Hexavalent chromium synthesized polyaniline nanostructures: Magnetoresistance and electrochemical energy storage behaviors

Hongbo Gu\textsuperscript{a,b,1}, Huige Wei\textsuperscript{a,c,1}, Jiang Guo\textsuperscript{a,1}, Neel Haldolaarachige\textsuperscript{d}, David P. Young\textsuperscript{d}, Suying Wei\textsuperscript{a,c,*}, Zhanhu Guo\textsuperscript{a,**}

\textsuperscript{a} Integrated Composites Laboratory (ICL), Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, TX 77710, USA
\textsuperscript{b} School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin, Heilongjiang 150001, China
\textsuperscript{c} Department of Chemistry and Biochemistry, Lamar University, Beaumont, TX 77710, USA
\textsuperscript{d} Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA 70803, USA

**Abstract**

In this work, the oxidant Cr(VI) dose was observed to have influenced the polyaniline (PANI) nanostructures as well as the crystallization structure. The temperature dependent resistivity study revealed a quasi 3-dimensional variable range hopping (VRH) electrical conduction mechanism. The permittivity was found to be affected by the PANI nanostructures. The observed positive MR at room temperature in the synthesized PANI samples was analyzed by the wave-function shrinkage model. The electrochemical energy storage was investigated using the cyclic voltammetry (CV) and galvanostatic charge–discharge measurements. The highest gravimetric capacitance of 298.5 F g\textsuperscript{-1} was obtained in the prepared PANI sample using 3 mmol K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} derived from the CV at a scan rate of 5 mV s\textsuperscript{-1} and the maximum value of gravimetric capacitance of 330.2 F g\textsuperscript{-1} was achieved in the galvanostatic charge–discharge measurements at a current density of 0.5 A g\textsuperscript{-1}. After applying an external magnetic field, the capacitance decreased due to the observed positive magnetoresistance phenomenon. The cyclic stability studies revealed that the synthesized PANI samples exhibited good durability and retained around 80% of the capacitance even after 1000 charge–discharge galvanostatic cycles.

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1. Introduction

Recently, owing to the climate change and the depletion of fossil fuels, such as oil, coal and natural gas, the design of new energy storage systems is imperatively required [1–3]. Electrochemical capacitors (ECs) have been extensively studied as the new generation of energy storage systems [4] due to the high energy and power density as well as long cycle life [5,6], which can be used in the electric vehicles and portable electronic device [7,8]. Generally, there are two types of ECs depending on the charge storage mechanisms as well as the active electrode materials [9]. One is called electrical double-layer capacitors (EDLCs), which has the high power density (power per unit volume) with long cycling life and is predominately due to the double-layer charging effects [10] arising from the electrolyte ion adsorption [11]. However, this kind of capacitor (commonly used materials are activated carbon materials with large specific surface area) has the low energy density (energy per unit volume, typically 5–10 Wh kg\textsuperscript{-1}), which limits its applications. Another one is called pseudocapacitors or supercapacitors, which is based on the Faradaic process. Pseudocapacitance is an interfacial phenomenon, which is related to the specific surface area of the electroactive materials and achieved by the charge transfer through the surface Faradaic (redox) reaction [12]. And the pseudocapacitors have higher specific capacitance than EDLCs [13].

Conducting polymers have been considered as the promising pseudocapacitor electrode materials due to their low cost, easy synthesis process, flexibility and high capacitance [14]. The commonly studied conducting polymers include polythiophenes (PTs), polypyrrole (PPy), poly(DNTD) [15,16], and polyaniline (PANI) [17,18]. Among these conducting polymers, PANI is the most investigated for supercapacitor application because of its high conductivity, good environmental stability, versatile redox behavior and high pseudocapacitance [19,20]. The specific capacitances of PANI-based electrode materials are strongly dependent on the fabrication method [21]. Generally, PANI is synthesized by chemical or electrochemical oxidation polymerization of aniline monomers.
followed by the head to tail formation mechanism [22]. The commonly and widely used oxidant for PANI in the chemical polymerization method is ammonium persulfate (APS) [23,24]. The oxidants such as ferric chloride (FeCl₃) [25], hydrogen peroxide (H₂O₂) [26], perchloric acid (HClO₄) [13], vanadic acid [27], manganese dioxide (MnO₂) [28,29], tetrachloroaurate (AuCl₄⁻) [30] and hexavalent chromium (Cr(VI)) [31] have been reported to prepare PANI as well [31]. Cr(VI) is a strong oxidant in the acidic solution due to its high redox potential (1.33 V) and can be reduced to the stable Cr(III) species [32]. Though the Cr(VI) has served as an oxidant in preparing multi-walled carbon nanotubes (MWNTs) nanocomposites [31], the Cr(VI) dose effect on the polymerization of aniline and properties including permittivity and magnetoresistance of synthesized PANI has not been reported yet together with the electrochemical capacitive properties and energy storage behavior.

In this work, different PANI nanostructures were prepared by using different doses of Cr(VI) in Cr(VI) aqueous solution. The chemical structure and crystallinity as well as the properties of PANI synthesized by different doses of Cr(VI) were studied using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and scanning electron microscope (SEM), respectively. The frequency dependent permittivity, temperature dependent resistivity and magnetic field dependent resistivity (MR) were also studied. The electrochemical performances of the synthesized PANIs for the energy storage device applications were studied using cyclic voltammetry (CV), galvanostatic charge-discharge measurements and electrochemical impedance spectroscopy (EIS) techniques. An equivalent circuit was also proposed to disclose the nature of the capacitive behavior. The effects of oxidant doses and the magnetic field on the electrochemical energy storage as well as the stability were also investigated systematically.

