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Effect of Temperature on Electrochemical Degradation of Polyaniline

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Polyaniline (PANI) as active material of batteries possesses excellent electrochemical reversibility. It is a promising candidate for a rechargeable battery with a high performance. The polyaniline (PANI) was deposited onto the platinum electrode by cyclic voltammetry. The electrochemical degradation of PANI was studied in 1.0 M sulfuric acid aqueous solution at different temperatures. The higher temperatures lead to the irreversible change of some redox characteristic peaks. The experimental results indicate that the electrochemical degradation of PANI is first-order reaction in 1.0 M sulfuric acid solution. The degradation rate of PANI is greatly affected by temperature, which increases by approximately 4.6 times at 45°C than that of at 15 °C. The first-order degradation rate constants (k) and half-period ($\tau_{1/2}$) were calculated based on the change of the relative peak current over the course of the study. The morphology, structure and electrochemical properties of the PANI are also greatly affected by the temperature. Higher temperatures ($\geq 35\ ^{o}$C) promote the overoxidation of the PANI, which results in decreasing the electrochemical activity of the PANI in sulfuric acid solution and the reversibility of PANI during the charge and discharge cycles, and damaging the conjugated structure of PANI. The overoxidized PANI film has a higher R_{ct} (charge transfer resistance). Higher temperatures also destroy the porous structure of PANI. It is suggested that the optimum electrochemically operating temperature of PANI should be below 35 ^{o}C in the aqueous sulfuric acid solution.

Keywords: polyaniline, degradation, kinetics, electrochemistry, temperature

1. INTRODUCTION

Polyaniline (PANI), as a kind of conductive polymers with a variety of chemical structures, unique doping mechanism, good stability, cheap monomer and simple synthesis, etc., is considered to be one of the most promising conducting polymer materials. PANI is widely used in electrochemical catalysis [1-2], electrochromic display devices and metal corrosion protection [3-4], chemical [5] and biological sensors [6], electrode materials in the secondary battery [7], capacitors [8-9] and EMI shielding [10]. However, the degradation of PANI has limited its application in many aspects, especially in the application of the secondary battery [11-13]. Therefore, a lot of researchers have paid more and more attention to study the stability and degradation of conducting PANI [14-16].

Some current researches have been focused on the electrochemical stability and thermal stability of the PANI. Maeda *et al* firstly studied the electrochemical and thermal behavior of PANI in 1M $ZnSO_4$ aqueous solution, and the thermal response is mainly attributed to the entropy change for two electrochemical processes. A decrease of entropy is due to the doping of SO_4^{2-} at lower potential and an increase of entropy is attributed to the proton elimination at higher potential [17]. Luo *et al* suggested that the PANI-EB molecules appear to undergo a crosslinking reaction at about 250 ^oC [18]. Trchova *et al* considered that the counter-ions influence the thermal stability of films and the decrease of the conductivity during ageing is caused by gradual deprotonation [19]. They concluded that the PANI films after the thermal treatment at 80 ^oC undergo deprotonation, oxidation and crosslinking reactions among PANI molecules in three months. PANI bases are more stable than PANI salts, and the ageing of PANI salts undergo dedoping, desulfonation and structural changes [20]. Bhadra *et al* revealed the mechanism for doping, dedoping, oxidation, chain scission and crosslinking [21].

The group of Malinauskas studied the degradation of PANI at anodic potentials with *in situ* UV-Vis spectroscopy of polymer-coated ITO glass electrodes at first [22]. They performed the kinetic study on the degradation of PANI at different pH values and electrode potentials with the use of electrochemical technique [23] and Raman spectroscopy [24]. Nakayama *et al* studied the electrochemical polymerization of aniline and the degradation of PANI on the platinum electrode in aqueous solutions by means of *in situ* Fourier-transform Infrared Spectroscopy [25]. Among those methods, electrochemical technique as a simple, efficient and accurate method is used most to study the degradation of PANI. There are many evaluations of PANI degradation by electrochemical technique. Cui *et al* suggested that the extent of degradation could be evaluated by the ratio of the second anodic peak current to the first, i_B/i_A, in the voltammograms of PANI redox [26-27]. Zhang *et al* reported that the ratio of the sum of the second and third anodic current peaks to the first anodic current peak, $(I_{p,B1}+I_{p,B2})/I_{p,A}$, in the cyclic voltammograms of PANI, is used to measure the extent of PANI degradation [28]. However, the relative peak current $(I_{p,A})$ is a more intuitive way to show the degradation of PANI [23].

