Electrical resistance response of polyaniline films to water, ethanol, and nitric acid solution*

Yin Hong-Xing(尹红星), Li Meng-Meng(李蒙蒙), Yang He(杨 贺),
Long Yun-Ze(龙云泽)†, and Sun Xin(孙 欣)‡

College of Physics Science, Qingdao University, Qingdao 266071, *China*

(Received 3 November 2009; revised manuscript received 22 January 2010)

This paper reports on electrical resistance vs. aging time for the response of polyaniline films under exposure to water, ethanol and nitric acid (HNO_3) solution. Camphor sulfonic acid-doped polyaniline films were prepared by a "doping-dedoping-redoping" method, the morphology and microstructures of the films were characterized by a scanning electron microscope and an x-ray diffractometer, the electrical resistance was measured by a four-probe method. It was found that a lower amount of water molecules infiltrating the film can decrease the film's resistance possibly due to an enhancement of charge carrier transfer between polyaniline chains, whereas excessive water molecules can swell inter-chain distances and result in a quick increase of resistance. The resistance of the film under exposure to ethanol increases and becomes much larger than the original value. However, HNO_3 solution can decrease the film's resistance sharply possibly owing to doping effect of protonic acid. These results can help to understand the conduction mechanism in polyaniline films, and also indicate that the films have potential application in chemical sensors.

Keywords: polyaniline films, conducting polymers, conductivity

PACC: 8120S, 7280L

1. Introduction

Conducting polymers such as doped polyacetylene, polyaniline (PANI), polypyrrole and polythiophene have drawn much attention due to their excellent physical and chemical properties and have been studied extensively in fundamental and applied researches.[1−10] Among these conducting polymers, PANI has caught much attention by its diversiform configuration,[11] good stability,[12] unique mechanism of doping and extensive prospect of technical applications.[13−15]

By now, the electrical resistance response of PANI to different vapours such as moisture, methanol vapour and ethanol vapour has been studied.[16−24] Kahol *et al.*[21] reported that the existence of water molecules in PANI can reduce the boundary region between the "metallic islands" (where polymer chains are much ordered), thereby enhancing the conductivity of PANI. Tan *et al.*[17−19] found that methanol or water vapour can result in an increase in conductivity of emeraldine salt and the interaction between vapour and PANI was completely reversible. According to Pinto *et al.*,[22] the resistivity of metallic PANI film was shown to depend very sensitively on the presence of moisture. Tarachiwin *et al.*[23] also found that the specific conductivity of PANI films responded with positive increments upon exposure to water and ethanol, and the similar result was obtained by Zhou *et al.*[24] who explored the interaction between PANI nanotube pellets and water/ethanol molecules. Due to the sensibility to vapours and reversibility of interactions with vapours, PANI films, pellets, nanostructures and composites have been studied as promising candidates for gas/chemical sensors in recent years.[25−30]

However, the concentration of vapour or moisture in most published papers is usually not very high. In order to explore the influence of excessive liquid or solution on the conductivity of PANI films, in this paper, we studied the resistance changes of camphor sulfonic acid (CSA)-doped PANI films under exposure to excessive water, ethanol and nitric acid solution. Compared with PANI films doped with other protonic acids such as HCl, PANI–CSA film shows a relatively high electrical conductivity at room temperature ($\sim$ 200 S/cm), and its temperature dependence of conductivity has been reported in previous publications.[22,31,32]

*Project supported by the Program for New Century Excellent Talents in University of China (Grant No. NCET-07-0472) and the National Natural Science Foundation of China (Grant Nos. 10604038 and 10910101081).

†Corresponding author. E-mail: yunze.long@163.com

‡E-mail: qdwlxsx@163.com

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2. Experimental details

The CSA-doped PANI films were prepared by a "doping-dedoping-redoping" method.[31] Aniline monomer was distilled under reduced pressure. Other reagents, such as ammonium persulphate as oxidant, HCl and CSA as dopants, and NH_4OH as dedopant, were used as received materials. Highly conducting and soluble CSA-doped PANI was synthesized as follows. The PANI doped with HCl was first synthesized by a common method reported by MacDiarmid *et al.*,[33] and then converted into its emeraldine base form (EB) after being dedoped with 3-wt% NH_4OH for about 6 h. The resulting EB was further redoped with CSA by a method reported by Cao *et al.*[34] to prepare the soluble and conductive PANI–CSA/m-cresol solution. The PANI films of thickness about 18–26 μm were obtained by casting the solution onto a glass plate. After dried at room temperature in air for several days, the films were peeled off the glass substrate to form freestanding films.

