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Electrochemical preparation of polyaniline doped with hydrochloric acid

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Abstract. In this paper, ITO conductive glass was used as working electrode; polyaniline was synthesized in cyclic voltammograms electrochemical method. He factors of electrolyte. scanning rate are analyzed ,microcosmic morphology, redox reversibility and conductivity of polyaniline can be affected by appropriate adjustment. The experiment focuses on the analysis of the relationship between the reduction of monomer concentration in the electrolyte and oxidation properties of polyaniline, cyclic voltammetry, Tafel curve test method of polyaniline were used into the test analysis. The result served that the when scan rate is 0.05v/s, the PANI film has uniform particles with good oxidation resistance at the concentration of hydrochloric acid for 0.3mol/l, the concentration of aniline is 0.3mol/l.

1. Introduction

In the 21 century, conducting polymers have become as one of hot spots in current material range. In the conducting polymer , polyaniline (PANI) has obtained many cautions from a lot of researchers because of low costs ,industrial preparation supported ,excellent conductivity and unique redox characteristic[1].There are two major preparation ways of PANI ,including chemical oxidation[2] and electrochemical preparation[3].Chemical oxidation is usually used when a lot of PANI industrial produces are needed[4].In addition ,electrochemical ways are usually used when unique characteristics of PANI are needed in the domain of science.[5-7].Chemical redox ways are including template polymerization and emulsion polymerization[8].

The advantages of emulsion polymerization are it can control the particle size efficiently and the reaction rate. In addition, water is usually used as reaction solvent, and water together with soluble initiator can control reaction heat efficiently. And it can discharge the heat in the reaction efficiently in time if water is used as reaction medium .However; there are also some defects in emulsion polymerization. For example, the products need demulsification, which can affect the conductivity of PANI seriously because of the add of emulsifier in the reaction. In the microemulsion, the dosage of the emulsifying agent is one of major factors of preparation and property of PANI, while the decision of PANI property is the dosage ratio of water and emulsifier. The shape and particle size can be control efficiently by the changing the ratio of water and emulsifying agent. Shorter time can lead to the nano size of the particle size of PANI, regular arrayed production and the greater degree of crystallization. But it is bad for the conductivity of PANI because of the less molecular weight.

Template polymerization: The polymerization place of this ways is different; the polymerization place of this ways is porous membrane. The PANI can be adhered to the porous membrane because of the hydrophobic lipophilic property, and then the porous membrane is dipped into the reaction system containing protonic acid and oxidizer which the aniline can make chain propagation on. The major functions of the membrane are it can offer a environment of PANI polymerization and it can control the shape and particle size efficiently. The PANI fiber generated on the porous membrane have a great

combining power with the porous membrane, and the composites made up of PANI fiber and porous membrane have excellent electrochemical property. Electrochemical polymerization: the electrolyte of the polymerization of PANI is made of different ratio of aniline and protonic acid. Open the electrochemical workstation and set the parameters such as scan voltage range and scan rate. Then aniline can polymerize on the positive electrode and PANI fiber or layer of PANI power can appear on the positive electrode. In the procedure of electrochemical preparation of PANI ,the major factors of PANI electrochemical polymerization are the protonic acid doping contention ,the kind of conducting anions ,the concentration of aniline ,the polymerization thermometer and the scan rate and so on[9].

In this paper, HCl as the doping acid, using aniline as the monomer, the PANI can be electrochemical polymerize in cyclic voltammetry ways. And a layor of PANI fiber can appear on the ITO glass. Then through the analytic of the CV curves of PANI fiber generated, we can judge the reversibility of that reaction by the peak current and peak voltage. Then we can obtain the UV absorption spectrum of the PANI by using the ultraviolet spectrophotometer. And we can analyse the micro morphology and structure by the UV absorption has been obtained.

2. Experiment Section

2.1. Reagent

Anline, alcohol and HCl is analytical grade and Double distilled water was used throughout the experiment to prepare the solutions.

2.2. PANI Preparation

First, using some aniline monomer had been weighed; 50ml aniline solution was prepared. Then HCl which concentration had been known was weighed, and then was added to aniline solution with agitation into an electrolyte containing 0.3mol/L aniline monomer and 0.7mol/L protonic acid. After that, take 50ml electrolyte what have been made into the beaker and make the three electrodes into the electrolyte. Make green clip connected to ITO glass red clip connected to platinum wire electrode, and white clip connected the reference electrode. After electric circuit has been connected, open the electrochemical workstation and set the electrochemical parameters. Finally, aniline can be oxidative polymerization into the PANI.

