Electrochemical Degradation of Polyfuran in Wet Acetonitrile and Aqueous Solutions

Xiao-Bo Wan, Liang Li, Jin-Bo He, Dong-Shan Zhou, Gi Xue, Tian-Wei Wang

Department of Polymer Science and Engineering, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

ABSTRACT: The degradation of polyfuran in a wet acetonitrile solution and in an aqueous solution has been investigated with a cyclic voltammetry technique, along with Fourier transform infrared and Fourier transform Raman spectroscopy techniques. Infrared spectroscopy shows that the main defects that exist in polyfuran after cycling in dried acetonitrile are mainly saturated C—H structures, whereas those after cycling in an aqueous solution are mainly carbonyl groups in the polymer chain. This may be because polyfuran can undergo degradation through a crosslinking mechanism in a dried acetonitrile solution, whereas in an aqueous solution, it undergoes degradation through a nucleophilic attack mechanism. Raman spectroscopy shows that not all the furan rings are involved in the degradation process, although the electrochemical activity of polyfuran is totally lost in an aqueous solution after only one cycle. The sites that are sensitive to the degradation process may be the electrochemically active sites, that is, the positively charged sites in polyfuran chains. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3160–3165, 2002

Key words: degradation; FTIR; Raman spectroscopy

INTRODUCTION

Conducting polymers have many potential applications, such as new materials for battery electrodes,[1] gas sensors,[2] biological sensors,[3] ion seiving,[4] corrosion protection,[5] and microwave shielding.[6] However, the stability of conducting polymers seems to be the main limiting factor in their practical applications. Therefore, their degradation properties under different conditions have been studied extensively.[7] Most studies have been focused on the overoxidation of conventional conducting polymers, such as polypyrrole,[8–14] polythiophene,[15–17] and polyaniline.[18–20] The degradation of these polymers always takes place at potentials higher than that for the reversible electrochemical process.

Polyfuran (PFu), because of the great difficulty of its synthesis, is rarely characterized. Recently, we successfully prepared PFu in a binary solvent system containing boron trifluoride ethyl ether (BFEE) and additional ethyl ether[21] and found that when both were cycled in a similar potential range, PFu underwent electrochemical deactivation rapidly in an aqueous solution but was electroactive in an acetonitrile (MeCN) solution. In this study, experiments were conducted to determine the role of water in the deactivation of PFu.

EXPERIMENTAL

Materials

Furan (Fluka, Buchs, Switzerland; 99%) was distilled under an atmosphere of N_2 twice before use. Ethyl ether was dried and distilled in the presence of sodium. BFEE was freshly distilled before use. Tetrabutylammonium tetrafluoroborate (TBABF$_4$) was dried in vacuo. MeCN was purified according to the literature.[22]

Electrochemical experiments

The electrochemical examinations and polymerizations were performed in a one-compartment, three-electrode cell with an EG&G M273 potentiostat (Princeton, NJ) under the control of a computer. The galvanostatic method was used for the electrochemical polymerizations. All the films were deposited at a current density of 1 mA/cm^2, and the thickness of the deposited films was controlled by the electric charge passed during film growth (the thickness of the film prepared at a current density of 1 mA/cm^2 for 1 h was about 10 μm). Electrochemical measurements were carried out with a platinum disc (0.5-mm-diameter) electrode that was polished and cleaned, as mentioned

earlier, before each experiment. Ag/AgCl was used as the reference electrode, and TBABF$_4$ was used as an electrolyte in organic solvents in all cases. Each solution containing furan was degassed by the bubbling of dry argon before the experiment, and a slight argon overpressure was maintained during the experiment.

Cyclic voltammetry (CV) experiments of PFu films in aqueous solutions containing sodium tetrafluoroborate (NaBF$_4$) and in MeCN solutions containing TBABF$_4$ and trace amounts of water (MeCN/H$_2$O = 100:1, 20:1, or 10:1 v/v) were recorded. All the PFu films used in CV tests were deposited onto Pt disc electrodes at a current density of 1 mA/cm^2 for 600 s.

Spectroscopy

To investigate the influence of water on the possible structural changes in PFu during the redox process, we electrochemically cycled all the PFu films subjected to the spectroscopy examination, in both dried MeCN and wet MeCN solutions and in the aqueous solution, for 100 cycles. All the Raman spectra were measured with an RFS-100 spectrometer (Bruker, Karlsruhe, Germany) with 1064-nm excitation, and the power of the laser was fixed at 100 mW. The PFu films used in Raman tests were deposited onto an Au electrode (with a 3-mm diameter) for 10 min. Fourier transform infrared (FTIR) spectra were recorded on an IFS-66V spectrometer (Bruker) in vacuo. PFu films used in FTIR tests were deposited onto a stainless steel electrode (area = 1.5 × 2 cm^2) at a current density of 1 mA/cm^2 for 30 min, and they were then stripped off from the electrode, washed with acetone, and dried in vacuo at room temperature after CV scans.