A four-probe method was used to measure the conductivity of PANI films at room temperature. Figure 1 shows the schematic diagram of the standard four-probe method. A constant current was supplied between probes 1 and 4 and the resultant voltage was measured across the probes 2 and 3. All the probes

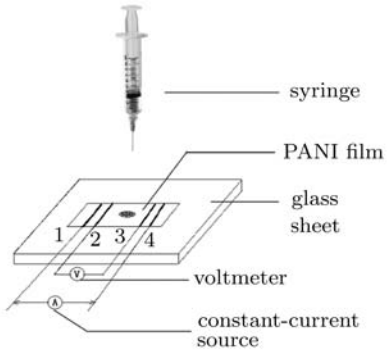


Fig. 1. A standard four-probe method to measure electrical resistance of PANI film.

(Cu wires) were fixed on the PANI film by highly conductive silver paste. The electrical resistance of the PANI film between the probes 2 and 3 is calculated from $R = V/I$, where V is the voltage, I is the supplied current. Several pieces of PANI–CSA films were used to measure the resistance changes under exposure to a drop ($\sim$15 μL) of water, ethanol and HNO_3 solution by syringe, respectively. The water and ethanol used were of analytical grade. The concentration of the HNO_3 solution was 0.985 wt%. All experiments were carried out under atmospheric conditions. The morphology of the PANI films was characterized by scanning electron microscopy (SEM, JSM-6390). The crystallinity degree of the PANI films was characterized by x-ray diffraction (XRD, MAC Science M18AHF with a CuK_α radiation).

3. Results and discussion

The electrical conductivity of the PANI film is about 200 S/cm at room temperature. Previous studies[21,32] have demonstrated that the microstructures and electronic transport properties of PANI films can be described by metallic islands model or inhomogeneous disorder model.[21,35–37] Namely, the polymer film is composed of ordered crystalline parts and disordered amorphous parts. The polymer chains in crystalline state are arranging in an orderly manner and have a higher electrical conductivity, but the polymer chains in amorphous state are disorderly arranged and show a lower conductivity. This model will help us to understand the electrical resistance response of PANI films to different vapours or liquids.

3.1. Effect of water

Figure 2(a) shows the electrical resistance vs. aging time for the response of PANI film to water. This curve indicates that there are three processes for the effect of water molecules on the film's resistance versus aging time.

First, the resistance ratio R/R_0 (R_0 is the original resistance value of the PANI film) falls from 1 to 0.988 in the first 30 seconds, as shown in Fig. 2(b) clearly. The decline of the resistance of the PANI film is due to the rise of the relative humidity in its surrounding. Jain *et al.*[38] studied the relationship of the resistance of conducting polymers and the relative humidity, and found that the resistivity of the conducting polymers was seen to reduce as the level of relative humidity was increased. We can use the metallic islands model to explain this phenomenon, a lower amount of water molecule entering the PANI film produce crosslink points to construct PANI chains and conducting channels between metallic islands where water molecules act as carriers to transfer charge from one chain to another.[21] The charge–carrier–transfer results in an increase in the interchain charge mobility from one metallic island to another, so it is equivalent to decrease the resistance of the amorphous state, and decrease the macroscopic resistance of the PANI film.

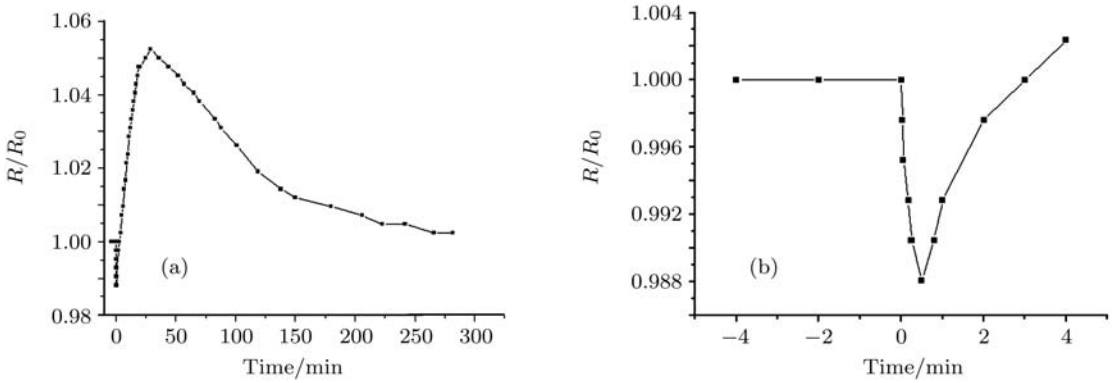


Fig. 2. (a) Electrical resistance vs. aging time for the response of PANI films to water. (b) The resistance response in the first 4 minutes. The resistance has been normalized.

