

Short Communication

Very High Pressure Synthesis – An Effective Way to Enhance the Capacitance and Rate Performance of Polypyrrole Films

Dawei Gu, Hongshun Sun, Pengwei Yin, Wenbo, Yuan, Jishu Li, Linjiang Shen*

School of Science, Nanjing Tech University, Nanjing 211800, P. R. China

*E-mail: ljshe@njtech.edu.cn

Received: 26 December 2014 / Accepted: 22 January 2015 / Published: 24 February 2015

Very high pressure (VHP) was employed to synthesize polypyrrole (Ppy) films. We observed high specific capacitance, excellent rate performance, and report the specific energy for Ppy films in supercapacitor electrodes. The Ppy film electrode synthesized under the VHP of 500 MPa exhibited high specific capacitance (526 F/g) at a scan rate of 2 mV/s. This specific capacitance was about two times higher than that was observed with electrodes prepared under ambient pressure in an acidic electrolyte. With an extremely high current density of 8 A/g, a specific energy of 109.8 Wh/kg was obtained for a Ppy film electrode synthesized under the VHP of 500 MPa. In addition, Ppy film electrodes prepared under the VHP of 500 MPa demonstrated cycling stability after 1000 charge-discharge cycles (potential window of -0.2 ~ 0.8 V, current density of 8 A/g) with 74.6 % retention of the initial capacitance. The stability of VHP-synthesized PPy film electrodes is superior to that of Ppy film electrodes prepared under ambient conditions.

Keywords: Very high pressure synthesis; Polypyrrole; Supercapacitor; Rate performance; Cycling stability

1. INTRODUCTION

Supercapacitors have been intensely investigated due to their ability to store energy through either electric double-layer capacitance (EDLC) or pseudocapacitance arising from fast reversible redox reactions.[1] The electrode material mainly determines the performance of a supercapacitor. Various electrode materials including porous or nanostructured carbon, transition metal-oxides and conducting polymers have been used.[2,3] Much attention has been focused on conducting polymers, such as polypyrrole (Ppy) and polyaniline (Pani), because of their low cost compared to noble metal oxides, their high charge density compared to active carbon, and their relatively simple synthesis and modification.[4] In the case of Ppy, many researchers have enhanced the properties of Ppy electrode

materials via chemical or electrochemical processes. Several novel technologies have been applied to the classical synthesis process: Tamm et al. employed simple redoping to enhance the redox capacity of Ppy films,[5] Sharma et al. obtained a Ppy film with specific capacitance of 400 F/g through pulsed polymerization,[6] Shinde et al. reported that a Ppy electrode, prepared by a simple chemical deposition, has an excellent electrochemical performance measured at low scan rate (5 mV/s).[7] In view of the existing literature, the properties of a supercapacitor can be improved by enhancing the specific surface area and the electrical conductivity of the electrode material.

We polymerized Ppy films in situ on substrates of Ta foil under very high pressure (VHP). This process was previously used to prepare high quality polyaniline films.[8-10] The introduction of VHP in the Ppy film polymerization process greatly improves the specific capacitance and rate performance of the electrode. The Ppy electrodes synthesized under a VHP of 500 MPa exhibit a high specific capacitance (526 F/g), about two times greater than those prepared under ambient pressure in an acidic electrolyte. It is important to note that electrodes of Ppy film synthesized at 500 MPa show a specific capacitance of 526 F/g at a scan rate of 2 mV/s. This is approximately two times greater than that of a Ppy film electrode prepared under ambient pressure. A surprising specific energy of 109.8 Wh/kg was obtained when this parameter was measured at an extremely high current density of 8 A/g.

2. EXPERIMENTAL

Synthesis of Ppy films under VHP was similar to the synthesis of Pani films as described previously.[8] Fig. 1 shows a schematic representation of the VHP synthesis method used to prepare the PPy material in thin film form. Briefly, pyrrole (35 μ L) and iron (III) chloride hexahydrate (0.311 g) were first dissolved in hydrochloric acid (50 mL, 0.1 M) to form a homogeneous solution. A 5.0mL volume of this solution was then added into the high-pressure reaction vessel. Subsequently, a well-cleaned square Ta foil substrate (1cm \times 1cm) was vertically immersed in the reaction solution. Finally, high pressure, introduced with a piston, was continually applied to the reaction vessel for 60 min. During the polymerization, the temperature of the reaction vessel was controlled between 0 and 5 $^{\circ}$ C. Upon completion of synthesis, the Ppy film that was deposited on the Ta substrate was washed with deionized water and dried at 25 $^{\circ}$ C for 12 h in a vacuum.

