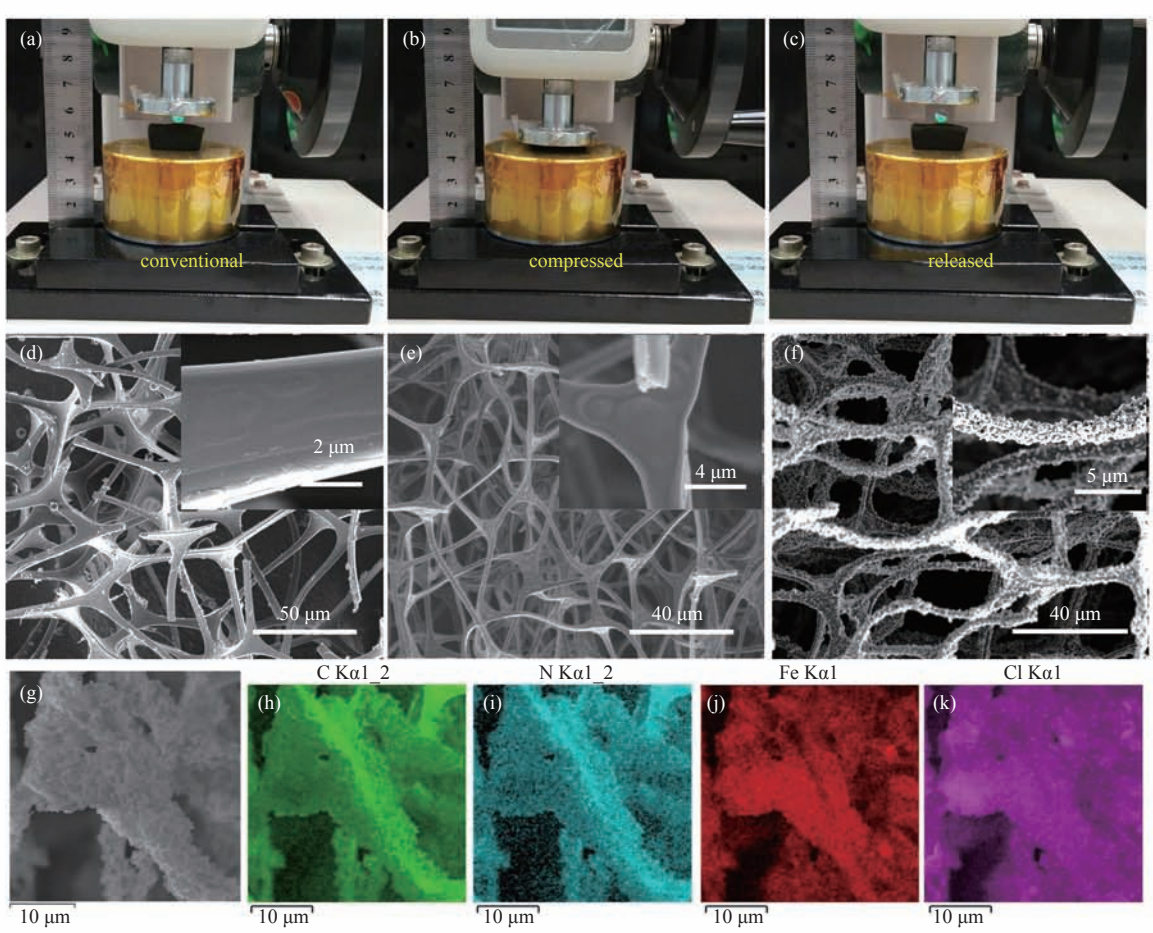

Fig. 1　(a)-(c) Digital photo of PPy/CMF electrode showing its compressibility; scanning electron microscopy (SEM) images of (d) MF, (e) CMF, (f) PPy/CMF; (g) SEM image of PPy/CMF electrode; (h)-(k) elemental mapping images of PPy/CMF in the area of (g)

(N), iron (Fe) and chlorine (Cl) are present in the electrode material, further indicating that we have successfully prepared the PPy/CMF electrode material by *in-situ* polymerization.