On the other hand, excessive water causes a side effect (e.g., swelling or disordering effect[39]) for the conducting PANI film. Its volume will swell, as shown in Fig. 3. From the comparison between Figs. 3(a) and 3(b), we can find that the distance between the bulges of the PANI film surface after soaking in water obviously becomes larger than that for the dry PANI film. Some conducting channels in the amorphous regions or interfaces may be blocked by the excessive water molecules, which results in the increase of the film's resistance. This process lasts about half an hour, the resistance ratio R/R_0 of the PANI film raises to 1.052. This change is more obvious than that of decrease at the beginning.

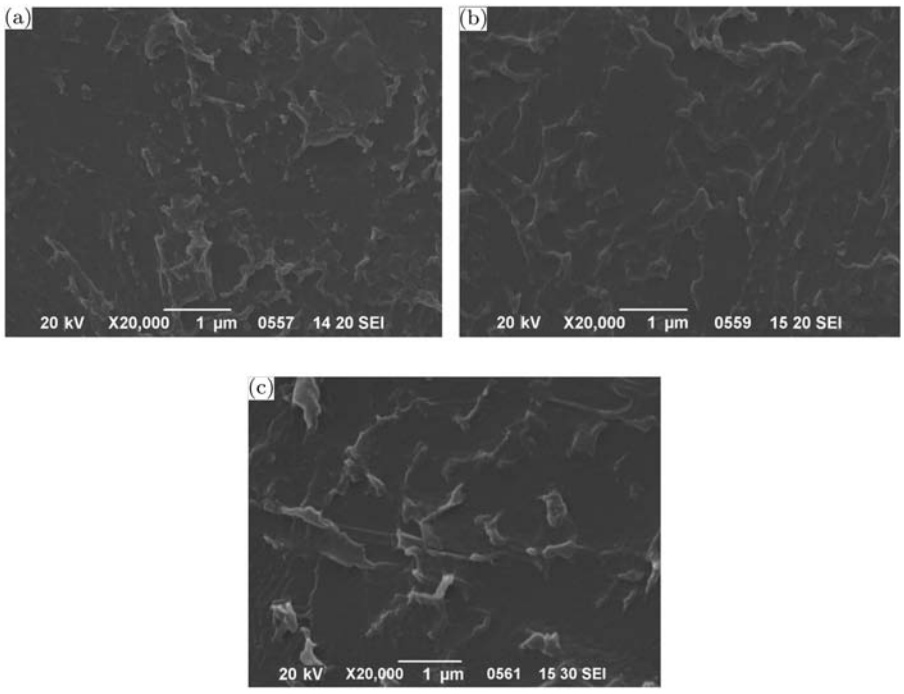


Fig. 3. The SEM images of the surfaces for (a) pure PANI film, (b) PANI film after soaking in water, and (c) PANI film after soaking in HNO_3 solution.

Since the PANI film is exposed to the air, the water molecules in the PANI may evaporate into atmosphere, resulting in changes of the water concentration and the volume of PANI film. Therefore, the side effect of excessive water which increases the resistance of the PANI film is weakened gradually, and then the resistance falls down. The slope of decline of the resistance ratio becomes smaller and smaller, and the resistance is down to the original value after about 5 hours.[16] Here it is noted that the x-axis in Fig. 2, in fact, corresponds to the change of water concentration. So, figure 2 also displays the influence of the

concentration of the solvents on the film's resistance.