Micromorphology of Ppy films was observed by means of atomic force microscopy (AFM) with a CSPM5500 Scanning Probe Microscope (Beijing Nano-Instruments LLC, China.) and the electrical conductivity of Ppy samples was measured using a 2602 SYSTEM SourceMeter (Keithley Instruments Inc., United States).

Electrochemical measurements were carried out in a conventional three electrode cell setup: Ta foil substrate loaded with Ppy film was the working electrode, platinum was the counter electrode, Ag/AgCl with saturated KCl solution was the reference electrode, and H₂SO₄ solution (0.5 M) was the electrolyte. The cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) were performed on a ZENNIUM Electrochemical Workstation (ZAHNER-Elektrik GmbH & Co. KG. Germany). The potential range for CV and GCD measurements was from - 0.2 to 0.8 V.

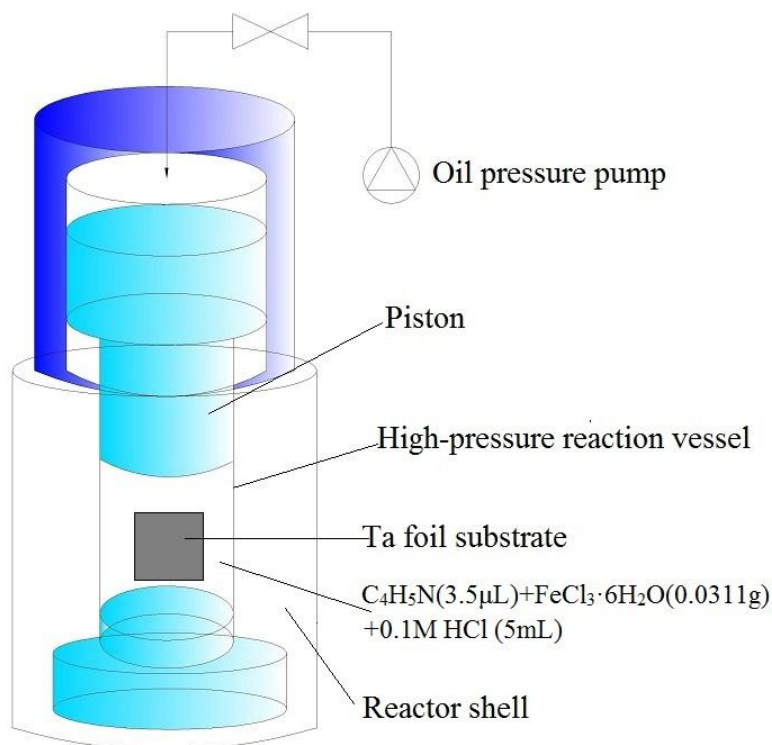


Figure 1. Schematic representation of the experimental VHP synthesis set up used to prepare Ppy thin films.

3. RESULTS AND DISCUSSION

AFM was used to provide information about the polymer's morphology. AFM images of Ppy films deposited onto Ta foil under different reaction pressures, obtained in contact mode, are shown in Fig. 2 (a-f). The micrographs show that the surface morphology of Ppy films prepared under different reaction pressures exhibit highly porous nanoparticle features. As a representative result, the nanoparticle size from samples at each reaction pressure was analyzed using Imager 4.60 Offline Software (CSPM5500 AFM analysis software, Beijing Nano-Instruments LLC, China) and plotted in Fig. 3. It is evident from these results that the nanoparticle size of the Ppy films decreased, from 49.6 nm to 38.3 nm, with increasing reaction pressure. In contrast, the electric conductivity of Ppy films improved as the reaction pressure increased, behavior that was similar to that seen with Pani films in earlier reports.[8-10] The relationship between the electrical conductivity of Ppy films and the reaction pressure is plotted in Fig. 3. With reaction pressures in the range of 500 MPa, the electrical conductivity for Ppy films increased from 8.3 S/cm to 22.1 S/cm. Ppy films synthesized at 500 MPa provide higher surface area and electrical conductivity, properties that have been shown to improve the electrochemical performance of supercapacitors.[11]