RESULTS AND DISCUSSION

Retention of the redox activity of PFu in wet MeCN solutions

The synthesis of PFu with an electrochemical method in conventional solvents always encounters unconquerable difficulties because of the extremely high oxidation potential of furan, the low aromaticity of the furan ring, and its sensitivity toward acids and bases. Recently, we successfully prepared PFu in a novel binary solvent system containing BFEE and additional ethyl ether with a conventional anodic coupling method. The obtained film showed a well-defined conjugated structure and fairly good mechanical strength.[21]

PFu shows fairly good long-term stability of the redox activity in organic solvents such as MeCN; as shown in Figure 1(A), the peak separation of anodic and cathodic peaks is small. The retention of the redox activity of PFu after cycling in MeCN for 100 times is
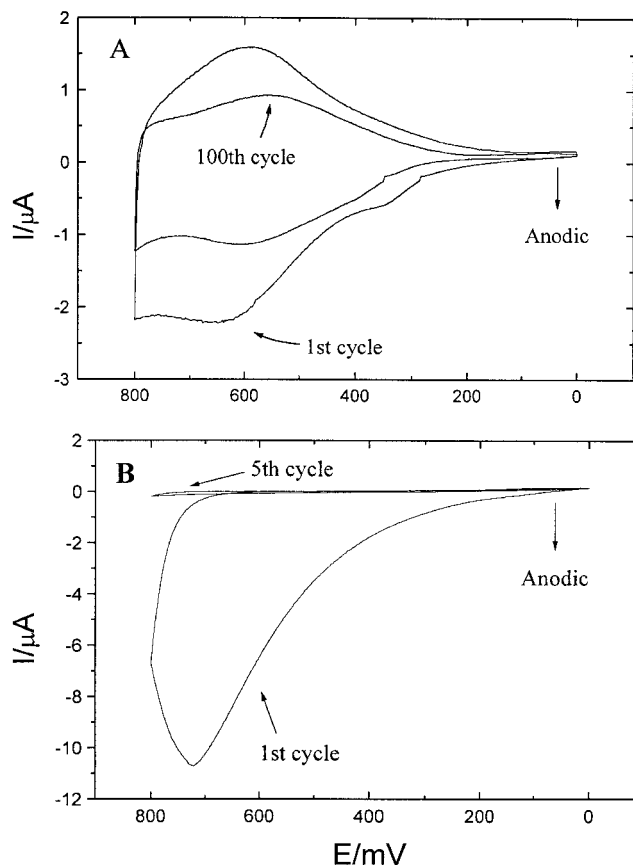

Figure 1 (A) First and 100th CV scans of PFu in an MeCN solution containing 0.05M Bu$_4$NBF$_4$ and (B) first and fifth CV scans of PFu in an aqueous solution containing 0.1M NaBF$_4$. The scan rate was 20 mV/s, and the reference electrode was Ag/AgCl.

about 51.3%. However, when PFu is cycled in an aqueous solution, it shows a very large anodic peak current around 0.7 V, but no reversible cathodic peak current is observed [Fig. 1(B)]. This implies that PFu undergoes an irreversible anodic oxidation process, and the redox activity is almost totally lost during this process. This process is independent of the pH value of the aqueous solution, and this implies that water molecules are involved in the process.[21]

The CV of PFu in MeCN/H$_2$O solutions with different volume ratios was studied. Figure 2(A–C) shows the retention of the redox activity of PFu in wet MeCN solutions containing different amounts of water. The volume ratio of MeCN to water is set to 100:1, 20:1, and 10:1, respectively. It is evident that the anodic current in the first redox cycle increases with the increasing amount of water in the MeCN solutions. About 50% of the redox activity of PFu remains after 100 cycles in a 100:1 MeCN/H$_2$O solution, after 40 cycles in 20:1 MeCN/H$_2$O, and after 15 cycles in 10:1 MeCN/H$_2$O, respectively. This indicates that the losing rate of redox activity increases with the increasing