2. Experimental

2.1. Materials

Aniline (C₆H₇N) and p-toluene sulfonic acid (PTSA, C₇H₈O₃S) were purchased from Sigma Aldrich. Potassium dichromate (K₂Cr₂O₇) was purchased from Alfa Aesar Company. Carbon Conductive Tabs with a diameter of 6 mm, PELCO Tabs™, were provided by Ted Pella, Inc. Carbon paper — 2050-A 10 cm × 10 cm was obtained from Fuel Cell Store. All the chemicals were used as-received without any further treatment.

2.2. Synthesis of PANI by different doses of Cr(VI)

The PANI was synthesized by different doses of Cr(VI). Specifically, the PTSA (15 mmol) and K₂Cr₂O₇ (0.75, 3, 4.5 or 9 mmol) were added into 100 mL deionized water in an ice-water bath for half an hour mechanical stirring (SCILOGEX OS20-Pro LCD Digital Overhead Stirrer, 300 rpm) combined with sonication (Branson 8510). Then the aniline solution (18 mmol in 25 mL deionized water) was mixed with the above solution and mechanically stirred and sonicated continuously for additional 1 h in an ice-water bath for further polymerization. The final product was vacuum filtered and washed with deionized water. The precipitate was further washed and dried with 1 mol L⁻¹ PTSA. The final powders were dried at 60 °C in an oven overnight. The samples synthesized from different K₂Cr₂O₇ doses were named PANI-0.75, PANI-3, PANI-4.5 and PANI-9, respectively.

2.3. Preparation of PANI Electrode

About 1 mg PANI samples synthesized by different doses of Cr(VI) were weighed using microbalance (UMX2 ultra-microbalance, METTLER TOLEDO company) and pressed uniformly onto a PELCO Tabs™ carbon conductive tape with a diameter of 6 mm on a carbon paper substrate. Each sample was weighed for five times within a deviation of ±3% to obtain the average value.

2.4. Characterizations

The morphology of the synthesized PANI was observed in the JEOL JSM-6510LV SEM after coated with carbon. The FT-IR spectrometer coupled with an ATR accessory (Bruker Inc., Vector 22) was used to characterize the chemical structure of the synthesized PANI in the range of 4000—500 cm⁻¹ at a resolution of 4 cm⁻¹. The visible absorption (XRD) analysis was carried out with a Bruker AXS D8 Discover diffractometer with GADDS (General Area Detector Diffraction System) operating with a Cu-Kα radiation source filtered with a graphite monochromator (λ = 1.5406 Å). Data were collected in a range of 5—30°. Permittivity was investigated by an LCR meter (Agilent, E4980A) equipped with a dielectric test fixture (Agilent, 16451B) at the frequency of 20—2 × 10⁶ Hz at room temperature. The synthesized different PANI samples were pressed in a form of disc pellet with a diameter of 25 mm by applying a pressure of 50 MPa in a hydraulic presser and the average thickness was about 6 mm. The same sample for LCR measurement was also used to measure the resistivity (ρ) by a standard four-probe method from 100 to 290 K. The temperature dependent resistivity was used to determine the electrical conduction mechanism in the PANI-0.75 and PANI-3 samples. Magnetoresistance was carried out using a standard four-probe technique by a 9-T Physical Properties Measurement System (PPMS) by Quantum Design at room temperature. The four probes were 0.002 inch diameter platinum wires, which were attached by silver paste to the sample. And the magnetic field was applied perpendicular to the current. The UV—vis spectra were performed on a Jasco V-670 spectrophotometer. The sample was dissolved in the N-methyl-2-pyrrolidone (NMP) solution (1 mg of PANI samples diluted in 10 mL of NMP).

The electrochemical behaviors were evaluated using cyclic voltammetry (CV), galvanostatic charge—discharge measurements, and electrochemical impedance spectroscopy (EIS) techniques on an electrochemical working station VersaSTAT4 potentiostat (Princeton Applied Research). A typical electrochemical cell consisting of a reference electrode (saturated calomel electrode (SCE)), a working electrode, and a counter electrode (a platinum (Pt) wire) was employed. The CV was scanned from −0.2 to 0.8 V vs SCE at a series of scan rates in 1.0 mol L⁻¹ H₂SO₄ electrolyte aqueous solution. EIS was carried out in the frequency range from 100,000 to 0.01 Hz at an amplitude of 5 mV referring to the open circuit potential. The endurance of the composites was also assessed using galvanostatic charge-discharge measurements at a current density of 8 A g⁻¹ for 1000 cycles. The whole electrochemical cell was fixed between two magnetic poles of an electromagnet (EM4-HVA H-Yoke, Lake Shore Cryotronics, Inc., USA) to test the electrochemical property of the materials in a magnetic field [33]. The magnetic field flux density was controlled through tuning the magnitude of the current, which was measured to be 305.0 G (or Oe) by a Gauss/Tesla meter (7010 Gauss/Tesla meter, Sypris).