3.2. Effect of ethanol

The resistance ratio R/R_0 of the PANI film rises sharply after the ethanol drop was dripped onto the PANI film, as shown in Fig. 4. Since the polarity of ethanol molecule is not weaker than that of water molecule, ethanol molecules enter the PANI film more easily and quickly than water molecules. Tarachiwin *et al.*[23] studied the Fourier transform infrared (FTIR) spectra of PANI films exposed to pure ethanol, and found that the PANI film exposed to ethanol, no new peak occurred in the FTIR spectrum, which suggested that ethanol molecules did not permanently change with the PANI emeraldine salt. The process of producing crosslink points to construct PANI chains and conducting channels is weak and ethanol molecule has a lower ability to cause the charge–carrier–transfer than water molecule.[23] However, the process that the resistance of amorphous regions is increased by volume expansion is much faster.[39] As a result, the resistance ratio R/R_0 of the PANI film increases from 1 to 1.413 in the first 1.1 min. Then, the resistance ratio R/R_0 falls to 1.008 quickly in the following 3 minutes, because the ethanol molecules are more easily evaporated into atmosphere than water molecules. From the comparison of the results shown in Figs. 2 and 4, it is obvious that the resistance of PANI film is more sensitive to ethanol than water.

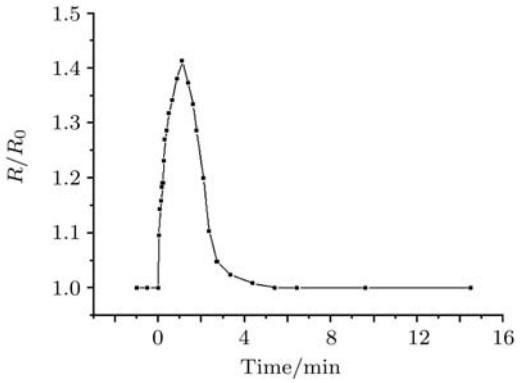


Fig. 4. Electrical resistance vs. aging time for the response of PANI film to ethanol.

3.3. Effect of HNO_3 solution

We also studied the electrical resistance response of PANI film to protonic acid solution. Figure 5 exhibits the electrical resistance vs. aging time at room temperature for response of PANI film to HNO_3 solution. The resistance of PANI film declines sharply in the first 2 minutes after the HNO_3 solution was dropped onto the film. The resistance ratio R/R_0 falls to 0.977. For comparison, the resistance ratio R/R_0 of PANI film exposed to water is only down to 0.988, as shown in Fig. 2. From this comparison we can find that the existence of protonic acid can more significantly reduce the resistance of PANI film due to two possible reasons. The first reason is similar to the first process for the effect of water molecules on the PANI–CSA film, as discussed above, a lower amount of water molecule entering the inside of PANI film produces crosslink points to construct PANI chains and conducting channels between metallic islands where water molecules act as carriers to transfer charge from one chain to another. The second reason is that the protonic acid entering into the PANI results in redoping, namely, protonation on some quinoid segments generates polarons which can conduct current in the polymer chains, therefore can improve the conductivity of PANI film.[40,41] Compared with the effect of water, we propose that the second reason leads to the fact that the resistance of the PANI film exposed to HNO_3 solution shows a larger decline.

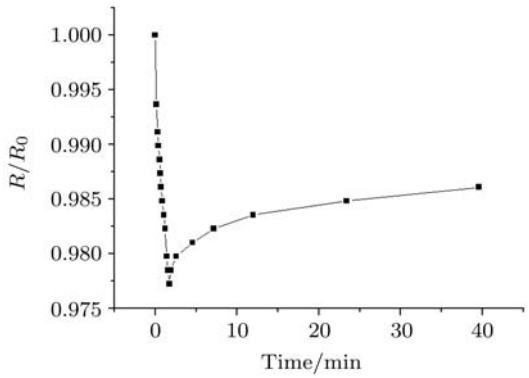


Fig. 5. Electrical resistance vs. aging time for the response of PANI film to HNO_3 solution.

Figure 5 also shows that the film's resistance increases gradually after 2 minutes. This transition is quite similar with the transition shown in Fig. 2(b). The possible reason is that excessive water molecules entering the PANI film, swell the film's volume (Fig. 3(c)), and enlarge the distance of PANI chains.[39] The effect of this process increases the resistance of the film. However, owing to the doping effect of the protonic acid, the resistance of the film exposed to HNO_3 solution is only increasing slowly, and is still much less than the original resistance even after 40 minutes. It is noted that the value of the resistance will rise to the original value finally after about 5 days' aging treatment at room temperature possibly due to the evaporation of water molecules and partly dedoping.

3.4. Further studies on microstructures of PANI films

Here we note that the resultant PANI films are not homogeneous. Some surface seems to be smooth (as shown in Fig. 3), but some surface seems to be a bit rough. The microstructures of the polymer films are dependent on the synthesis conditions, aging time, and other factors. For comparison, we show some other SEM images of the cross section (Fig. 6(a)) and the surface (Figs. 6(b) and 6(c)) for the PANI films. It is obvious that some crystal-like or granular structures were observed. The formation of these structures may be ascribed to the PANI crystallization.[11] It also should be noted that a porous structure (as shown in Fig. 6(d)) could be formed possibly due to the swelling effect if excessive water molecules penetrate the PANI film.