amount of water in MeCN solutions. Another feature that can be seen in Figure 2 is the change in the anodic peak current I_{pa} in different solutions. When the amount of water in the solution increases, the current I_{pa} of overoxidation increases. This implies that the oxidation process becomes more irreversible, and this may be caused by the destruction of conjugated structures.
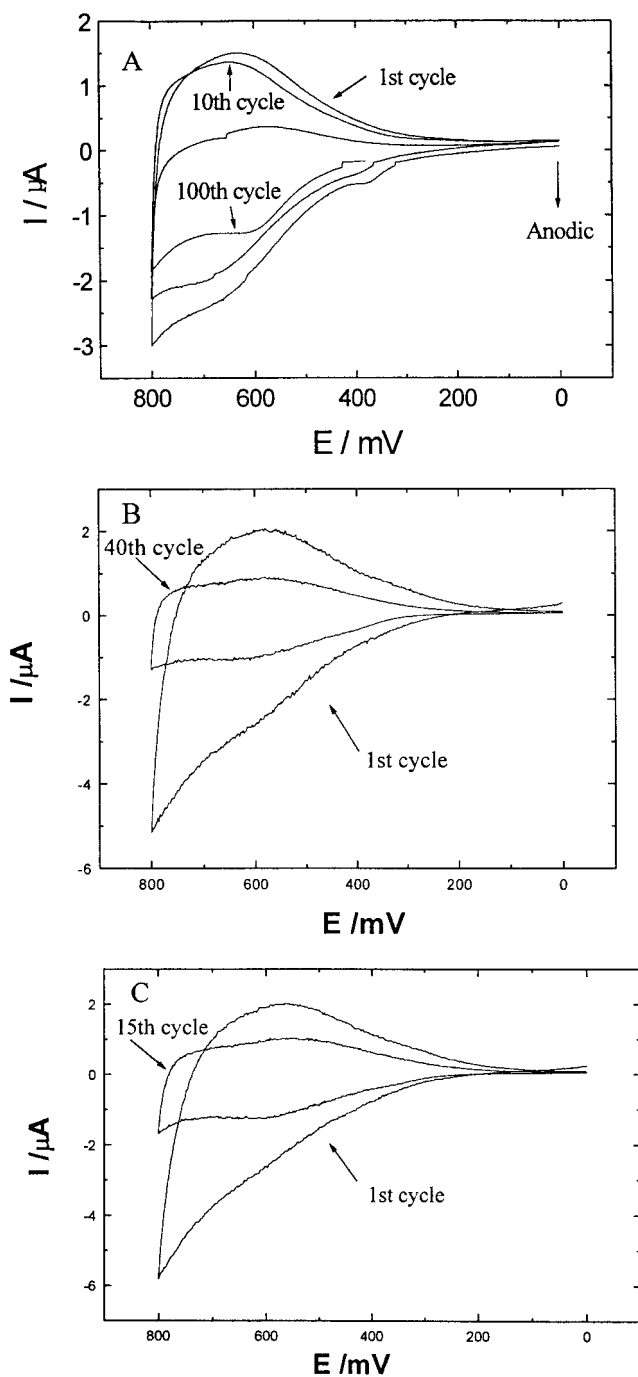

Figure 2 CV scans of PFu in MeCN/H_2O with different volume ratios: (A) 100:1, (B) 20:1, and (C) 10:1. The scan rate was 20 mV/s, and the reference electrode was Ag/AgCl.
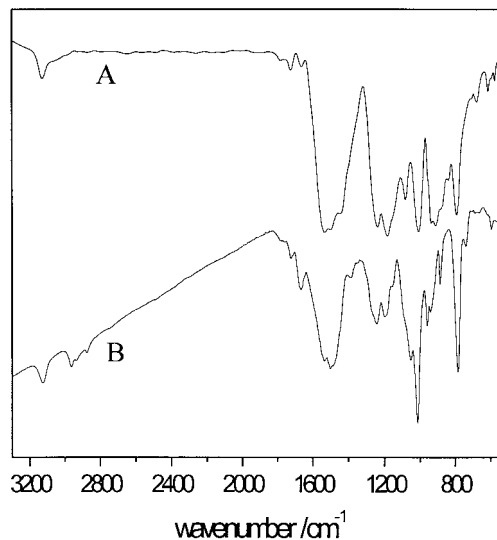

Figure 3 FTIR spectra of (A) as-prepared PFu and (B) PFu electrochemically cycled in a dried MeCN solution.