3. Results and discussion

3.1. Morphology, FT-IR, X-ray diffraction, UV—vis spectra

Fig. 1 shows the SEM images of the PANI-0.75, PANI-3, PANI-4.5 and PANI-9 samples. Different morphologies are observed for the PANI nanostructures fabricated by different doses of Cr(VI). The particle size of PANI increases with increasing Cr(VI) doses and the PANI becomes more ordered with increasing Cr(VI) dose.
Fig. 2 shows the FT-IR spectra of the PANI nanostructures synthesized by different doses of Cr(VI). The strong absorption peaks at 1547 and 1453 cm\(^{-1}\) for the PANI-3 sample, correspond to the C–C stretching vibration of the quinoid and benzenoid rings, respectively [34,35]. The bands at 1287 and 1235 cm\(^{-1}\) are related to the C–N stretching vibration of the benzenoid unit [36] and the C–H in-plane vibration of the quinoid rings, respectively [31]. The out-of-plane bending of C–H in the substituted benzenoid ring is reflected in the band at around 785 cm\(^{-1}\) [31]. These characteristic peaks (1547, 1453, 1287 and 1235 cm\(^{-1}\)) are also observed in the PANI-0.75 sample and prove that the PANI-3 and PANI-0.75 are the emeraldine (EB) salt form [37]. However, in the FT-IR spectra of PANI-4.5 and PANI-9 samples, the new peaks within the marked region with pink color (in web version) (around 1140-1180 cm\(^{-1}\)) appear obviously, which are assigned to the carbon–nitrogen vibration in the full oxidation form of PANI, i.e., pernigraniline (PB) form of PANI, indicating the over oxidation of PANI for the PANI-4.5 and PANI-9 samples by Cr(VI) [37].

The X-ray diffraction (XRD) is shown in Fig. 3. For all the synthesized PANI nanostructures, three obvious diffraction Gaussian shaped peaks are observed in the XRD patterns [38]. The peaks around 2\(\theta\) = 15, 20.4, and 25.4\(^{\circ}\) correspond to the (0 1 0), (1 0 0), and (1 1 0) crystallographic planes of the partially crystallized PANI [39]. The crystallinity is calculated by dividing the total area of crystalline peaks by the total area under the diffraction curve (crystalline plus amorphous peaks). % Crystallinity = (total area of crystalline peaks)/(total area of all peaks) \times 100. The obtained crystallinity for PANI-0.75, PANI-3, PANI-4.5, and PANI-9 is 48.6, 57.6, 26.1, and 57.3%, respectively. These results indicate that the dose of Cr(VI) can affect the crystallization structure of the synthesized PANI.

Fig. 4 shows the UV–vis absorption spectra of all the synthesized PANI samples. Normally, in UV–vis of PANI samples, the spectrum of EB form presents two absorption peaks, one is located around 634 nm (1.96 eV) and another one is around 320 nm (3.75 eV) [40]. The former peak is due to the exciton formation in the quinoid rings (oxidized unit), and the latter one is assigned to the \(\pi – \pi^*\) transition in the benzoid structure (reduced unit) [41]. In this work, for PANI-0.75 and PANI-3 samples, both oxidized and reduced units exist, which indicate that both PANI-0.75 and PANI-3
samples are EB form. For PANI-4.5 and PANI-9 samples, there is oxidized peak in their UV–vis spectra, however, the reduced unit peak almost disappears, which illustrates that the synthesized PANI-4.5 and PANI-9 samples are PB form. These results are consistent with the FT-IR results.

3.2. Temperature dependent resistivity, electrical conduction mechanism and magnetoresistance

The temperature dependent resistivity of PANI-0.75 and PANI-3 samples is measured from 100 to 290 K and depicted in Fig. 5(a). Generally, in the conducting polymer systems, the charge transport is due to the hopping between polaronic clusters by the dopant ions, which serve as a tunneling bridge between the neighboring chains [42]. The electrical conduction mechanism is investigated by Mott variable range hopping (VRH) approach and presented in Equation (1) [39]:

$$\sigma = \sigma_0 \exp \left[-\left(\frac{T_0}{T}\right)^{1/n+1}\right], \quad n = 1, 2, 3$$  \hspace{1cm} (1)$$

where the pre-exponential factor \(\sigma_0\) is a constant, which represents the conductivity at infinite low temperature limit, \(T\) is the Kelvin temperature, \(T_0\) is the characteristic Mott temperature and expressed as Equation (2):

$$T_0 = \frac{24}{\pi k_B N(E_F) a_0^3}$$  \hspace{1cm} (2)$$

where \(k_B\) is Boltzmann constant, the \(N(E_F)\) is the density of states at the Fermi level, and \(a_0\) is the localization length of the localized wave function of charge carriers. The \(n\) value of 3, 2 and 1 in Equation (1) represents three-, two-, and one-dimensional systems, respectively. The \(\sigma_0\) and \(T_0\) can be calculated from the intercept and the slope of the plot \(\ln(\sigma) \sim T^{-1/n+1}\) [23]. For the measured pressed disc pellet samples (PANI-0.75 and PANI-3), the temperature dependent resistivity (Fig. 5(a)) follows a linear relationship of \(\ln(\sigma)\) vs \(T^{-1/4}\). Fig. 5(b), indicating a quasi 3-dimensional \((n = 3)\) VRH hopping mechanism. The obtained \(\sigma_0\) values for PANI-0.75 and PANI-3 are 31,044.91 and 71.65, respectively. The calculated \(T_0\) values for PANI-0.75 and PANI-3 are \(2.49 \times 10^5\) and \(4.84 \times 10^5\) K, respectively. The larger \(T_0\), which means the stronger charge carrier hopping barrier [43], leads to a higher resistivity. Thus, the resistivity of PANI-0.75 is higher than that of PANI-3.

The room temperature magnetoresistance (MR) for PANI-0.75 and PANI-3 samples (the MR of the PANI-4.5 and PANI-9 samples cannot be obtained due to the insulating nature for the PB form of PANI) is calculated from MR\% = \(\Delta R/R = (R(H) - R(0))/R(0) \times 100\) (where \(R(0)\) and \(R(H)\) are the resistance at zero magnetic field and at any applied magnetic field \(H\), respectively) and shown in Fig. 6. The MR of PANI-0.75 and PANI-3 samples exhibits the positive value within the measured magnetic field range (0–9 T) and magnetic field \((H)\) dependent property. The MR value of PANI-3 increases with increasing \(H\); however, the MR value of PANI-0.75 increases as \(H\) increases to 3.5 T with a highest value of 4.70% and then decreases as \(H\) increases to 9 T (around 3.61%). Normally, the slope at low \(H\) (around 0.5 T) can reflect the sensitivity of the materials to the applied \(H\) [44]. This slope for PANI-0.75 and PANI-3 is 5.21 and 10.56, respectively, which means PANI-3 is much sensitive to the applied \(H\) than PANI-0.75. The materials with high sensitivity to the \(H\) can be used as magnetic field sensors [23].

