Electrochemical energy storage by polyaniline nanofibers: high gravity assisted oxidative polymerization vs. rapid mixing chemical oxidative polymerization

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Polyaniline (PANI) nanofibers prepared by high gravity chemical oxidative polymerization in a rotating packed bed (RPB) have demonstrated a much higher specific capacitance of 667.6 F g\(^{-1}\) than 375.9 F g\(^{-1}\) of the nanofibers produced by a stirred tank reactor (STR) at a gravimetric current of 10 A g\(^{-1}\). Meanwhile, the cycling stability of the electrode is 62.2 and 65.9% for the nanofibers from RPB and STR after 500 cycles, respectively.

Introduction

Due to their easy production, good environmental stability, unique redox behaviors,\(^1\text{-}^3\) high conductivity, and excellent electrochemical and optical properties, intrinsically conducting polyaniline (PANI) nanostructures exhibit enhanced performances in their potential wide applications including sensors,\(^4\text{-}^6\) electrodes,\(^7\) electrochromic smart windows,\(^8\text{-}^9\) and supercapacitors\(^10\text{-}^14\) arising from their larger interfacial area.\(^15\) However, these applications have not been widely exploited due to the lack of facile and reliable methods to obtain high-quality structural PANI nanomaterials.

Among the reported methods to prepare PANI nanostructures including electrochemical oxidative polymerization,\(^20\text{-}^22\) interfacial polymerization,\(^23\text{-}^25\) rapid mixing polymerization,\(^26\) and seeding polymerization,\(^27\) chemical oxidative polymerization is the commonly used method for preparing PANI nanomaterials.\(^16\text{-}^19\) However, these methods usually require low temperature, low monomer concentration, and a long reaction time to obtain PANI nanomaterials of good morphology and performances due to the poor mixing process prior to the induction period of polymerization.\(^28\text{-}^31\) Additionally, the microwave-assisted synthesis method has the advantage of reducing the reaction time to several minutes though it merely produces micron-sized PANI,\(^32\) whereas the sonochemical synthesis technique produces PANI nanofibers of poor morphology with many irregular particles despite favoring the mixing process.\(^33\) The uniformity of mixing greatly influences the nucleation mode of polymerization and the morphologies of the subsequently formed PANI nanostructures.\(^34,35\) Reaction conditions favoring heterogeneous nucleation cause aggregation of the PANI particles as the new polyaniline molecules are deposited on the pre-formed particles. However, homogeneous nucleation resulting from sufficient mixing of raw materials prior to the induction period of polymerization ensures a continuous yield of PANI nanofibers. Unfortunately, most of the aforementioned production methods involve the usage of magnetic stirrers or agitators that have difficulty in providing sufficient mixing for the homogeneous polymerization.

A rotating packed bed (RPB), a high-gravity device, can generate an acceleration of up to 1–3 orders of magnitude larger than the gravitational acceleration on earth.\(^36,37\) It is regarded as an ideal reactor for preparing nanoparticles due to its distinctive advantages of short residence time and effective intensification of both mixing and mass transfer processes.\(^38,39\) The micromixing characteristic time (ca. 10\(^{-4}\) s) in RPB is much lower than the nucleation induction period in aqueous solutions.\(^40,41\) In addition, the high-gravity field and shear force generated in the RPB produce a uniform supersaturated solution required for the homogeneous nucleation.\(^39,42\) More importantly, the preparation process by use of RPB is easy for scale-up.\(^43\) The feasible and effective preparation of PANI nanofibers by high gravity chemical oxidative polymerization
Preparation of electrodes

The working electrode was prepared by dropping a nafion-impregnated sample onto a glassy carbon electrode. Typically, 10 mg of active material was dispersed in 1000 μL of absolute alcohol followed by the addition of 100 μL of nafion solution (0.5 wt%) and sonicated for 45 min. Finally, the working electrode was obtained by dropping 10 μL of the as-prepared suspension onto a glassy carbon electrode with a diameter of 3 mm. The electrode dried naturally at room temperature, and the loading density of PANI was 1.29 mg cm⁻².