The electrochemical degradation of PANI is influenced by many factors, such as electrode potential, polarization time, pH, doping anion and temperature. But only a few researchers studied the effect of temperature on electrochemical degradation of PANI. Mondal *et al* [29] reported that the cyclic voltammograms and electrochemical impedance spectra was firstly performed and then heated at 80 ^oC in the air for deposited PANI electrode. Following this, the electrode was cooled to ambient temperature and dipped in 0.5 M aqueous sulfuric solution before recording the cyclic voltammograms and impedance spectra again.

To our knowledge, there is no on-the-spot research work published for the effect of temperature on electrochemical degradation of PANI in aqueous sulfuric solution, which is very important for practical applications. In this paper, we reported the electrochemical degradation of PANI by cyclic voltammetry at different temperatures in 1.0 M aqueous sulfuric solution, and other characterizations such as electrochemical impedance spectra, FT-IR, UV-vis spectroscopy and scanning electron microscopy (SEM) of the degraded PANI films removed from the cells (or scraped off from the electrodes). Our results have two distinct features compared to previous reports: first, PANI exhibited the considerable electrochemical degradation with the change of temperatures in aqueous sulfuric solution; second, this degradation is a first-order reaction at different temperatures.

2. EXPERIMENTAL

2.1 Materials

Aniline, sulfuric acid (H_2SO_4) and N, N-dimethylformamid (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals used were analytical grade. The monomer aniline was distilled under reduced pressure and stored in refrigerator (about 4 ^oC) before use. All aqueous solutions were prepared using doubly distilled water.

2.2 Electropolymerization of PANI films

The electropolymerization of the aniline was performed on a CHI 660D electrochemical workstation (CHI Instruments, USA) with a three-electrode system, containing a 5mm×5mm platinum plate as the working electrode, a 10mm×10mm platinum plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. All potentials recorded are referred to this reference electrode. PANI films were prepared on the platinum working electrode by the cyclic voltammetry within the potential of -0.2 V to 1.0 V for 10 cycles in a solution containing 0.2 M aniline and 1.0 M sulfuric acid. And the potential scan rate of electropolymerization was controlled at 50 mV/s. After the electropolymerization of the aniline, the PANI electrode was repeatedly washed with acetone and the doubly distilled water until the washing liquid was completely colorless, during which the degradation product of small molecular generated during polymerization was removed. Finally, the PANI electrode was dried at 50 ^oC.

2.3 Electrochemical degradation of PANI films

After the electropolymerization of the aniline, the electrochemical degradation was performed on CHI 660D electrochemical workstation by cyclic voltammetry with a potential range from -0.2 V to 1.0 V for 35 cycles in 1.0 M sulfuric solution, and the potential scan rate was controlled at 20 mV/s. The PANI degradation time was just 10 minutes for 5 cycles. In our study, a high potential limit of 1.0 V was chosen to shorten the reaction time. And the effects of temperature on the degradation of the PANI were more clearly. The peak currents of the first anodic peaks of PANI were taken into account and used in the following calculations. The peak currents of the first anodic peaks in the 5th, 10th, 15th, 20th, 25th, 30th and 35th cycles were chosen to study the kinetics of PANI degradation. Considering the reproducibility of the cycle curves, the peak current of the 5th was used as the reference standard. So the relative peak current of the n cycle was taken as the radio of $I_{p,A}$ (n) to $I_{p,A}$ (5).

2.4 Characterization of PANI films

The electrochemical impedance spectroscopy (EIS) was recorded at the open circuit potential (OCP) in the frequency range from 100 kHz to 10 mHz with an amplitude of 10 mV in a electrochemical workstation (AutoLab, Nova 1.9, Metrohm). The charge and discharge tests of PANI were also performed in the range of 0 V to 0.7 V (vs. SCE) at 2 mA/cm^2 by the chronopotentiometry method on CHI 660D electrochemical workstation with a three-electrode system. FT-IR (Tensor 27, Bruker, Switzerland) spectra were recorded by a KBr sample holder method. The PANI samples were dissolved in DMF and the UV-vis spectra (Shimadzu UV-2550) were measured in the range from 200 to 800 nm at room temperature. A Hitachi S-4800 scanning electron microscope (SEM) was used to examine the surface morphologies of PANI.

3. RESULTS AND DISCUSSION

3.1 Electrochemical Characterization of PANI films

There are four pairs of redox peaks in the cyclic voltammograms of the PANI films (Figure 1). The A and A′ peaks correspond to the reversible transition between leucoemeraldine form and emeraldine form. The D and D′ peaks are attributed to the reversible transition between emeraldine form and pernigraniline form [16, 29-30]. The two peaks in the middle are caused by the degradation products. The peaks B and B′ as well as C and C′ are assigned to the presence of phenazine rings. The formation of phenazine structures in the polymer is attributed to the electropolymerization of aniline at high potential, which is related to the reaction of aniline nitrenium cations in the ortho position on another ring or because of the cross-linking between two PANI chains [31]. The peak current values of C and C′ peaks are higher than that of B and B′ peaks at lower temperatures ($\leq 25\ ^oC$; Figure 1a, b), and they may be just the opposite at higher temperatures ($\geq 35\ ^oC$; Figure 1c, d), which is attributed to the effect of temperatures on the formation of degradation products.