Fig. 2(a) displays FTIR spectra of CMF and PPy/CMF compressible electrode, there are many characteristic bands are associated with PPy from the image. The PPy features band related with C=C stretching is located in 1 541 cm^{-1}, and the characteristic peak of PPy is assigned to C−N stretching vibration mode is located near in 1 448 cm^{-1}. Moreover, the features peak of PPy related with C−N stretching wagging vibration is located in 1 167 cm^{-1}, and the C−H vibration in-plane can observe in 1 047 cm^{-1} from the FTIR spectra of PPy/CMF. Furthermore, the characteristic peak of PPy correlated to ring deformation is attributed to 881 cm^{-1}[15,17-18]. It demonstrates that the presence of PPy in the PPy/CMF compressible electrode material. Fig. 2(b) presents the stress-strain curve of PPy/CMF compressible electrode material at strain of 50%. The volume of PPy/CMF compressible electrode material can restored to its initial volume after compression without any loss due to its three-dimensional network structure with high elasticity (according to the experiment), its stress-strain curve

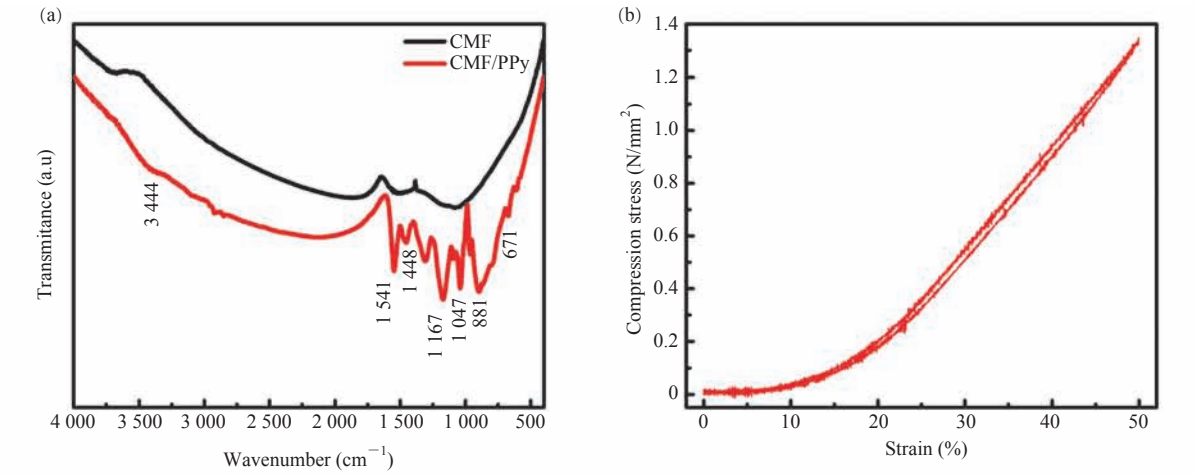

Fig. 2 (a) Fourier transform infrared spectroscopy (FTIR) spectra of CMF and PPy/CMF compressible electrode; (b) the stress-strain curve of PPy/CMF compressible electrode at strain of 50%