Spectroscopy proof of the destruction of the conjugated structure of PFu

Figure 3 shows the infrared spectra of as-prepared PFu and PFu cycled in dried MeCN solutions. It can be seen clearly in Figure 3(A) that the as-prepared PFu film contains a neglected saturated structure, as indicated by the extremely weak absorption in the saturated C—H stretching region. However, the weak absorption around 1700 cm^{-1} and another at 1665 cm^{-1} still show that some defects do exist in the as-prepared PFu film.[21] However, the intensity of the absorption around 2900 cm^{-1} increases after cycling, whereas that of the absorption around 1700 cm^{-1} remains almost the same. When the PFu is cycled in wet MeCN solutions, degradation becomes more complicated. Figure 4 illustrates the FTIR spectra of PFu cycled in wet MeCN solutions 100 times, along with the spectra of as-prepared PFu and PFu cycled in aqueous solutions 100 times. What is most significant is that the intensity of the absorption located at 1665 cm^{-1} increases gradually with an increasing amount of water in the solutions. The intensity of the absorption at 1710 cm^{-1} remains very weak when PFu is cycled in wet MeCN solutions and increases sharply when PFu is cycled in aqueous solution. However, the intensity of the aliphatic C—H stretching absorption located around 2900 cm^{-1} increases when the volume ratio of MeCN/ H_2O decreases from 100:1 to 20:1, as shown in Figure 4(B,C). It decreases when the water content in the MeCN solution is further increased to 10:1 and decreases further when PFu is electrochemically cycled in an aqueous solution, as shown in Figure 4(D,E), respectively.

It is well known that the degradation of a conducting polymer is a complex process that is related to the
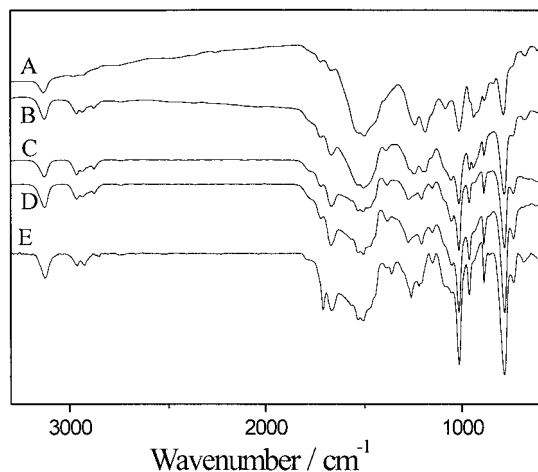
Figure 4 FTIR spectra of (A) as-prepared PFu, (B–E) PFu electrochemically cycled in MeCN/H$_2$O with different volume ratios (100:1, 20:1, and 10:1, respectively) 100 times, and (E) PFu cycled in an aqueous solution 100 times.

nature of the conducting polymer itself, the synthetic conditions, the nature of the solvent, and the counteranions. However, the mechanism of degradation is not clear yet. For polypyrrole and polythiophene, the investigation of their degradation was mainly focused on the extended potential range, in which the reversible redox process and the irreversible degradation process could be distinguished clearly. For example, the degradation of polypyrrole always takes place at potentials higher than 0.7 V versus saturated calomel electrode (SCE), whereas the reversible redox process of polypyrrole happens around 0 V versus SCE.[8–14] In the case of PFu, FTIR spectra (Fig. 3) show that when PFu is cycled in a dried MeCN solution from 0 to 0.8 V versus Ag/AgCl, saturated C—H structures are produced in the polymer chains. The degradation process takes place in the same potential range in which the reversible redox process occurs. This implies that the degradation of conjugated structures occurs when PFu is oxidized from its undoped state (insulating state) to a doped state (conducting state). The loss of the electrochemical activity of PFu in MeCN solutions, as shown in Figure 1(A), is sure to be related to the production of saturated C—H structures in the polymer chains.

It is also certain that the absorptions at 1665 and 1710 cm^{-1} reflect the defect existing in the PFu chains, and the absorption at 1710 cm^{-1} presents the C=O stretching vibration. This observation has already been made in studies on polypyrrole[10–12] and was ascribed to the formation of carbonyl groups at the β position of pyrrole rings with the oxidation of the polymer. Because there are no reports on PFu degradation, we speculate it is also true for PFu. However, the assignment of the absorption at 1665 cm^{-1} is more difficult. It may be attributed to the stretching vibra-

tion of isolated C=C in the polymer chain. However, it has been reported that the carbonyl peak observed in 1H-pyrrol-3(2H), the tautomeric form of 3-hydroxylpyrole, is at 1675 cm^{-1}.[23] It is more likely that this peak in PFu is the characteristic absorption of 3-hydroxyfuran. When PFu is reduced in ammonia, this peak is very strong,[21] but when PFu is electrochemically cycled in MeCN solutions, this peak is weakened, as shown in Figure 3. It seems that the appearance of this absorption is also related to the attack of water molecules on the positively charged polymer chains.