In addition, as the temperature increasing, the peak current values of A′ and D′ peaks decrease, and the peak current values of A and D peaks almost don’t change, indicating that the emeraldine form and the pernigraniline form of the PANI are difficult to be reduced to leucoemeraldine form and emeraldine form at higher temperatures ($\geq 35\ ^oC$), respectively. So the higher temperatures promote the overoxidation of the PANI, and the degradation of the PANI may mainly occur in the emeraldine form and the pernigraniline form. In other words, the higher temperatures lead to the irreversible transformation between A and A′ peaks as well as D and D′ peaks, which results in the overoxidation of PANI at the same time.

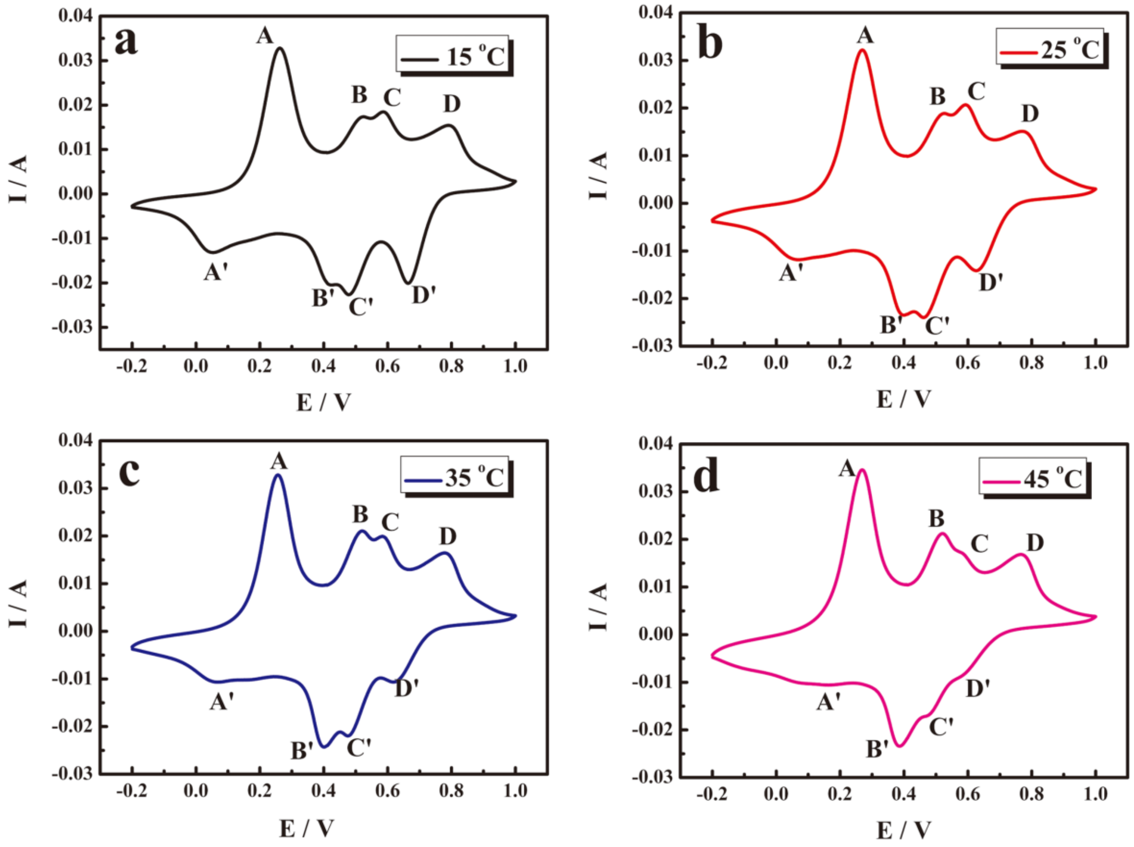

Figure 1. Cyclic voltammograms for PANI films in the second cycle (a-d) in 1.0 M H_2SO_4