Cyclic voltammetry (CV) is an effective tool to investigate the capacitive behavior of electrode materials. To evaluate the capability of Ppy electrode materials synthesized under various reaction pressures, CV curves of above-mentioned samples have been recorded over - 0.2 V to 0.8 V versus

Ag/AgCl at various scan rates in 0.5 M H₂SO₄ aqueous electrolyte. As can be seen in Fig.4, redox peaks are present for the all the Ppy film electrodes at slow scan rate (2 - 20 mV/s). These peaks can be attributed to a pseudocapacitive mechanism and reveal a capacitive behavior for Ppy films. Remarkably, the capacitive area for the CV curves expands with an increase in reaction pressure. When the scan rate is increased to the 100 mV/s (Fig. 4(f)), CV curve of Ppy film electrode synthesized under 500 MPa still shows the relatively clear redox peaks. Furthermore, the CV enclosed area for Ppy synthesized under VHP of 500 MPa is larger than other Ppy electrodes, demonstrating a much higher capacitance. PPy synthesized under VHP of 500 MPa exhibits better electrochemical capacitive characteristic and superior reversible redox reaction than other PPy samples due to the contribution of both double layer and the pseudo-capacitance.

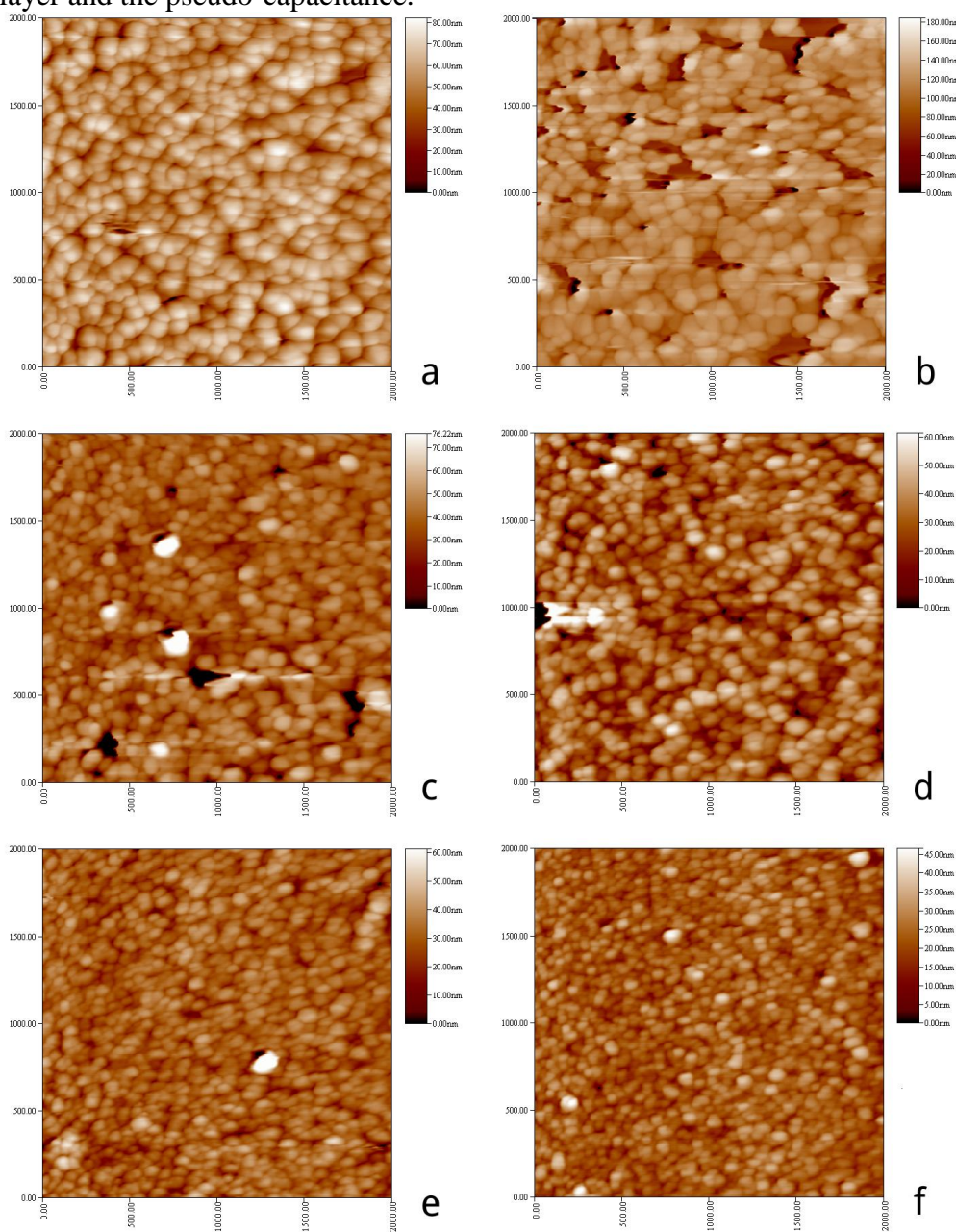


Figure 2. AFM images of Ppy films synthesized under different reaction pressures: (a) 0.1 MPa, (b) 100 MPa, (c) 200 MPa, (d) 300 MPa, (e) 400 MPa, and (f) 500 MPa, respectively.