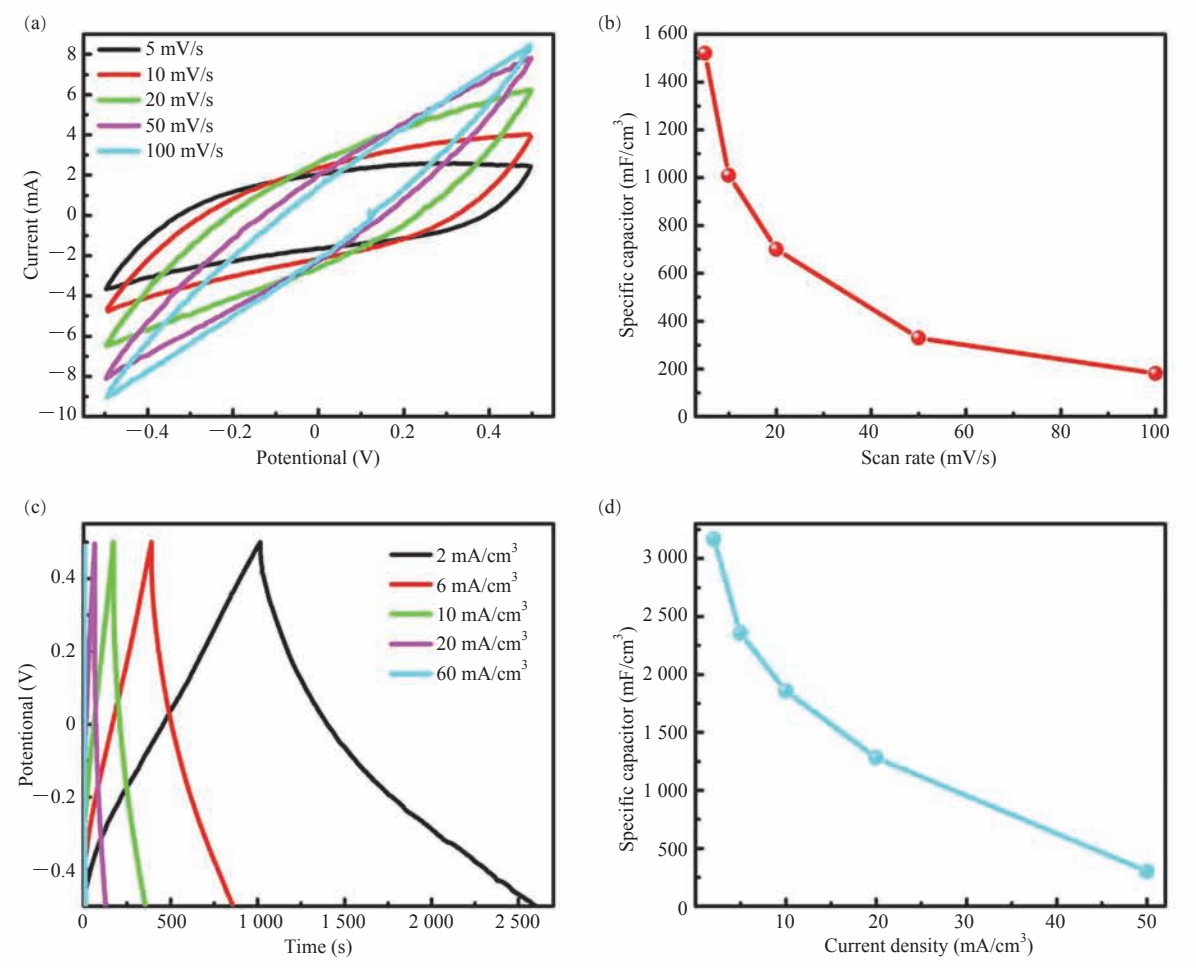

Fig. 3 (a) Cyclic voltammetry (CV) curves of PPy/CMF at various scan rates; (b) volume specific capacitance variation atvarious scan rates; (c) galvanostatic charge-discharge (GCD) curves of PPy/CMF at various current densities; (d) volume specific capacitance versus current densities

further explained the experimental phenomenon.

Fig. 3 displays the electrochemical property of PPy/CMF elastic material. Outstanding material properties correspond to excellent microstructure. The rectangular shape of CV curve is corresponds to a double-layer capacitor from PPy/CMF elastic materialas shown in Fig. 3(a). The shapes of CV curves have no significant change with increase of scan rate, and volume specific capacitance of PPy/CMF elastic electrode can achieve 1 520 mF/cm^3 at 5 mV/s. Furthermore, the electrochemical performance of PPy/CMF was measured by GCD curve. Fig. 3(c) and Fig. 3(d) describe GCD curves and volume specific capacitances of PPy/CMF at various current densities, volume capacitance gradually decreases with current density. The symmetrical GCD curve is performed for PPy/CMF electrode, indicating the high volume capacitance and excellent coulombic efficiency of PPy/CMF. The discharge time of PPy/CMF gradually decreases with current density and remains 64 s at 20 mA/cm^3. The volume specific capacitance of PPy/CMF can achieve 3 168 mF/cm^3 at 2 mA/cm^3. These electrochemical performances illustrate that PPy/CMF is an exceptionalel ectrode for compressible supercapacitor.