Characterizations

The morphologies of the PANI nanofibers were characterized by scanning electron microscopy (SEM, JSM-6701F) while their molecular structures were analyzed by Fourier transform infrared spectroscopy (FTIR, Nicolet model 8700 spectrometer) with KBr pressed disks, and UV-Vis spectroscopy (UV-5200PC) using water as the solvent. X-ray diffraction (XRD) analysis was performed using a Bruker D8A X-ray diffractometer. The specific surface areas of the samples were obtained by the Brunauer–Emmett–Teller (BET) method (Quadrasorb SI) at room temperature. The conductivities of the samples were measured using a four-probe technique on a digital multimeter (SX1934). The samples were compressed into tablets at a pressure of 10.0 MPa on a desktop tablet pressing machine (DY-30) driven by a motor. The molecular weights of the dedoped PANI samples were measured by gel permeation chromatography (GPC, Agilent 1200 Series) at room temperature. Dimethyl formamide was used as the solvent and mobile phase (1.0 mL min⁻¹) and the system was calibrated with polystyrene standards. The electrochemical performances of the as-prepared electrodes were tested by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), electrochemical impedance spectroscopy (EIS) and cycling stability using a VersaSTAT 4 electrochemical workstation. The electrolyte used was a 1.0 M H₂SO₄ aqueous solution. A platinum wire and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. EIS was carried out in the frequency range from 100 kHz to 0.01 Hz at an amplitude of 5 mV referring to the open circuit potential. All the characterizations were carried out at room temperature in air.

Calculations

The specific capacitance of PANI was calculated from the CV and GCD curves according to eqn (1) and (2):

\[
C_m = \frac{\int I dV}{m V} \tag{1}
\]

where \(C_m\) is the specific capacitance based on the mass of electro-active materials in F g⁻¹, \(I\) is the response current in A, \(V\) is the scanned potential window in V, \(v\) is the potential scan rate in V s⁻¹, and \(m\) is the mass of the active materials on the electrode in g.

\[
C_m = \frac{(I \times \Delta t)}{(m \times V)} \tag{2}
\]

where \(C_m\) is the specific capacitance in F g⁻¹, \(I\) is the discharge current in A, \(\Delta t\) is the discharge time in s, \(m\) is the mass of the active materials in the electrode in g, and \(V\) is the potential window (excluding the IR drop at the beginning of the discharge process) in V.

Results and discussion

Fig. 2 shows the SEM images of RPB-PANI and STR-PANI. It is evident that RPB-PANI have uniform morphology [Fig. 2A] with a diameter of about 30–50 nm and length of 1 μm, while most of the STR-PANI [Fig. 2B] show rod-like structure (50–100 nm in diameter and 0.5 μm in length). The formation of PANI nanofibers is as a result of homogeneous nucleation while the irregular PANI is due to heterogeneous nucleation. Therefore, the rapid mixing polymerization could not ensure sufficient...
mixing at such high aniline concentration. To prove this, PANI was also prepared at a low aniline concentration of 0.025 M in a RPB and a STR, respectively, and their reaction processes are shown in Fig. 3. Compared with the STR, the RPB obviously not only promoted the reaction, but also mixed the reactants more efficiently. The specific surface area was found to be 49.1 and 38.9 m² g⁻¹ for RPB-PANI and STR-PANI, respectively, showing that the nanofibers possess higher specific surface area than the rod-like structure.

The composition of the as-prepared PANI nanofibers was studied by FTIR and UV-Vis spectroscopy. Fig. 4(A) shows the FTIR spectra of PANI nanofibers. Both nanofibers show nearly identical peaks. The main characteristic peaks of PANI located at 1563 and 1484 cm⁻¹ are assigned to the C—C stretching vibration of quinoid rings and benzene rings, respectively. Other peaks located at 3438, 1298, 1128, and 799 cm⁻¹ are due to the N—H stretching vibration, C—N stretching mode, N—Q—N stretching mode (with Q representing the quinoid ring), and C—H bonds of benzene rings, respectively. The UV-Vis spectra of these two samples are shown in Fig. 4(B). It is evident that both have similar characteristic peaks. The peaks of PANI located at 352, 442, and 850 nm are attributed to the π—π* transition of the benzenoid rings, polaron—π*, and π—polaron transitions, respectively. The strong peak centered at ca. 850 nm confirms the formation of doped PANI (i.e., emeraldine salt). Fig. 4(C) shows the XRD patterns of the PANI nanofibers prepared in RPB and STR. Four characteristic peaks located at 2θ = 9.2, 15.3, 20.7, and 25.1° are identified, further illustrating that the products are in highly doped emeraldine salt form. No significant difference is observed in the intensities of both RPB-PANI and STR-PANI, indicating that both processes yielded fibers of the same crystallinity.

The molecular weights of RPB-PANI and STR-PANI are shown in Table 1. Both samples are observed to have similar molecular weight (ca. 10 000 g mol⁻¹). However, the polydispersity of STR-PANI is slightly lower than that of RPB-PANI, indicating that STR-PANI has a narrower molecular weight distribution. Overall, the difference between these two samples in the molecular weight is quite small.