Electrochemical impedance spectroscopies (EIS) for the PANI films after degradation are shown in Figure 2. All curves contain a semicircle and a line, and the diameter of the semicircles increase with the increasing temperatures. The semicircles at the high frequency region are attributed to the double layer capacitance in parallel with the charge transfer resistance (R_{ct}) due to the ion exchange for charge compensation at the PANI-electrolyte interface [32-34]. The R_{ct} increases with the increasing temperatures, which is due to high temperatures leading to the overoxidation of PANI and the decrease of PANI electrochemical activity. The vertical lines ($\leq 25\ ^{o}C$) at the lower frequency slightly deviated from the ideal vertical line, which is caused by irregular geometry of the PANI electrode surface [35]. In the meanwhile, the vertical line indicated that the property of the system is close to an ideal capacitance (the faradaic pseudocapacitance of the PANI) behavior at lower temperatures ($\leq 25\ ^{o}C$) [33] and the electrode process is mainly controlled by charge transfer process (electrochemical reaction steps). Higher temperatures ($\geq 35\ ^{o}C$) cause severe degradation of PANI, not only leading to an increase of R_{ct} by nearly 10 times, but also making the angles of the lines present 45^{o} at the low frequency, which indicates that the electrode process is controlled by charge transfer and Warburg diffusion processes at this point [32, 35-36]. For clarity, the inset of Figure 2 indicates the EIS at Higher temperatures.

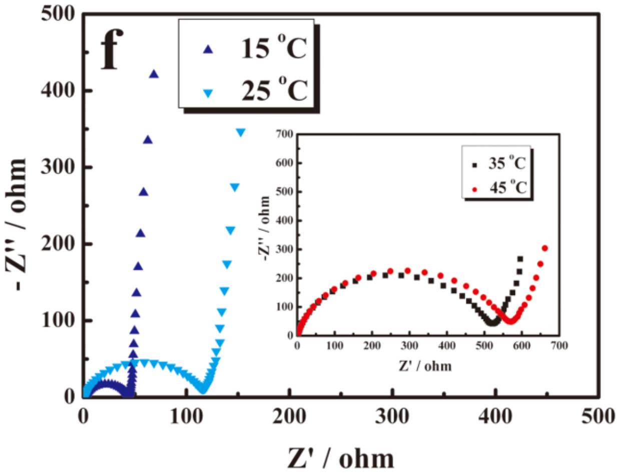

Figure 2. Impedance spectroscopies for the PANI films after the degradation at different temperatures in 1.0 M H_2SO_4

Figure 3a-d shows the charge and discharge curves of PANI at different temperatures. The charge-discharge curves of PANI have good symmetry at lower temperatures ($\leq$ 25 ^{o}C), which indicates that the PANI has a good charge-discharge reversibility. However, higher temperatures ($\geq$ 35 ^{o}C) destroy the reversibility, and the charge curves in the first cycle appeared a “charge plateau” (Figure 3c, d). The higher the temperature is, the longer the time of plateau is. The platform disappeared at the fifth cycle and the charge and discharge time of the PANI became shorter. When the temperature reaches 45 ^{o}C, the potential range of the discharge reduces to 0.62 V in the fifth cycle, indicating that PANI is overoxidized and the electrochemical activity of PANI decreases after a period of the plateau.

Only the emeraldine form after the proton doping shows the electrical conductivity. While the leucoemeraldine form and pernigraniline form cannot be doped with proton, so they don’t show the electrical conductivity. The leucoemeraldine form after being oxidized to emeraldine form is doped with the proton to form PANI salts at higher potentials, and the emeraldine form after dedoping undergoes the reduction reaction to the leucoemeraldine form at low potentials. The charge and discharge processes are reversible under a certain condition. However, the PANI bases are more stable than the PANI salts, so the PANI degradation came mainly from PANI salts nucleophilic attack by H_2O molecules [15, 25, 37]. Due to higher temperatures promoting PANI salts nucleophilic attack by H_2O molecules, the PANI salts are severely overoxidized and the proton and sulfate ions are dedoping from the PANI chains. The higher temperatures destroy the dynamic equilibrium of doping and dedoping processes, resulting in that the PANI is difficult to be charged to high potentials (0.7 V vs. SCE). The surface of PANI is overoxidized so fast, which is due to the nucleophilic attack by a large amount of water molecules in the aqueous solution. However, the inner layer of PANI is overoxidized more slowly, for only a small amount of H_2O molecules can reach them in the pores [29]. The occurrence of overoxidation is manly on the surface of the PANI in the first cycle, and the overoxidation of PANI occurs mainly in the inner layer in the subsequent cycles. So the plateau appears in the first cycle and disappears in the fifth cycle. It is concluded that the temperature should be below 35 ^{o}C in the process of the charge-discharge of PANI.