Fig. 4(a) presents GCD cycle curves of PPy/CMF before and after 1 000 cycles at 20 mA/cm^3, and Fig. 4(b) displays volume specific capacitance variation with cycle numbers. According to GCD cycle curves, the discharge time in first cycle is 61 s and finally cycle is 53 s, which displays the volume specific capacitance retention of 86.88% even after 1 000 cycles. It may be that the strong binding force between the polypyrrole particles and the CMF fibers, and there is no phenomenon in which the polypyrrole is largely detached during the electrochemical cycle. According to Fig. 4(b), volume capacitance of PPy/CMF decreases slowly with the increase of cycles, indicating the excellent cycle stability of PPy/CMF. In order to investigate compression stability of PPy/CMF, we tested its electrochemical properties under different compressions. Fig. 4(c) and Fig. 4(d) exhibit the CV and GCD curves of PPy/CMF at different compressions. According to the CV curve, there is no evident change in shapes and areas of curve at various compressions. The discharge time of PPy/CMF does not exhibit obvious change at different compressions, demonstrating the excellent compression stability of PPy/CMF. These results reveal PPy/CMF is an excellent material for compressible electrode. Volume specific capacitance variation with compressions (as shown in Fig. 4(e)) further illustrates the compression stability of PPy/CMF. Fig. 4(f) presents Nyquist plot of PPy/CMF, according to previous literature reports, the internal resistance (Rs) containing active material and electrolyte resistance as well as contact resistance between the surface of active material and current collector can be revealed by the real axis intercept in the high frequency region[21-23]. The semicircle in the high frequency region can attribute to the charge transfer resistance, which is associated with the rate performance of acquired elastic material. The straight line slope at low frequency region is corresponds to the ion diffusion resistance during electrochemical testing.

4 Comparison

Compressible supercapacitors based on carbon nanotube sponges, graphene aerogels and melamine