Generally, the wave-function shrinkage model is often used to describe the positive MR value for the case when the resistivity obeys the Mott VRH law. In this model, the MR ratio \(R(H)/R(0)\) is
given in terms of the percolation parameter $\xi_c(H)$ (also known as the optimum hopping probability parameter) by Equation (3) [45]:

$$R(H,T)/R(0,T) = \exp\{[\xi_c(0)/\xi_c(HT) - 1]\}$$

(3)

where $\xi_c(0) = (T_0/T)^{1/4}$ for the 3-d Mott VRH system, $\xi_c(HT)/\xi_c(0)$ is the normalized hopping probability parameter and is a function of $H/T_c$ for the Mott VRH system, $H$ is the magnetic field, $P_c$ is the fitting parameter, which is the normalizing characteristic field and can be expressed as Equation (4) for the Mott VRH mechanism [46]:

$$P_c = 6h/\left[e\alpha_0^2\xi_c(0)\right] = 6h/\left[e\alpha_0^2(T_0/T)^{1/4}\right]$$

(4)

where $e$ is electron charge, $h$ is the reduced Planck’s constant. In the low $H$ limit, Equation (4) is simplified to Equation (5) [23]:

$$R(H,T)/R(0,T) = 1 + t_2 H^2/\left[T_0/T\right]^{1/4}$$

(5)

And MR is defined as Equation (6):

$$MR = \frac{R(H,T) - R(0,T)}{R(0,T)} = t_2 H^2/\left[T_0/T\right]^{1/4} = \frac{e^2\alpha_0^4/\left[T_0/\left(T/T_0\right)^{3/4}\right]}{H^2}$$

(6)

where the $t_2$ is predicted to be $\approx 5/2016 = 0.00248$. According to Equation (6), the localization length $\alpha_0$ for PANI-3 is calculated to be 138.43 and 101.70 nm at $H$ of 0.47 and 0.99 T, respectively. The calculated $\alpha_0$ at different $H$ for PANI-0.75 and PANI-3 samples is listed in Tables S1 and S2, respectively, and is observed to decrease with increasing $H$. Generally, the hopping probability between the localized states is related to the density of states at the Fermi level $N(E_F)$ [47]. The higher $N(E_F)$, the more hopping probability of the charge carriers is obtained [43]. The $N(E_F)$ can be calculated from Equation (7) using the calculated $\alpha_0$:

$$N(E_F) = 24/\left[\pi k_BT_0\alpha_0^3\right]$$

(7)

The calculated $N(E_F)$ for PANI-3 is $5.56 \times 10^{-32}$ and $2.20 \times 10^{-32}$ (J cm$^{-1}$)$^{-1}$ at $H$ of 0.47 and 0.99 T, respectively. The calculated $N(E_F)$ for the different $\alpha_0$ of PANI-0.75 and PANI-3 samples is listed in Tables S1 and S2, respectively, and increases with increasing $H$. The average hopping length $R_{hopp}$ can be obtained from Equation (8) by $T_0$, $T$ and $\alpha_0$ [48]:

$$R_{hopp} = (3/8)(T_0/T)^{1/4}a_0$$

(8)

The calculated $R_{hopp}$ for PANI-3 is 331.78 and 243.76 nm at $H$ of 0.47 and 0.99 T, respectively. The obtained $R_{hopp}$ for different $\alpha_0$ of PANI-0.75 and PANI-3 samples is also listed in Tables S1 and S2, respectively, and is observed to decrease with increasing $H$. Normally, the MR in the hopping system is due to the charge carrier hopping conduction arising from the contraction of the charge carrier wave function and the subsequent reduced average hopping length [23].

### 3.3. Permittivity

The dielectric materials can be used for storing the electrical energy via charge separation when the electron distributions around constituent atoms or molecules are polarized upon an applied external electric field [49]. Recently, polymer and polymer nanocomposites dielectric materials are intensively used for the energy storage [48,49]. Thus, it’s important to investigate the dielectric property of the synthesized PANI samples. Fig. 7 shows the real permittivity ($\varepsilon’$), imaginary permittivity ($\varepsilon”$) and dielectric loss tangent ($\tan\delta$), where $\tan\delta = \varepsilon”/\varepsilon’$ as a function of frequency range for room temperature for PANI-0.75, PANI-3, PANI-4.5, and PANI-9 samples. In Fig. 7(A), the $\varepsilon’$ for all the PANI nanostructure samples shows the positive values and decreases with increasing frequency within the measured frequency range of 20–2 × 10$^6$ Hz. PANI-3 sample shows the highest $\varepsilon’$ with a value of 2.03 × 10$^5$ at a frequency of 20 Hz and 3.50 × 10$^5$ at a frequency of 2 × 10$^6$ Hz. Fig. 7(A)-b. The value of $\varepsilon’$ for PANI-0.75 changes from 4.88 × 10$^4$ at a frequency of 20 Hz to 77.85 at a frequency of 2 × 10$^6$ Hz, Fig. 7(A)-a. PANI-4.5 (Fig. 7(A)-c) and PANI-9 (Fig. 7(A)-d) samples show the lowest $\varepsilon’$ values (from 80.19 to 61.0 and 36.14 to 4.96 within the frequency range of 20–2 × 10$^6$ Hz, respectively) and the $\varepsilon’$ of PANI-4.5 is higher than that of PANI-9. These results indicate that the different nanostructures can affect the permittivity of PANI. The frequency dependent permittivity behavior arises from the interfacial polarization, where the charge carriers are accumulated at the internal interfaces arising from the Maxwell–Wagner–Sillars polarization effect [23]. Fig. 7(B) shows the $\varepsilon”$ of PANI-0.75, PANI-3, PANI-4.5, and PANI-9, respectively. The $\varepsilon”$ value of all the synthesized PANI samples also shows the frequency dependent property and decreases with increasing frequency at frequency range from 20 to 2 × 10$^6$ Hz. For the PANI-3 sample, Fig. 7(B)-b, the $\varepsilon”$ value shows the highest value of 2.02 × 10$^4$ at frequency of 20 Hz and 291.19 at frequency of 2 × 10$^6$ Hz. The $\varepsilon”$ of PANI-0.75 is from 6.40 × 10$^5$ (20 Hz) to 85.86 (2 × 10$^6$ Hz), Fig. 7(B)-a. PANI-4.5 sample changes the $\varepsilon”$ value from 376.48 (20 Hz) to 0.99 (2 × 10$^6$ Hz), Fig. 7(B)-c. PANI-9 shows the lowest $\varepsilon”$ value of 236.07 at frequency of 20 Hz to 0.72 Hz at frequency of 2 × 10$^6$ Hz, Fig. 7(B)-d.