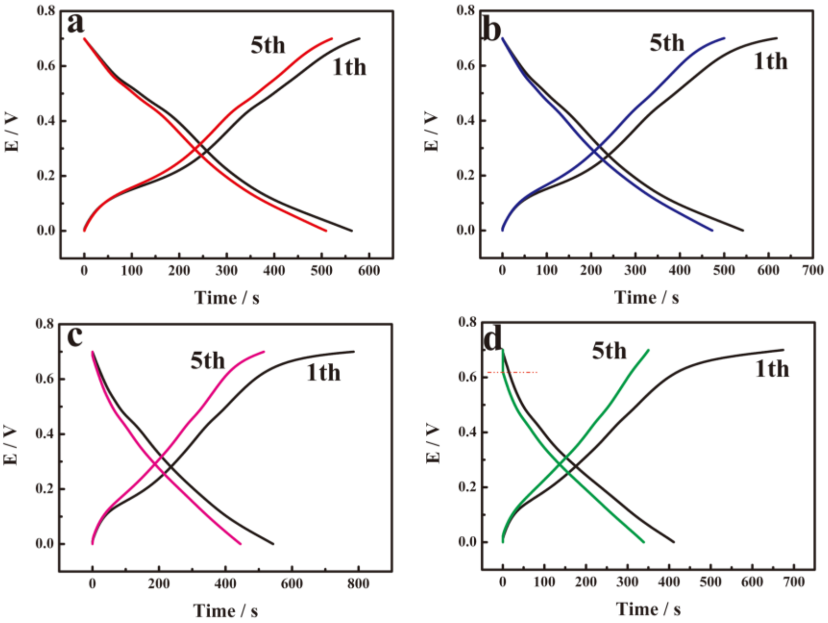

Figure 3. The charge and discharge curves (the first cycle and the fifth cycle) of PANI (a, b, c, d) at different temperatures. (a: 15 ^{o}C; b: 25 ^{o}C; c: 35 ^{o}C; d: 45 ^{o}C;) in 1.0 M H_2SO_4

3.2 Degradation kinetics of PANI films

The relative peak current is used to evaluate the extent of electrochemical degradation of the PANI. Figure 4(a) presented the changes of the relative anodic peak current for PANI films at different temperatures. As temperatures increase during the degradation processes, the relative anodic peak current of PANI decreases greatly and the slopes of the lines increase in semilogarithmic coordinates, which indicated that higher temperatures promote the degradation of the PANI. At relatively lower temperatures, the slope of the line became smaller. However, the PANI film degraded so significantly at low temperatures as well. The extent of degradation of PANI is affected by many factors, such as electrode potentials, concentration of sulfuric acid, doping anions and temperature. Lower temperatures can reduce the extent of the degradation of PANI, but not completely inhibit the degradation of PANI. In other words, the higher electrode potential or concentration of sulfuric acid will also cause the overoxidation and the hydrolysis of PANI at a lower temperature. If the concentration of the acid is reduced and the range of the potential is narrowed, the slopes of the lines will become smaller at low temperatures.

When the temperature continued to rise in the redox process of PANI, higher temperatures promote the occurrence of the overoxidation of PANI chains, and the overoxidized PANI chain can never return to the emeraldine form or the pernigraniline form of PANI, which leads to the relative anodic peak current decreasing faster.

There is a linear relationship between logarithm of the relative anodic peak current and time in Figure 4(b), which indicates that the degradation of PANI follows a first-order reaction kinetic. The rate of degradation is first order to the PANI with electrochemical activity. The first-order degradation rate constants (k) can be obtained by the equation [23]:

$$k = -\frac{\Delta \ln I_{pa(rel)}}{\Delta \mathrm{t}}$$

The obtained data were listed in Table 1. According to *k*, the values of a half-period of the PANI degradation ($\tau_{1/2}$) were calculated. It is seen that the degradation rate of PANI increases by approximately 4.6 times at 45 °C than at 15 °C, which further illustrates that the degradation of PANI is greatly affected by temperature.