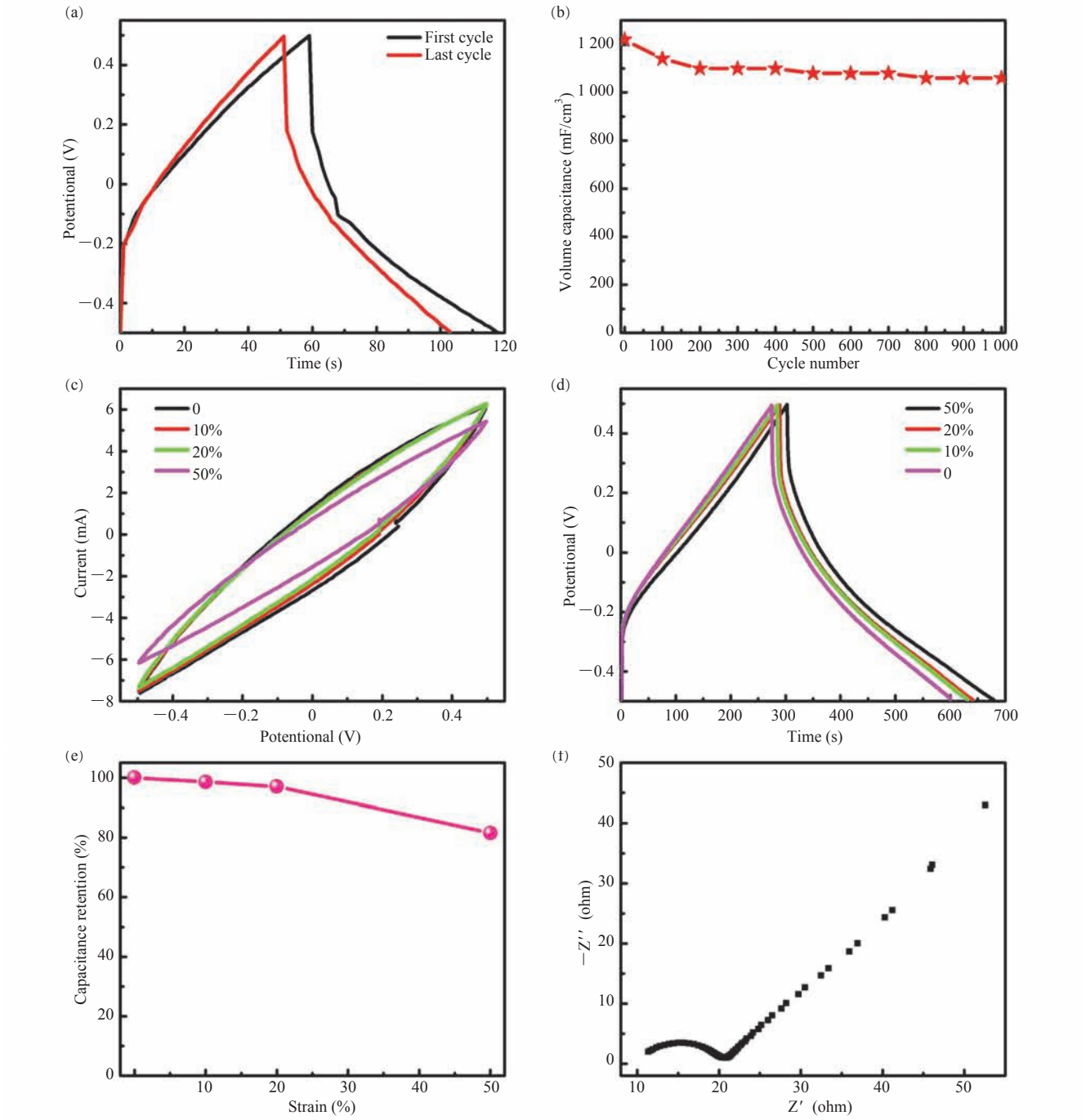

Fig. 4 (a) GCD curves of PPy/CMF before and after 1 000 cycles at 20 mA/cm^3; (b) volume specific capacitance variation with cycle numbers; (c) CV curves of PPy/CMF with different compressions at 100 mv/s; (d) GCD curves of PPy/CMF with different compressions at 10 mA/cm^3; (e) volume specific capacitance variation with compressions; (f) Nyquist plot of PPy/CMF

foam have been investigated by many researchers. However, the mechanical and electrochemical properties of the electrode material cannot be taken into account at the same time, hindering the rapid development of compressible supercapacitors. Melamine foam has been used as substrate for preparing compressible supercapacitor electrode material, which electrochemical performance is a

major obstacle to its application in compressible supercapacitors[6-7]. In this work, we report an electrode material based on melamine foam, which electrochemical performance was improved by depositing a uniform layer of polypyrrole electrochemically active material on the surface of CMF. The electrochemical properties of electrode materials have improved compared to other foam-based electrode materials, however, their cycle stability needs to be further improved.

5 Conclusion

A compressible electrode based on commercial melamine foam was successfully prepared by high temperature carbonization and *in-situ* polymerization. We performed the electrochemical performance and compression stability of PPy/CMF electrode. Its volume capacitance can reach 3 168 mF/cm^3 at 2 mA/cm^3. PPy/CMF exhibits a volumetric capacitance retention of 86.88% even after 1 000 GCD cycles. Furthermore, the compression stability was tested at different compressions, its CV and GCD curves have no significant change at different compressions, which indicates that PPy/CMF displays high compression stability. These results demonstrate that PPy/CMF is an excellent electrode for compressible supercapacitor.

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