2.3. The Characterization of the Example

By the analysis of the CV curve when the sample is being prepared, a preliminary conclusion about the property of PANI can be made .Tafel curve is made to analyse the electrochemical corrosion property.The relevant UV adoption curve can be made by UV-2600 UV-Vis spectrophotometer.

3. The Results and Discussing

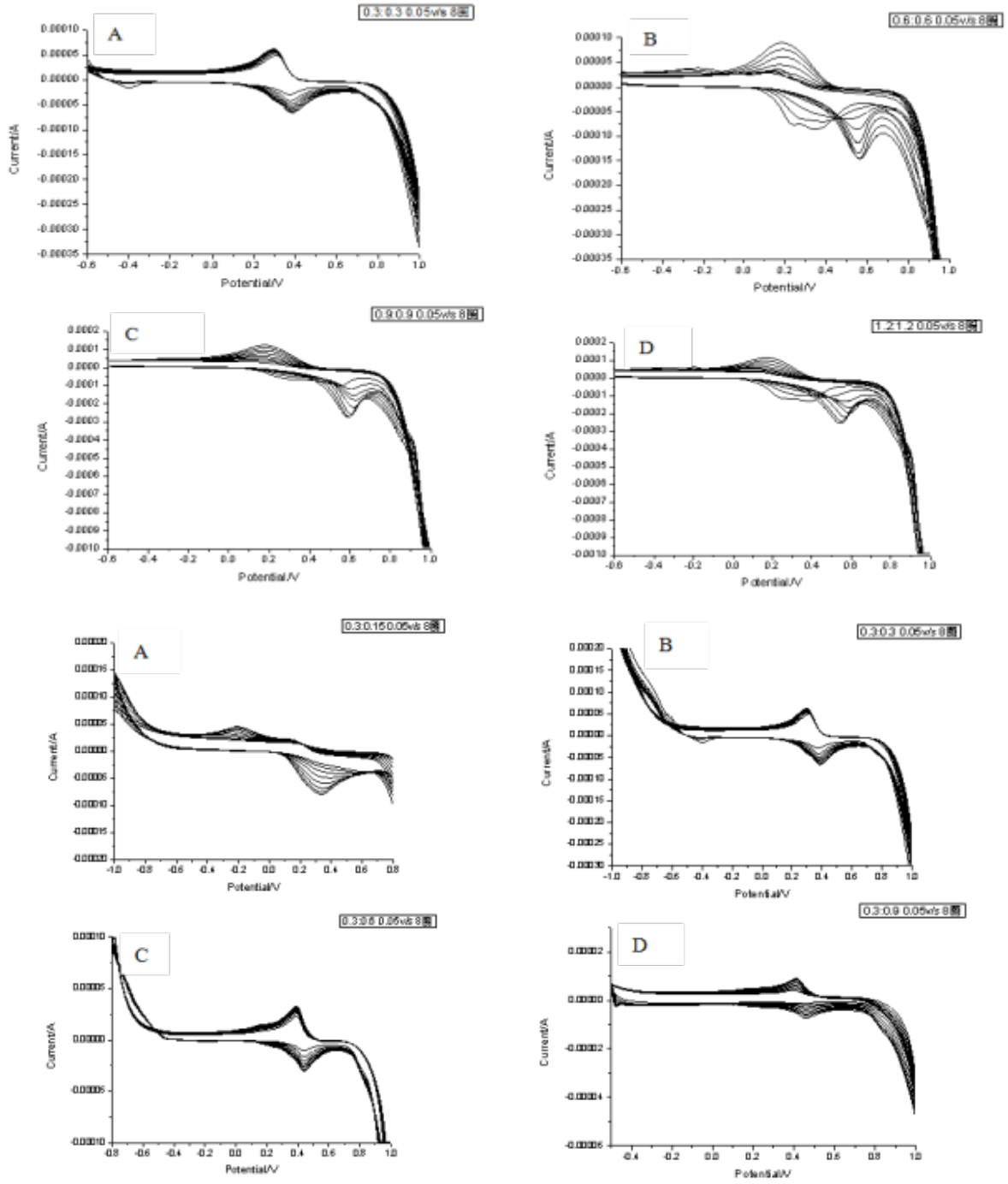
3.1. Cylic Voltammetry

Picture2-3The CV curve in the procedure of the cyclic voltamme

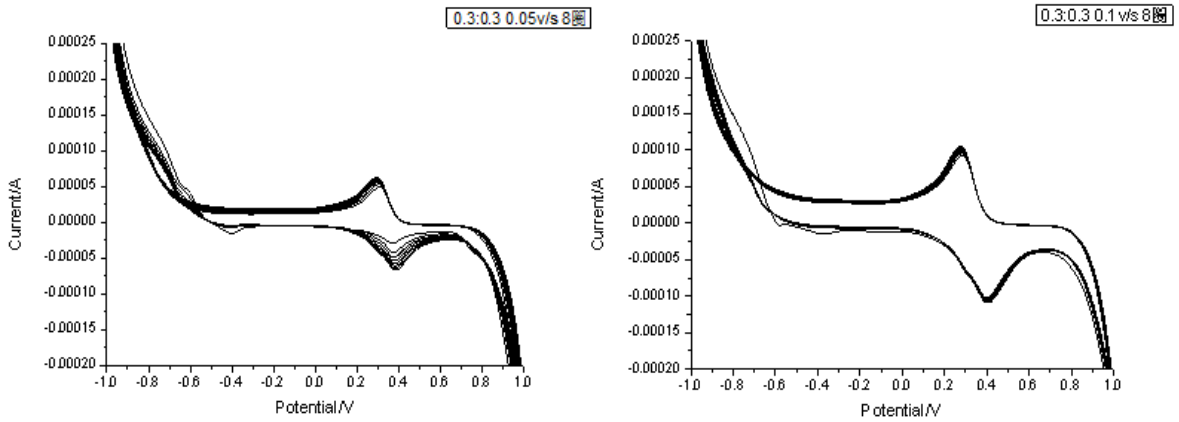
From the upper figure, we can see that the influence of the concentration of solute on the PANI is obvious, which reflect on the difference of the symmetry of redox peak on the CV curve. The symmetry of the redox in the figure A is best ,which is accord with (59/n)mv(n is the number of electrons taking part in the reaction).And the current of oxidation peak is equal to the reduction peak ,which reflect that the redox reversible degree is high in this concentration. Every CV curve is similar and uniform, which reflect the uniformity of the PANI fiber and PANI particle size that have been made. In addition, from the CV curve of the A picture ,we can see that gradually increasing reversibility after the third circle of CV curves comparing with the CV scanning curve at the beginning. The appearance of CV curves probably is closely relevant to the PANI which has different molecular chain structure.

While the symmetry of the CV curves in the B and C figure is not good and the curve is dispersive. The current is larger with the scanning. The reason of this phenomenon is the redox polymerization is greater with the scanning going on in the environment where the aniline monomer and the protonic