Fig. 7(C) shows the frequency dependent $\tan\delta$ from 20 to 2 × 10$^6$ Hz for different nanostructures of PANI. Interestingly, the $\tan\delta$ for PANI-0.75 (Fig. 7(C)-a) and PANI-3 (Fig. 7(C)-b) increases to certain frequency (10$^2$ and 10$^3$ Hz for PANI-0.75 and PANI-3 samples, respectively) and then reaches a peak value, after that the $\tan\delta$ decreases with increasing frequency. The appearance of the peak in the $\tan\delta$ is due to the resonance effect, in which the system tends to oscillate with greater amplitude than others at certain frequencies [43]. The $\tan\delta$ of PANI-0.75 shows the highest value from 1.31 × 10$^2$ (20 Hz) to 1.11 (2 × 10$^6$ Hz). PANI-3 sample shows the lower value of 99.29 (20 Hz) to 0.83 (2 × 10$^6$ Hz). However, the $\tan\delta$ of PANI-4.5 and PANI-9 samples decreases with increasing frequency and has much lower values (from 4.70 at 20 Hz to 0.16 at 2 × 10$^6$ Hz and 6.53 at 20 Hz to 0.14 at 2 × 10$^6$ Hz, respectively) than that of PANI-0.75 and PANI-3 samples. The materials with low...
energy loss have the potential application in the microelectronic devices [31].

3.4. Electrochemical properties

3.4.1. Cyclic voltammetry (CV)

The CV was studied using the classical three electrode method in 1.0 mol L\(^{-1}\) H\(_2\)SO\(_4\) aqueous electrolyte solution to measure the capacitance of the synthesized PANI samples. The specific capacitance of the samples can be calculated from CV curves at different scan rates from −0.2 to 0.8 V (vs SCE) using Equation (9):

\[
C_s = \frac{\int idV}{2 \times m \times \Delta V \times S}
\]

where \(C_s\) is the specific gravimetric capacitance in F g\(^{-1}\), \(\int idV\) is the integrated area of the CV curve, \(m\) is the mass of the active materials in the single electrode in g, \(\Delta V\) is the scanned potential window in V, and \(S\) is the scan rate in V s\(^{-1}\).

Fig. 8 (left) shows the CV curves of PANI-0.75, PANI-3, PANI-4.5, and PANI-9 samples at a voltage sweeping rate of 5, 10, 20, 50, and 100 mV s\(^{-1}\). PANI-3 sample exhibits three well defined redox peaks, i.e., A/A', B/B', and C/C', indicating the typical pseudocapacitance character of the PANI [50]. A/A' and C/C' are due to the transition from leucoemeraldine salt (LS) to emeraldine salt (ES) and ES to pernigraniline salt (PS), respectively [51]. B/B' is correlated to a two-dimensional polymer with phenazine rings formed by a cross-linking reaction between PANI chains or the insertion of nitrenium cations of aniline [52]. This cross-linking reaction results in an interruption in the delocalization of both the charges and electrons along the PANI chains [52]. These characteristic redox peaks are not obvious in PANI-0.75 sample, however, they can be observed in the PB form of PANI-4.5 and PANI-9 samples. Fig. 8 (right) shows the corresponding \(C_s\) calculated from Equation (9). The \(C_s\) is observed to decrease with increasing potential scan rate from 5 to 100 mV s\(^{-1}\) [53]. The drop in the \(C_s\) with increasing scan rate is attributed to the slow ion diffusion [8]. At the high scan rate, the electrolyte ions on the surface of electrode decrease dramatically with increasing the scan rate, while the slow diffusion of the ions in the electrolyte is hard to complement the ions required near the interface between electrolyte and electrode during charge–discharge process [54]. The PANI-0.75 sample shows the highest \(C_s\) of 298.5 F g\(^{-1}\) at a scan rate of 5 mV s\(^{-1}\). This value is even higher than the reported 260 F g\(^{-1}\) for the hybrid supercapacitors consisting of polyaniline and activated carbon even though the scan rate is little bit higher, 10 mV s\(^{-1}\) [55]. The \(C_s\) for the synthesized PANI samples at a scan rate of 5 mV s\(^{-1}\) obeys the following relationships: PANI-0.75 (298.5 F g\(^{-1}\)) > PANI-4.5 (193.7 F g\(^{-1}\)) > PANI-3 (188.2 F g\(^{-1}\)) > PANI-9 (115.9 F g\(^{-1}\)). Even the PANI-4.5 is in the PB form, which is insulating in nature, it was reduced to the conductive EB salt form during the CV scan. Meanwhile, as aforementioned in XRD part, the crystallinity of PANI-4.5 (26.1%) is lower than that of PANI-3 (57.6%), the ions can easily diffuse from the electrolyte to the electrolyte/electrode interface [56], which leads to an increased capacitance compared with PANI-3. However, for the PANI-9 sample, the conductivity is too low due to the over oxidization by Cr(VI), the efficiency charge transport within the material is impeded, resulting in a decreased \(C_s\).