For a quantitative comparison of the electrochemical capacitance of different Ppy films, their specific capacitance, C_s , was evaluated using CV. CV curves were analyzed using the relationship: $C_s = (2m \times \Delta V \times S)^{-1} \int idV$, Where $\int idV$ is the integrated area of a CV curve, m is the mass of active PPy material, ΔV is the potential range, and S is the scan rate, respectively.[12]

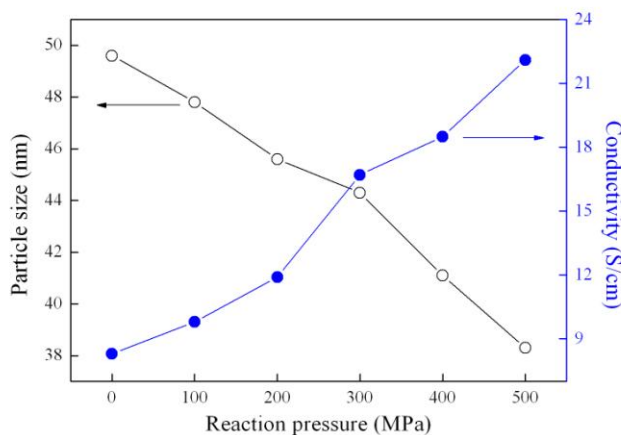


Figure 3. Influence of reaction pressure on the particle size and electrical conductivity of Ppy films.

The variation of specific capacitance with respect to the scan rate for all Ppy film electrodes is shown in Fig. 5(a). A considerable improvement in specific capacitance is observed as the reaction pressure increases regardless of scan rate. A comparison of the C_s values of different Ppy film electrodes at a scan rate of 2 mV/s shows a continuous increase in C_s from 247 F/g to 526 F/g as the reaction pressure increases from 0.1 MPa to 500 MPa (Fig. 5(a) inset). By further increasing the scan rate to 100 mV/s, the specific capacitances of these samples are still as high as 95, 97, 127, 142, 148 and 223 F/g. Generally, the specific capacitance decreases with an increase in potential scan rate. It is well accepted that this is due to the fact that electrode materials cannot sustain the redox transitions at higher scan rates.[13] The maximum specific capacitance value of 526 F/g, observed for the Ppy film synthesized at 500 MPa, is about two times larger than the maximum specific capacitance of the samples prepared at ambient pressure and distinctly higher than published reports for pure Ppy.[6,7]