acid are certain.



From the figure 2-4, we can see that the concentration of the protonic acid can affect the preparation obviously when the concentration of PANI is certain. When the concentration of protonic acid is 0.15mol/L, the protonic acid's chief influence to the PANI is the redox reversibility ,which is a disadvantage to the redox reversibility of PANI. When the concentration of protonic is more than 0.3mol/L ,the concentration of protonic acid have a chief influence on the uniformity of the particle size of PANI.It reflects that the level of uniformity of PANI fiber is decreased because the CV curve of B and D figure is more scattered than others. Though there have a most symmetrical CV curve when the concentration of the protonic acid is 0.6mol/L, the curve is much scattered. After comprehensive comparison, the PANI fiber what we have made have the best property when aniline is 0.3mol/L, protonic is 0.3mol/L.



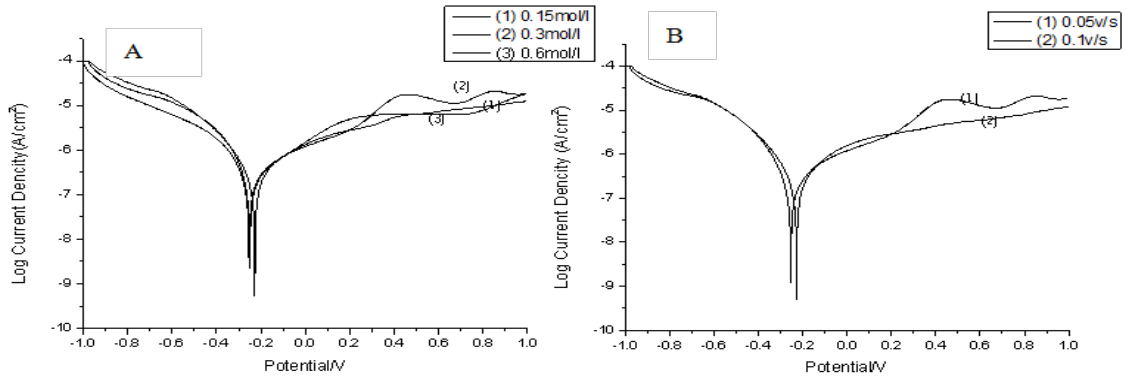
The figure 2-5 the cv curve of PANI prepared in different scan rate when the solute concentration ratio is 0.3:0.3

After the analysis upper, we investigate the influence of the scan rate to the preparation of PANI when we take the aniline is 0.3mol/L, protonic is 0.3mol/L. From the 2-5 figure, we can know that the change of scan rate mainly appear on the uniformity of PANI fiber in unchangeable concentration of solute. We can see in the 2-5 figure, the PANI fiber that made by cyclic voltammetry is more compact and uniform when the scan rate is 0.1v/s.