3.4.2. Galvanostatic charge–discharge measurement

The galvanostatic charge–discharge measurement has been performed by chronopotentiometry (CP) on the PANI-0.75, PANI-3, PANI-4.5, and PANI-9 in the 1.0 mol L\(^{-1}\) H\(_2\)SO\(_4\) electrolyte to evaluate the electrochemical performance of the samples using Equation (10) [57]:

\[
C_s = \frac{(i \times t)/(m \times \Delta V)}
\]

where \(C_s\) is the specific gravimetric capacitance (F g\(^{-1}\)), \(i\) is the discharge current (A), \(t\) is the discharge time (s), \(m\) is the mass of the materials in the single electrode (g), and \(\Delta V\) is the scanned potential window (V) (excluding the IR drop at the beginning of the discharge process). Fig. 9 shows the potential responses of the
synthesized PANI samples under different current densities on the left and the corresponding calculated $C_s$ according to Equation (10) at different current densities on the right. It's observed that the $C_s$ has the current density dependent property and decreases with increasing current density, which is due to the comparatively slow rate of redox reactions and the slow ion diffusion at high current densities [58]. The PANI-0.75 sample also shows the maximum $C_s$ with a value of 330.2 F g\(^{-1}\) at a current density of 0.5 A g\(^{-1}\), which is found to be much higher than that for the pure PANI even at lower current density of 0.2 A g\(^{-1}\) (216 or 298 F g\(^{-1}\)) [59,60]. The $C_s$ for the synthesized samples at a current density of 0.5 A g\(^{-1}\) shows the following relationships: PANI-0.75 (330.2 F g\(^{-1}\)) > PANI-4.5 (240.1 F g\(^{-1}\)) > PANI-3 (174.2 F g\(^{-1}\)) > PANI-9 (119.1 F g\(^{-1}\)), which is consistent with the results obtained from the CV curves. All the obtained $C_s$ values of the synthesized PANI samples at different current densities are listed in Table 1.
Fig. 9. Charge–discharge curve (left) and current density dependent areal capacitance (right) of (a) PANI-0.75, (b) PANI-3, (c) PANI-4.5, and (d) PANI-9.
Equations (11) and (12) are also listed in Table 1 and the plot of density of 24.1 Wh kg$^{-1}$ is comparable to the results reported in the literature (an energy density of 38.4 Wh kg$^{-1}$ at a power density of 399 W kg$^{-1}$ for pure PANI) [5]. PANI-9 has the lowest values of $E$ and $P$. The $E$ and $P$ values for the PANI-3 and PANI-4.5 samples are close to each other, only have a small difference. This is due to the different crystallization structures and conductivity of the PANI-3 and PANI-4.5. As aforementioned, PANI-3 is ES form of PANI and has a good conductivity, but higher crystallinity (57.6%). However, PANI-4.5 is PB form and insulating in nature, but lower crystallinity (26.1%). These differences may lead to the little difference in $C_i$ and discharge time, thus, similar $E$ and $P$ are obtained.

### 3.4.3. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a powerful technique to explore the phenomenon occurred at the electrode/electrolyte interfaces [62]. In EIS, the Nyquist plot (imaginary impedance, $Z_{im}$, vs real impedance, $Z_{re}$) is obtained, in which the specific information regarding the charge transfer resistance (i.e., the resistance to the charge transfer of the Faradaic process, $R_{ct}$) [63] and the equivalent series resistances (ESR, $R_{e}$, which includes the active and interfacial layer resistance, the electrode resistance, and various contact and interconnect resistances [ESR, $R_{e}$]) can be obtained. Generally, there are three types of Nyquist plots: (1) a semicircle, standing for the charge-transfer-limited process [65]; (2) a straight line, representing the diffusion-limited process [66]; (3) a semicircle at high frequency region accompanied by a straight line at low frequency region. Fig. 11 depicts the obtained Nyquist plots for the PANI-0.75, PANI-3, PANI-4.5, and PANI-9 samples. The Nyquist plots for all the synthesized PANI samples show the small semicircle at the high frequency region accompanied by a straight line at the low frequency region. Normally, for the semicircle Nyquist plot, the $R_{e}$ represents the high-frequency intercept and $R_{ct} + R_{e}$ is the low-frequency intercept on the $Z_{re}$ axis [62]. Thus, the diameter of the semicircle can reflect the $R_{e}$ value. A bigger diameter corresponds to a larger $R_{e}$ [67]. Thus, according to the results obtained in Fig. 11, the $R_{e}$ follows the relationships: PANI-0.75 $>$ PANI-3 $>$ PANI-4.5 $>$ PANI-9 and $R_{ct}$ obeys the following relationships: PANI-0.75 $<$ PANI-3 $<$ PANI-4.5 $<$ PANI-9. The higher the $R_{ct}$, the higher the charge transfer resistance, leading to a lower capacitance [68]. Generally, a capacitance element corresponds to a $90^\circ$ line, and a Warburg resistance element corresponds to a $45^\circ$ line [69]. The angle estimated from the value of $|\Delta Z_{im}|/|\Delta Z_{re}|$ in the low frequency region is 80.70, 90.00, 72.09, and 68.53° for PANI-0.75, PANI-3, PANI-4.5, and PANI-9 samples, respectively, which also indicates different ion diffusion rates.