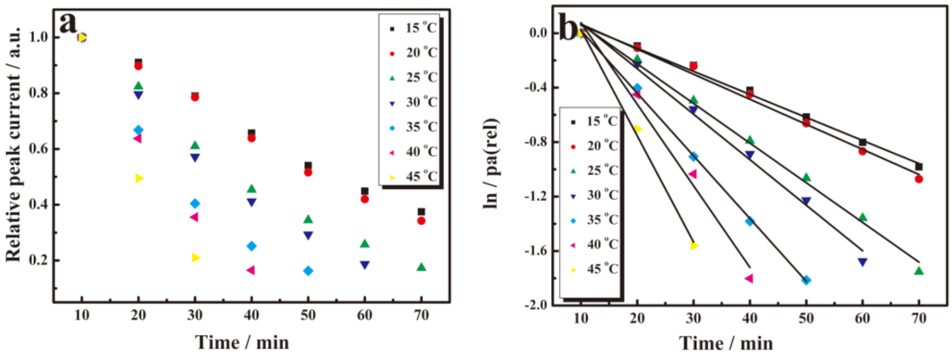

Figure 4. Time dependence of a relative anodic peak current for PANI films (a) and logarithm of the relative anodic peak current changes with time (b) ranging from 15 °C to 45 °C

Table 1. Rate constants (*k*) and half-period ($\tau_{1/2}$) of the PANI degradation

T (°C)	*k* (s^{-1})	$\tau_{1/2}$ (s)
15	1.69×10^{-2}	40.9
20	1.84×10^{-2}	37.7
25	2.91×10^{-2}	23.8
30	3.34×10^{-2}	20.7
35	4.61×10^{-2}	15.0
40	5.99×10^{-2}	11.6
45	7.80×10^{-2}	8.9

The dependence of rate constants on the temperature was shown in Figure 5. The change in the logarithm of degradation reaction rate constant of PANI with temperature shows a straight line with the correlation coefficient being 0.987, which indicates that the degradation of PANI proceeds at a remarkable rate with the increasing temperature. The activation energy (E_a = 42.66 kJ·mol^{-1}) of the degradation of PANI would be calculated by Arrhenius equation.

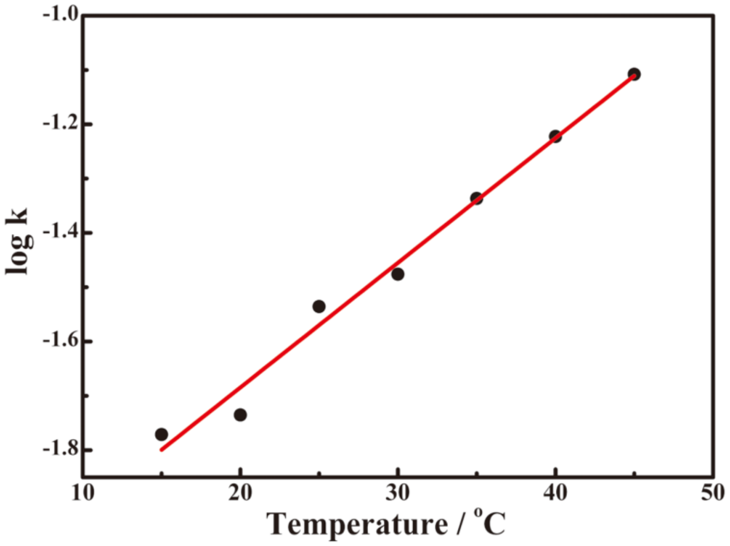

Figure 5. Dependence of logarithm of degradation reaction rate constant of PANI on the temperature

3.3 Structural and morphology characterizations of PANI films

As the FT-IR curves of PANI shown in Figure 6, five kinds of PANI have the similar characteristic absorption peaks. The relative intensities of the peaks at different wavenumbers were list in Table 2, and the relative intensity of one peak was the ratio of the intensity of this peak to the intensity of the peak at 575 cm^{-1}. The peak at 850 cm^{-1} is assigned to para-disubstituted benzene ring and the peak at 885 cm^{-1} is interpreted as the out-of-plane bending of C-H vibrations bonds on the aromatic rings in the backbone [38-39]. The peak at 1068 cm^{-1} is corresponding to S=O stretching vibration, which was due to the presence of sulfonic groups [19]. The peak at 1170 cm^{-1} is assigned to the $–NH^+=$ vibration in the protonated emeraldine form [21]. The peak observed at 1240 cm^{-1} is corresponding to a C-N stretching vibration in the polaron of the PANI, which is the characteristic band of the conducting protonated form [20]. The peak at 1290 cm^{-1} is assignable to π-electron delocalization induced by protonation in PANI [40]. The peaks at 1482 cm^{-1} and 1560 cm^{-1} are respectively corresponding to the C-C stretching vibration of the benzene ring and the quinoid ring [41-43]. The shoulder peak at 1610 cm^{-1} is assigned to the Raman-active C=C ring stretching vibration, and the C=C ring became infrared-active after the protonation process inducing conformational changes in the PANI chains [20, 40]. The relative intensities of the peaks at 1240 cm^{-1} and 1290 cm^{-1} decreases with increasing temperature, which suggests that higher temperature reduces the conducting protonated PANI and damages the conjugated structure with π-electron delocalization of PANI. The relative intensities of the peaks at 1482 cm^{-1}, 1560 cm^{-1} and 1610 cm^{-1} also decrease with increasing temperatures, which further indicates that the conducting structure of the PANI is destroyed and the electrochemical activity of PANI decreases. And the peak at 1612 cm^{-1} no longer a shoulder peak in Figure 6e may be assigned to C=O stretching vibration, which is due to the degradation of PANI [44].