The electrochemical performances of PANI nanofibers were evaluated by CV, GCD and EIS in a three-electrode system. The CV curves of both RPB-PANI and STR-PANI (Fig. 5A and B) exhibit three pairs of redox peaks, indicating the existence of pseudocapacitance. Also, the area of the CV curve of the RPB-PANI is larger than that of STR-PANI, indicating that STR-PANI has a narrower molecular weight distribution. Overall, the difference between these two samples in the molecular weight is quite small.

The specific capacitances of both samples decrease upon increasing the scan rate, and the specific capacitance of RPB-PANI is always larger than that of STR-PANI. The rate capacity of RPB-PANI and STR-PANI is 60.8% and 69%, respectively. Fig. 5D shows the GCD curves of the two samples at a gravimetric current of 10 A g⁻¹. Both RPB-PANI and STR-PANI show nearly symmetric charge–discharge curves. The IR drop of RPB-PANI (0.087 V) is lower than that of STR-PANI (0.112 V), indicating that the internal resistance of the PANI nanofibers is greatly reduced when RPB is used for their preparation. Moreover, the measured conductivity of RPB-PANI and STR-PANI being 108.1 and 93.8 S m⁻¹ by the four-probe method is consistent with the result of IR drop. Based on the GCD curves

<table>
<thead>
<tr>
<th>Samples</th>
<th>$M_m$ (g mol⁻¹)</th>
<th>$M_n$ (g mol⁻¹)</th>
<th>Polydispersity ($M_w/M_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPB-PANI</td>
<td>11 918</td>
<td>9573.6</td>
<td>1.24</td>
</tr>
<tr>
<td>STR-PANI</td>
<td>11 884</td>
<td>10 248</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Table 1 Molecular weight of the PANI nanofibers
of the electrodes, the specific capacitance of RPB-PANI and STR-PANI was 667.6 F g⁻¹ and 375.9 F g⁻¹, respectively, which agrees well with that deduced from the CV tests. The higher specific capacitance of RPB-PANI is ascribed to the low internal resistance, good conductivity and high specific surface, which could speed up the electrochemical reaction by increasing the speed of charge-transfer and electrode/electrolyte contact area.⁵²⁻⁵⁵

The cycling stability test of the two PANI nanofibers is presented in Fig. 5E. It is clear that the cycling stability of RPB-PANI (62.2%) is a little lower than that of STR-PANI (65.9%), consistent with the result of Fig. 5C. The reduction in the specific capacitance is due to the swelling and shrinkage of PANI during the charge–discharge process.⁵⁶⁻⁵⁸ Although the specific capacitance retention of PANI (62.2%) is not ideal, it is still much larger than most of the retention abilities of the PANI nanostructures reported by other synthetic methods.⁵⁹⁻⁶²

The Nyquist plots obtained from EIS tests are shown in Fig. 5F. From the x-intercept of the curve, the equivalent series resistance (ESR) of RPB-PANI and STR-PANI is about 5.48 and 8.95 Ω, respectively, supporting the result of the IR drop and conductivity. Furthermore, RPB-PANI shows a smaller semicircle in the high-frequency region and a larger slope in the low-frequency region as compared with those of STR-PANI. These results reveal that RPB-PANI nanofibers have better electrochemical performances because of their good electrical conductivity and ion diffusion behaviors.⁵⁸

Conclusions

In summary, PANI nanofibers were prepared by HGCOP in a RPB while a STR was used as a control experiment. The high-gravity field and shear force created in the RPB greatly intensified the mixing and mass transfer processes among the raw materials, hence ensuring homogeneous nucleation of PANI nanofibers. The morphology of RPB-PANI was uniform nanofibers while STR-PANI exhibited many irregular particles as a result of heterogeneous nucleation. The specific capacitance of RPB-PANI nanofibers was up to a maximum of 667.6 F g⁻¹ at a gravimetric current of 10 A g⁻¹ as compared to 375.9 F g⁻¹ for STR-PANI. The greatly enhanced specific capacitance was attributed to the low internal resistance, good conductivity and high specific surface of RPB-PANI nanofibers. After 500 cycles, the specific capacitance retention was decreased to 62.2% for RPB-PANI, a little lower than that of STR-PANI (65.9%). This research therefore provides a simple way to prepare PANI nanofibers with enhanced electrochemical performances.

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Notes and references