![Fig. 10. Ragone plots of PANI-0.75, PANI-3, PANI-4.5, and PANI-9.](image1)

![Fig. 11. Nyquist plots of PANI-0.75, PANI-3, PANI-4.5, and PANI-9 samples.](image2)

**Table 1**

<table>
<thead>
<tr>
<th>Current density (A g$^{-1}$)</th>
<th>PANI-0.75</th>
<th>PANI-3</th>
<th>PANI-4.5</th>
<th>PANI-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ (Wh kg$^{-1}$)</td>
<td>140</td>
<td>5.3</td>
<td>6.1</td>
<td>1.1</td>
</tr>
<tr>
<td>$P$ (W kg$^{-1}$)</td>
<td>1840.3</td>
<td>2244.3</td>
<td>2194.5</td>
<td>1953.7</td>
</tr>
<tr>
<td>$C_i$ (F g$^{-1}$)</td>
<td>186.1</td>
<td>47.0</td>
<td>56.8</td>
<td>12.9</td>
</tr>
<tr>
<td>$E$ (Wh kg$^{-1}$)</td>
<td>23.5</td>
<td>11.5</td>
<td>10.2</td>
<td>3.0</td>
</tr>
<tr>
<td>$P$ (W kg$^{-1}$)</td>
<td>1211.8</td>
<td>1321.8</td>
<td>1210.0</td>
<td>1204.4</td>
</tr>
<tr>
<td>$C_i$ (F g$^{-1}$)</td>
<td>259.2</td>
<td>106.2</td>
<td>113.1</td>
<td>33.4</td>
</tr>
<tr>
<td>$E$ (Wh kg$^{-1}$)</td>
<td>28.6</td>
<td>15.8</td>
<td>15.2</td>
<td>5.9</td>
</tr>
<tr>
<td>$P$ (W kg$^{-1}$)</td>
<td>837.9</td>
<td>904.2</td>
<td>894.1</td>
<td>865.8</td>
</tr>
<tr>
<td>$C_i$ (F g$^{-1}$)</td>
<td>293.8</td>
<td>138.7</td>
<td>136.9</td>
<td>56.4</td>
</tr>
<tr>
<td>$E$ (Wh kg$^{-1}$)</td>
<td>34.6</td>
<td>20.0</td>
<td>20.2</td>
<td>9.1</td>
</tr>
<tr>
<td>$P$ (W kg$^{-1}$)</td>
<td>435.8</td>
<td>457.6</td>
<td>424.2</td>
<td>418.0</td>
</tr>
<tr>
<td>$C_i$ (F g$^{-1}$)</td>
<td>328.1</td>
<td>172.2</td>
<td>202.8</td>
<td>93.9</td>
</tr>
<tr>
<td>$E$ (Wh kg$^{-1}$)</td>
<td>38.4</td>
<td>19.9</td>
<td>25.9</td>
<td>12.3</td>
</tr>
<tr>
<td>$P$ (W kg$^{-1}$)</td>
<td>228.7</td>
<td>226.7</td>
<td>220.2</td>
<td>215.9</td>
</tr>
<tr>
<td>$C_i$ (F g$^{-1}$)</td>
<td>330.2</td>
<td>174.2</td>
<td>240.1</td>
<td>119.1</td>
</tr>
</tbody>
</table>

The specific energy density ($E$) and the specific power density ($P$) are obtained from Equations (11) and (12) [61]:

$$E = \frac{1}{3.6} \frac{C_i \Delta V^2}{t}$$

$$P = \frac{3600E}{t}$$

where $E$ is the specific energy density (Wh kg$^{-1}$), $P$ is the specific power density (W kg$^{-1}$), $C_i$ is the specific gravimetric capacitance (F g$^{-1}$), $\Delta V$ is the scanned potential window (V) (excluding the IR drop at the beginning of the discharge process), and $t$ is the discharge time (s). The calculated $E$ and $P$ results according to Equations (11) and (12) are also listed in Table 1 and the plot of power density against energy density, also called Ragone plot, of the synthesized PANI samples is shown in Fig. 10. The $E$ value is found to decrease with increasing power density and current density, which is also observed in the graphene, magnetic graphene nanocomposites [33] and PANI/VO$_3$ nanocomposites [19]. The PANI-0.75 sample displays the highest $E$ while keeping a relatively high $P$. The maximum $E$ value of 38.4 Wh kg$^{-1}$ at a $P$ value of 228.7 W kg$^{-1}$ is obtained at the current density of 0.5 A g$^{-1}$, which is comparable to the results reported in the literature (an energy density of 24.1 Wh kg$^{-1}$ at a power density of 399 W kg$^{-1}$ for pure PANI) [5].
3.4.4. Magnetic field effect

The electrochemical performance of supercapacitors under the external magnetic field has been reported on the graphene and magnetic graphene nanocomposites, which have dramatically enhanced the capacitance of the graphene and magnetic graphene nanocomposites [33]. In this work, the magnetic field effects on the CV curves and the capacitance of the non-magnetic PANI-0.75 and PANI-3 samples are also investigated. Fig. 12(a&b) shows the CV curves of PANI-0.75 and PANI-3 samples, respectively. For the PANI-0.75 sample, Fig. 12(a), the shape of the CV curves has no obvious change and still there are no obvious redox peaks. However, for the PANI-3 sample, Fig. 12(b), after applying magnetic field, the CV curve has been changed dramatically compared with the results obtained in Fig. 8(b) (left) without magnetic field and the redox peak becomes less obvious. Generally, the magnetic field can affect the resistance of the materials (MR phenomenon) by changing the electron spin energy state [70], which can affect the electron transport efficiency at the electrolyte/electrode interface [33].