In addition, it is investigated that the influence of the different can rate to the PANI in the relative high concentration of protonic acid. The results can we see in the 2-6 figure that the change rule is similar to the curve in the 2-5 figure..But when we compare the 2-6 figure with the 2-3 figure, we find that the curve in the 2-3 figure is not accord with this rule when the scan rate is 0.05v/s, which reason is that the the number of free acid ion is relative high ,the stability of the reaction system decreased and the repeatability of the experiment decreased sharply when the concentric of protonic acid in the solvent is high.

3.2. Tafel Curve

In the upper two figures, the potential of the sharp pointing of the curve is named as Ecorr .On the right of the Ecorr (60-120mv) is the anode Tafel .We can obtain two straight lines by fitting linear of these pointing in these two areas. Then we can obtain the corrosion potential—Ecorr and the corrosion electric current—Icorr. And we can know the corrosion resistance property of ITO in 10% NaCl electrolyte is measured by the evaluation of the corrosion electric current and corrosion potential. Generally speaking ,the more corrosion electric current is, the more serious of the corrosion level.



In conclusion ,we can know when the aniline is 0.3mol/L, HCl is 0.3mol/Land the cylinder number is 16 ,the produced PANI fiber have the best property.In order to verify the influence of scan rate further ,we used 10% NaCl as the electrolyte and the voltage volt is -1V~1V, scan in the 0.05V/s and

0.1V/s ,then we obtain the Tafel in the B of 2-7picture.According to the experiment data, we obtain the Icorr,as -7.88,-7.56..So we can know when the scan rate is 0.05V/s ,the corrosion electric current is lowest.And we can judge that the corrosion resistance property of the produced PANI fiber is best when the scan rate is 0.05V/s.

4. UV Absorbance Text

In the two figures, we can know that the absorption density is decreased with the protonic acid concentration increasing when the monomer concentration is unchangeable. As we know, the effects of protonic acid in the reactive system as follows:(1)H+ is used to provide acid environment.(2)Cl- is used to improve the redox reversibility of the fiber and help fiber to obtain great geometrical regularity. The cause of the above phenomenon is probably that the aniline redox polymerization can be more full and the doping degree is better when the concentration of H+ is increased.The PANI fiber prepared have better uniformity. And the observance also became larger.But the experiment datas are opposed to the theory.In my opinion, I think the reason of this phenomenon is probably that when the H+ concentration is increased, it is bad to the stable of the concentration of the system and the PANI fiber is not uniform.So the greatest aniline concentration is 0.3mol/L, H+ is 0.3mol/L.

By comparing with the B figure,it can be discovered that the absorption is becoming larger with the scan going when the monomer concentration and protonic acid concentration is unchanged.The reason is there are more monomer polymerize in electrolyte and PANI fiber is prepared constantly on ITO ,which lead to the increase of the thickness of the fiber ,so the absorbance can becorm larger.

To conclude, it can be known that there have the best property of PANI when aniline monomer is 0.3mol/L,HCl is 0.3mol/L.

5. Conclusion

This experiment is mainly to study the electrochemical preparation of PANI fiber and its property characterization. It is mainly concentrated on the effects of aniline monomer concentration, concentration of the phonic acid, scan rate to the PANI fiber. By the analysis of CV curve, UV absorption curve and Tafel curve, it shows that the PANI fiber prepared have some effects of redox activity ,corrosion resistance and some UV absorption. But the effects of corrosion resistance and UV absorption is not ideal, which reason is probably the uniformity of the PANI fiber is not good. And the reason can be concluded into the bellow aspects:

(1) The reference electrode and the counter electrode don’t have a polarization treatment;

(2) The preparation of the electrolyte is not ideal, such as the solution of aniline and acid is not uniform;

(3) The ITO is probably not very clean because of my mistake, which affect the redox polymerization of the aniline.

Acknowledgement

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[10] In the English literature the concepts cyclic voltammetry and cyclic voltammogram have gained general currency. In the German literature the corresponding concepts are “Cyclovoltammetrie” and “Cyclovoltammogram” as well as the synonym “potentiodynamische Dreieckspannungs methode” (potentiodynamictriangle method).