The high value of specific capacitance for Ppy films can be attributed to the high surface area and electrical conductivity of nanosized Ppy as shown in Fig. 3. Both the particle size and electrical conductivity of Ppy play a crucial role in determining the ability of the electrolyte to enter and to enable local ion transfer. The smaller nanosized Ppy particles and higher electrical conductivity result in a shorter diffusion distance for ions penetrating entire particles. High surface area and electrical conductivity permit the rapid insertion/extraction of cations and anions from the interface between the electrode material and aqueous solution, even at the high scan rate of 100 mV/s. As the scan rate increased from 2 to 100 mV/s, the relative decrease in specific capacitance of the sample prepared under the VHP of 500 MPa is about 55.7%, this is in contrast to the 61.5% decrease observed for the sample synthesized at ambient reaction pressure. Hence, the higher reaction pressure used in the creation of our PPy electrode resulted in an excellent rate performance. The very high specific

capacitance at a high scan rate shows that our Ppy material, prepared under a VHP of 500 MPa, is a promising material for redox supercapacitors.

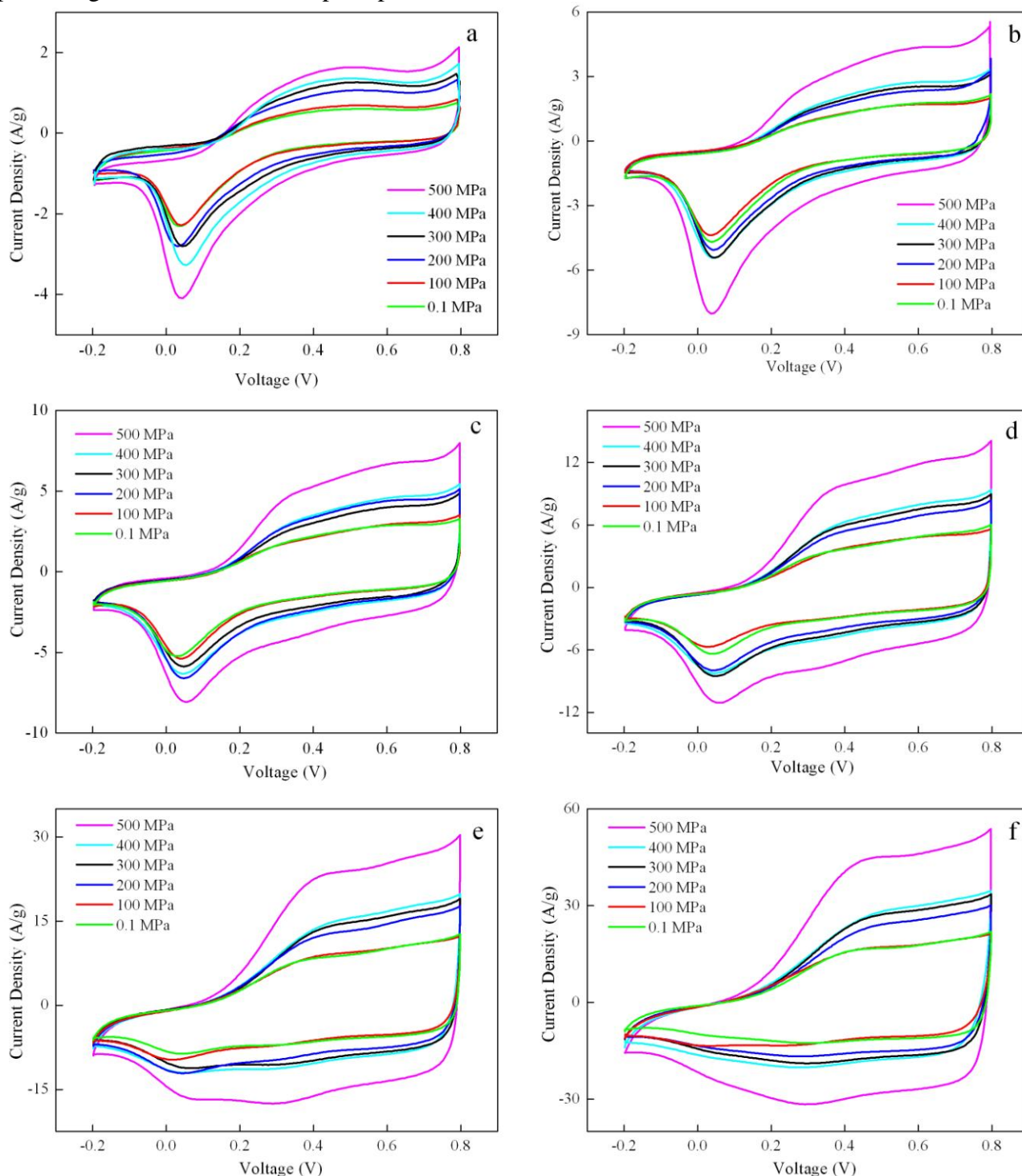


Figure 4. Typical cyclic voltammograms of Ppy electrodes synthesized under different pressures in a H₂SO₄ electrolyte (0.5 M) at different scan rate from 2 to 100 mV/s.(a) 2 mV/s, (b) 5 mV/s, (c) 10 mV/s, (d) 20 mV/s, (e) 50mV/s, (f) 100 mV/s.

The supercapacitor’s specific capacitance is also revealed by galvanostatic measurements. To evaluate the specific capacitance and rate performance of electrode materials prepared under different