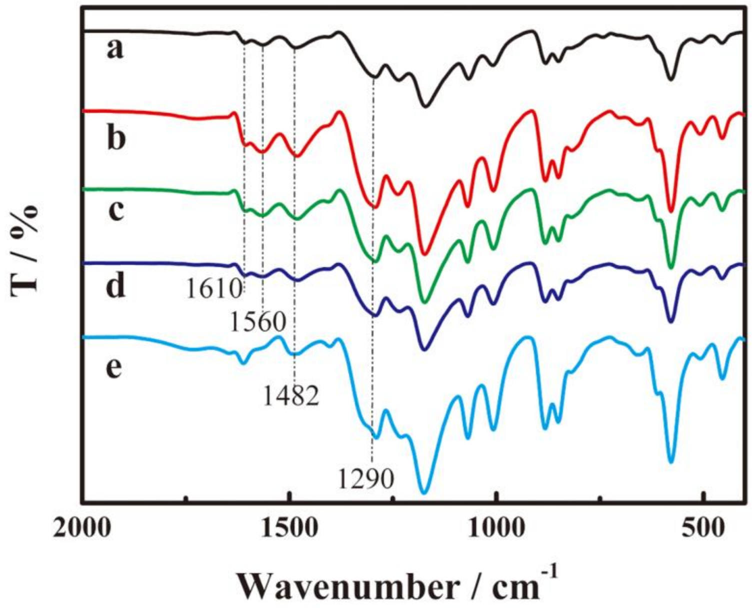

Figure 6. FT-IR spectra for undegraded PANI (a) and the PANI after the degradation process at different temperatures (b: 15 ^{o}C; c: 25 ^{o}C; d: 35 ^{o}C; e: 45 ^{o}C;)

Table 2. The relative intensities of the peaks at different wavenumbers

Entry	1240cm^{-1}	1290cm^{-1}	1482cm^{-1}	1560cm^{-1}	1610cm^{-1}
a	0.330	0.667	0.381	0.238	0.238
b	0.217	0.587	0.348	0.174	0.196
c	0.206	0.588	0.323	0.176	0.176
d	0.192	0.577	0.292	0.154	0.154
e	0.140	0.272	0.200	0.060	0.160

The UV-vis spectra of PANI are shown in Figure 7 and the intensities of different absorption peaks are shown in Table 3. The peak at 330 nm is assigned to the π-π* transition in the benzenoid structure of the PANI. The weak peak at 453 nm is interpreted as polaron peak, which is caused by the doping of PANI [45-47]. As the degradation temperature increasing, the intensities of the two peaks gradually decreased, which is attributed to the decrease of PANI after the degradation. The two peaks undergo obvious blue-shift with increasing temperature, which suggests that higher temperatures have broken the conjugated structure of PANI and decreased the ion doping level of the PANI chains. This result is consistent with the result concluded from FT-IR spectroscopy in Figure 6.

The scanning electron micrographs for the PANI are shown in Figure 8. It can be seen that the PANI prepared by electrochemical method shows the lamellar structure. And this kind of loose structure has many pores, which is advantageous to the doping and dedoping processes of the anions. So PANI is a good kind of cathode material for the secondary battery. However, with the temperature increasing, there are fewer and fewer pores on the surface of the PANI. And the structure is more compact.

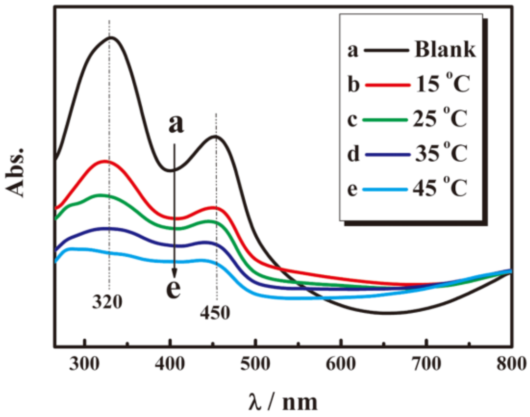

Figure 7. UV-vis spectra of undegraded PANI (a) and the PANI after the degradation at different temperatures (b-e)