The calculated $C_s$ values from CV curves for the PANI-0.75 and PANI-3 samples according to Equation (9) with and without magnetic field are listed in Table 2. From Table 2, the $C_s$ was observed to decrease dramatically after applying magnetic field to the electrodes. For example, for PANI-0.75 sample, the capacitance is 222.08 F g$^{-1}$ at a scan rate of 5 mV s$^{-1}$ under the magnetic field, which is much smaller than that obtained without magnetic field at the same scan rate (298.51 F g$^{-1}$). The decreased electrochemical performance of these samples is attributed to the induced MR phenomenon by the magnetic field to the samples. As aforementioned, the room temperature MR of PANI-0.75 and PANI-3 samples is positive. The increased resistance by the external magnetic field is not beneficial for the charge transfer of the electrodes, resulting in the decreased $C_s$. This is consistent with the obtained CV results.

In order to further study the magnetic field effect on the electrochemical properties of the electrode, typical EIS of PANI-0.75 sample with and without the magnetic field is presented in Fig. 12(c). The corresponding equivalent circuits are provided in the inset of Fig. 12(c) to obtain a fundamental understanding of the capacitive behaviors under two different experimental conditions. Without magnetic field, the EIS can be modeled as an equivalent circuit consisting of the $R_e$, $R_{ct}$, $C_{dl}$ and $C_p$ standing for the double layer capacitance on the electrode/electrolyte interface and the pseudocapacitance in the polymer, respectively [71]. After application of magnetic field, a different equivalent circuit is employed, which consists of $R_e$, double layer capacitance $C_{dl}$ in parallel to the charge transfer resistance $R_{ct1}$, and a Warburg diffusion element $Z_w$ arising from the diffusion of ions, a pseudocapacitance in the polymer $C_p$ and a charge transfer resistance from the polymer $R_{ct2}$.

Tables 3 and 4 summarize the fitting values from the EIS data. As
expected, the room temperature MR has little effect on $C_{eq}$, which is almost the same for PANI-0.75 with or without magnetic field. Interestingly, the $C_{eq}$ is dramatically reduced from 0.07642 to 0.00039 F under the magnetic field. Correspondingly, $R_{ct2}$ is introduced owing to the increased resistance by the aforementioned positive MR that is not beneficial for the charge transfer of the electrodes. It’s also worth noting that the magnetic effect can affect the ion diffusion reflected by the $Z_{eq}$, which is negligible for the electrode without magnetic field. Meanwhile, a remarkable increase in the charge transfer resistance is also found upon applying the magnetic field onto the material. The combined effects attribute to the decreased capacitance.

### 3.4.5. Stability of the electrodes

The stability of the PANI-0.75 and PANI-3 samples during the long term cycling is also investigated in this work and the capacitance retention of these two samples during the 1000 galvanostatic charge–discharge cycles at a current density of 8 A g$^{-1}$ are shown in Fig. 13. After 1000 galvanostatic charge–discharge cycles, about 76.8 and 81.7% of the capacitance are maintained for the PANI-0.75 and PANI-3 samples, respectively, which is much better than the stability of PANI film synthesized by electropolymerization (no energy storage function existed after 370 cycles) [1] and PANI nanofibers fabricated by the interfacial polymerization using ammonium persulfate (APS) as an oxidant (only 25.0% capacitance retention after 1000 cycles) [17]. The decreasing specific capacitance is attributed to the degradation of the electrode materials caused by the swelling and shrinkage during the long term charge–discharge process [72].

### 4. Conclusion

The PANI with different nanostructures have been successfully synthesized by different doses of Cr(VI) and the electrochemical performance as supercapacitor electrodes are evaluated. The FT-IR spectra results show that the PANI has different oxidation states due to the different doses of oxidant Cr(VI). PANI-0.75 and PANI-3 samples are EB salt form and PANI-4.5 and PANI-9 samples are PB form. The XRD results indicate that the synthesized PANI samples have different crystallization structure and degree. SEM images reveal that the synthesized PANI samples have different morphologies. The temperature dependent resistivity of PANI-0.75 and PANI-3 samples indicates a quasi 3-d VRH mechanism. Both PANI-0.75 and PANI-3 samples show positive MR values, which are analyzed using wave-function shrinkage model via decreases localization length $q_0$, increased density of states at the Fermi level $N(E_F)$, and decreased average hopping length $R_{hop}$. Different nanostructures of PANI exhibit different permittivity. In the 1 mol L$^{-1}$ acid H$_2$SO$_4$ electrolyte, the PANI-0.75 sample exhibits an optimum supercapacitive performance with a maximum gravimetric capacitance of 298.5 F g$^{-1}$ at a scan rate of 5 mV s$^{-1}$ obtained from CV test. Meanwhile, a highest value 330.2 F g$^{-1}$ of gravimetric capacitance is obtained for the PANI-0.75 sample in the galvanostatic charge–discharge measurement at current density of 0.5 A g$^{-1}$. A maximum energy density value of 38.4 Wh kg$^{-1}$ at a power density value of 228.7 W kg$^{-1}$ is obtained from the charge–discharge measurement at a current density of 0.5 A g$^{-1}$. The different crystallization structure of PANI can affect the ion diffusion and charge transfer, which further change the capacitance performance of PANI sample. The external magnetic field is found unfavorable for the electrochemical properties owing to the induced MR property and reduces the capacitance.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.08.020.