pressures, galvanostatic charge/discharge measurements with a high current density of 8 A/g were carried out (Fig. 5 (b)). Based on the charge/discharge curve, the specific capacitance can be calculated according to the following equation: $C_s = I\Delta t / m\Delta V$, where I is the discharge current, Δt is the discharge time, ΔV is the voltage change during the discharge process, and m is the mass of the active material, respectively. The specific capacitance of the electrodes as a function of reaction pressure is shown in Fig. 5(b), inset. It is clear that the specific capacitance of the electrodes increases with increasing reaction pressure. The Ppy electrode synthesized at 500 MPa has a maximum discharge capacitance of 480.7 F/g at the extremely high current density of 8 A/g. This is approximately four times greater than what was observed with the Ppy electrode prepared under ambient conditions. This result is consistent with the conclusion drawn from our cyclic voltammetry measurements.

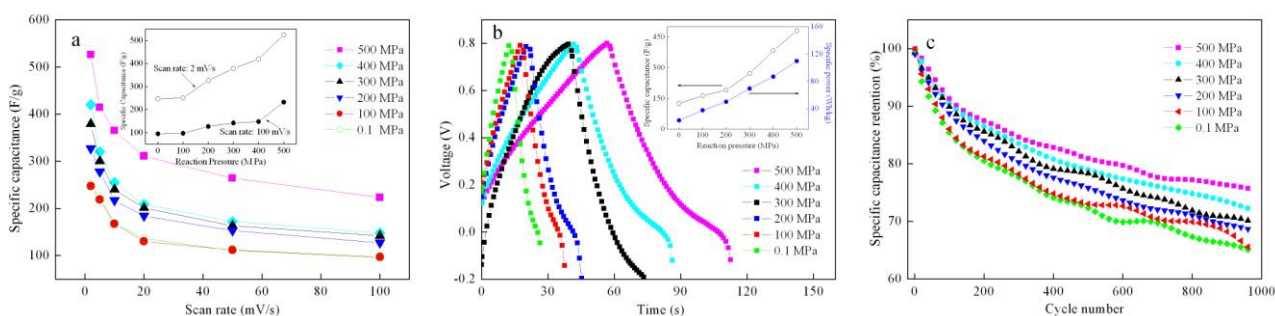


Figure 5. (a) Plot of specific capacitance vs. scan rate for Ppy electrodes synthesized at different pressures. Inset: The relationship between specific capacitance of Ppy electrodes and reaction pressure at scan rate of 2 mV/s and 100 mV/s, respectively. (b) Galvanostatic charge–discharge curves of Ppy electrodes synthesized under different pressures in a H_2SO_4 electrolyte (0.5 M) at a current density of 8 A/g. Inset: Influence of reaction pressure on the specific capacitance and specific energy of Ppy films. (c) Cyclic life analysis of different PPy film electrodes at 8 A/g in H_2SO_4 electrolyte (0.5 M).