Table 3. The intensities of different absorption peaks

Entry	λ_1 (nm)	Abs.	λ_2 (nm)	Abs.
a	330	1.564	453	0.879
b	327	0.731	449	0.425
c	318	0.507	446	0.333
d	323	0.287	440	0.192
e	293	0.149	434	0.075

Higher the degradation temperature is, severer the overoxidation of PANI is. When the temperature reach to 45 ^{o}C, the surface of PANI becomes a smooth film. Therefore, higher temperatures accelerate the structural damage of the PANI chains. The mechanism for the effect of temperature on the PANI morphologies is yet unclear. In addition, Mondal *et al* found that the H_2O molecules taken up by the heated sample does not occupy the same positions in the polymer as in the case of freshly prepared PANI. And the removal of original H_2O molecules by heating PANI at 80 ^{o}C leads to an irreversible electrochemical inactivation [29]. However, in our studies, the H_2O molecules in the original location are not removed from PANI and PANI is also nucleophilic attacked by H_2O molecules in the original location. So the degradation of PANI proceeds within the porous PANI network rather than at the outer PANI/electrolyte interface [48].

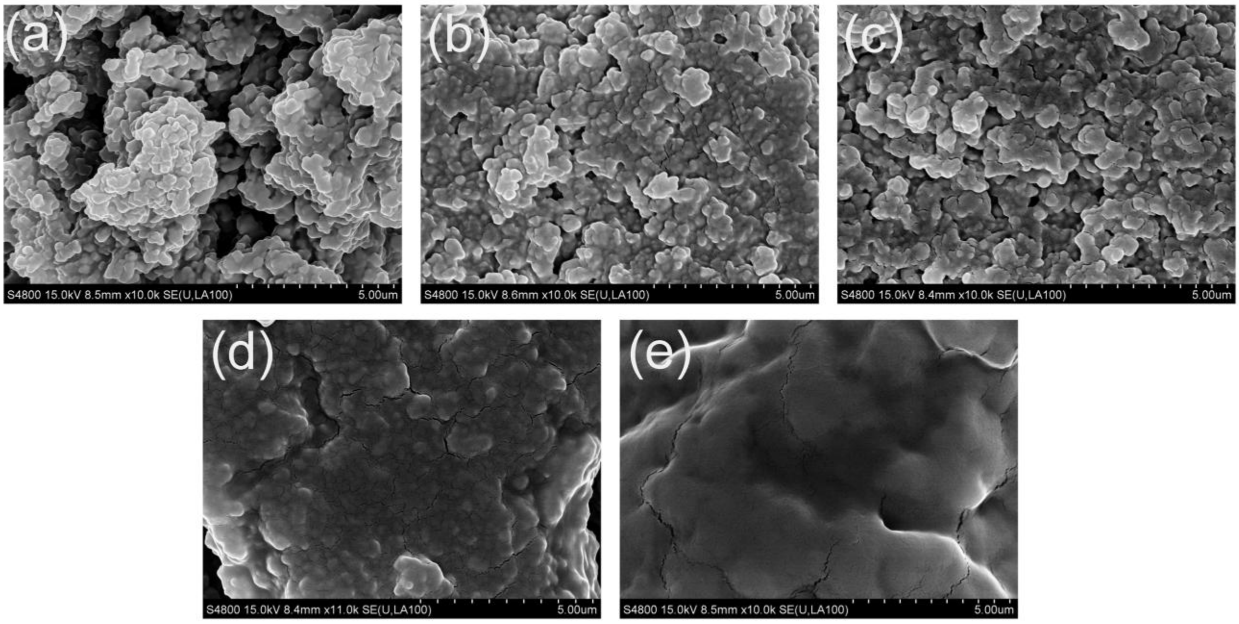

Figure 8. SEM micrographs for undegraded PANI (a) and the PANI after the degradation process at different temperatures (b: 15 ^oC; c: 25 ^oC; d: 35 ^oC; e: 45 ^oC;)

4. CONCLUSIONS

The electrochemical degradation of PANI prepared on the platinum electrode by the cyclic voltammetry is a first-order reaction. The degradation rate of PANI is greatly affected by temperature. And the degradation rate increases by approximately 4.6 times at 45 °C than at 15 °C. Higher temperatures ($\geq 35\ ^oC$) not only promote the overoxidation of the PANI, but also result in the decrease of the electrochemical activity of PANI and the reversibility in the charge and discharge cycles. The overoxidized PANI film also has a higher R_{ct}. Therefore, the optimum electrochemically operating temperature of PANI should be below 35 ^oC in the aqueous sulfuric acid solution. In a word, a reasonable temperature control can effectively reduce the extent of degradation of PANI during the electrochemical reaction. Further studies will focus on the inhibition of PANI degradation.

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