In addition, the crystallinity degree of the PANI–CSA films was characterized by XRD, as shown in Fig. 7. The XRD pattern shows that there are two crystalline diffraction peaks at 2θ around 19° and 25°. The XRD pattern indicates that the PANI–CSA film is partly crystalline but mainly amorphous. So, these results may exhibit evidence to the metallic islands model or inhomogeneous disorder model[21,32,35−37] of polymer films.

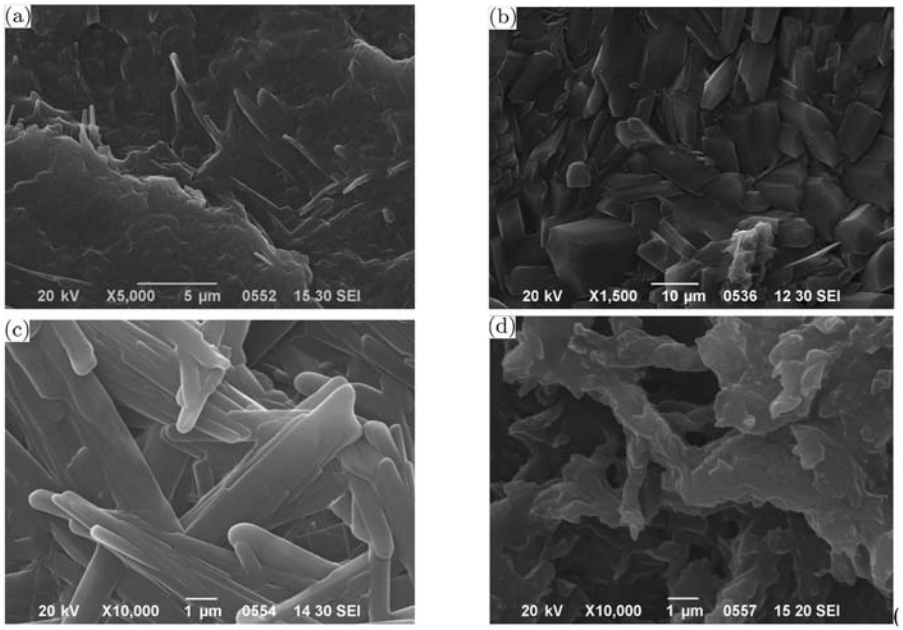


Fig. 6. The SEM images of the cross section (a) and the surface ((b) and (c)) for PANI films. (d) The SEM image of the surface of a PANI film after soaking in water.

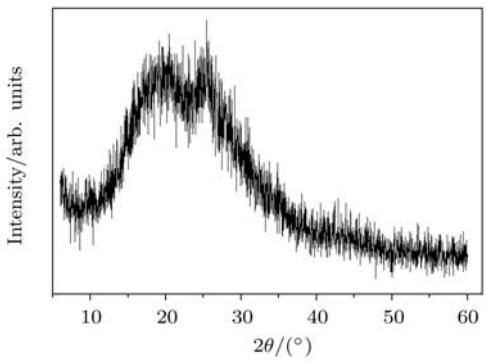


Fig. 7. The XRD patterns of the PANI films.

4. Conclusion

In summary, the influences of water, ethanol and HNO_3 solution on resistance response of polyaniline films have been studied under atmospheric conditions. The resistance response vs. aging time or concentration can be explained well from the viewpoint of interactions between PANI films and water, ethanol and HNO_3 solution. It was found that a lower amount of water molecules entering the PANI chains can decrease the film's resistance. The protonic acid in HNO_3 solution makes the film's resistance a much sharper decline than water because of the doping effect

of the protonic acid. Ethanol molecules do not permanently change with the PANI emeraldine salt and a lower ability to cause the charge–carrier–transfer than water molecules, so we do not observe the decrease of resistance. In addition, both excessive water and ethanol molecules entering into the film will increase the chain distance and swell the volume of the film, and thus make the film's resistance increasing. These results indicate that PANI films have potential application in chemical sensors.

Acknowledgement

The authors are grateful to Dr. Zhang Zhi-Ming (College of Chemistry and Chemical Engineering, Ocean University of China) for providing the PANI films.

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