In addition, the specific energy (SE) of Ppy films was calculated using the equation: $SE = I\Delta V\Delta t / m$, Where these parameters were introduced previously. The relationship between SE and reaction pressure at a high current density of 8 A/g is shown in Fig. 5(b), inset. The value of SE increases from 22.9 Wh/kg to 109.8 Wh/kg in the reaction pressure range of 0.1-500 MPa. In particular, the value of SE for Ppy films synthesized at 500 MPa is much higher than that previously reported. [7,14]

The cyclic stability of all the samples was evaluated by repeating the galvanostatic charge/discharge measurements at the current density of 8 A/g. As shown in Fig 5(c), after 1000 cycles, the degradation of the specific capacitance for PPy synthesized at 500 MPa was 25.4 %. In contrast, the capacity degradation of the PPy synthesized under ambient conditions was 35.6 %. This indicates that very high reaction pressure enhances the mechanical strength of the Ppy and delays the process of PPy chain destruction through the swelling and shrinking process induced by the long-term cycling.

4. CONCLUSION

We propose the use of VHP conditions during Ppy polymerization as an effective method for enhancing the capacitance, rate performance and cyclic stability of Ppy films. The smaller nanosized Ppy particles and higher electrical conductivity observed as a result of polymerization under VHP permit rapid insertion/extraction of cations and anions from aqueous solution. The results clearly show that the capacitance and rate performance of Ppy films were improved by employing very high reaction pressure during the preparation process. In particular, the Ppy film electrode synthesized at 500 MPa displays a specific capacitance of 526 F/g at a scan rate of 2 mV/s and a specific energy of 109.8 Wh/kg at a current density of 8 A/g. After 1000 cycles, the specific capacitance of Ppy films synthesized at 500 MPa is higher than the other Ppy electrodes measured. Therefore, this work presents a new and effective means of improving the performance of supercapacitor electrodes based on conducting polymers.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (No. 10774076), Universities in Jiangsu Province, China (No. 11KJB480003) and Priority Academic Program Development of Jiangsu Higher Education Institution (PAPD).

References

1. A. Kumar, R.K. Singh, H.K. Singh, P. Srivastava and R. Singh, *J. Power Sources*. 246 (2014) 800.
2. H.S. Kim, N. Branko and B.N. Popov, *J. Power Sources*. 104 (2002) 52-61.
3. J.P. Wang, Y. Xu, J. Wang and X.F. Du, *Synth. Met.* 161 (2011) 1141.
4. Y. Liu, Y. Zhang, G.H. Ma, Z. Wang, K.Y. Liu and H.T. Liu, *Electrochim. Acta*. 88 (2013) 519.
5. L.Z. Fan and J. Maier, *Electrochem Commun.* 8 (2006) 937.
6. R.K. Sharma, A.C. Rastogi and S.B. Desu, *Electrochem Commun.* 10 (2008) 268.
7. S.S. Shinde, G.S. Gund, V.S. Kumbhar, B.H. Patil and C.D. Lokhande, *Eur. Polym. J.* 49 (2013) 3734.
8. D.W. Gu, J.S. Li, J.L. Liu, Y.M. Cai and L.J. Shen, *Synth. Met.* 150 (2005) 175.
9. L.J. Shen, D.W. Gu and J.S. Li, *Synth. Met.* 155 (2005) 110.
10. J.S. Li, L.J. Shen and D.W. Gu, *React. Funct. Polym.* 66 (2006) 1319.
11. K.H. Lee, B.J. Park, D.H. Song, I.J. Chin and H.J. Choi, *Polym.* 50 (2009) 4372.
12. H. Cheng, Z.G. Lu, J.Q. Deng, C.Y. Chung, K. Zhang and Y.Y. Li, *Nano Research*. 3 (2010) 895.
13. C.C. Hu and T.W. Tsou, *Electrochem Commun.* 4 (2002) 105.
14. H.R. Ghenaatian, M.F. Mousavi and M.S. Rahmanifar, *Electrochimica Acta*. 78 (2012) 212.