It may be deduced from these results that the degradation of PFu in dried MeCN solutions mainly produces saturated C—H structures in the polymer chains, whereas the degradation of PFu in wet MeCN solutions results in more C=O structures and fewer saturated C—H structures in the polymer chains. When PFu is cycled in aqueous solutions, this phenomenon becomes more clear. This implies that there may be two mechanisms in the degradation of PFu: crosslinking and attack by nucleophilic species such as water molecules.[7] In dried MeCN solutions, because MeCN is a weak nucleophilic medium, the overoxidative degradation of PFu caused by the crosslinking mechanism prevails over the nucleophilic mechanism, resulting mainly in the saturated C—H structures. In wet MeCN solutions, the overoxidative degradation by the nucleophilic mechanism gradually obtains the leading position with increasing amounts of water in the solutions because of the extremely strong nucleophilic property of water molecules, resulting in the

A

B
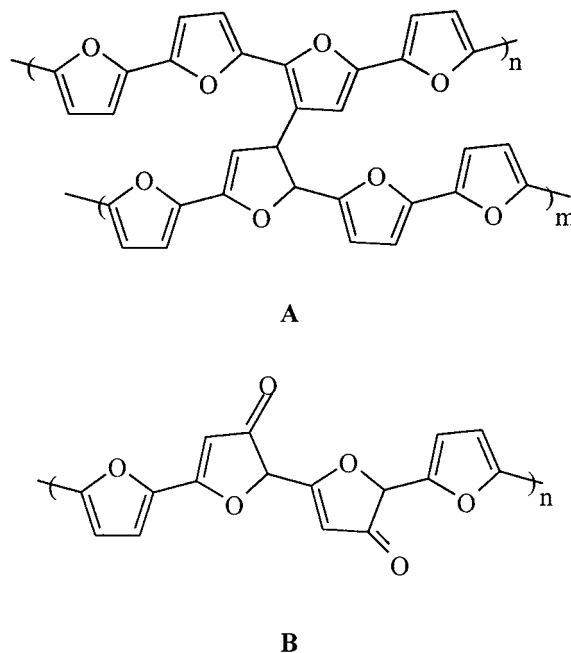
Scheme 1 Possible defects in PFu cycled in (A) a dried MeCN solution and (B) an aqueous solution.
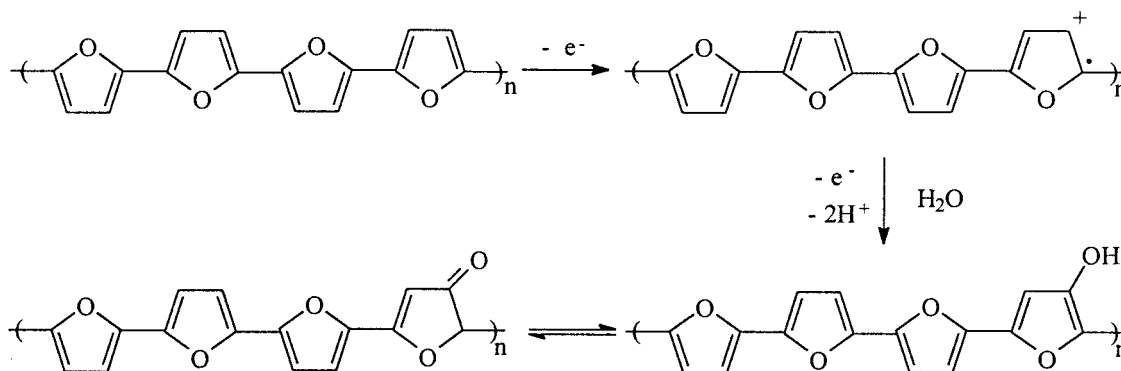
Scheme 2 Possible degradation mechanism of PFu cycled in an aqueous solution.

ketone structure. The possible byproducts produced by the two degradation processes may be described as shown in Scheme 1(A,B).

In the analysis of the degradation mechanisms of other conducting polymers such as polypyrrole, it is widely accepted that overoxidation takes place only at high potentials at which polypyrrole has already been oxidized to a bipolaron structure, and the resulting overoxidation product may be pyrrolinone. However, in the case of PFu, the overoxidation process happens at the same time as the oxidation process of the polymer chains. That is, the attack of water molecules takes place at the same time at which the first electron is removed from the polymer chains, and this may be due to the low aromaticity of the furan ring in comparison with that of pyrrole and thiophene. The possible process may be described as shown in Scheme 2.

Raman spectroscopy

Raman spectra of the as-prepared PFu and PFu cycled in wet MeCN solutions together with those of PFu cycled in aqueous solutions are given in Figure 5. The peak located around 1570 cm^{-1}, which is
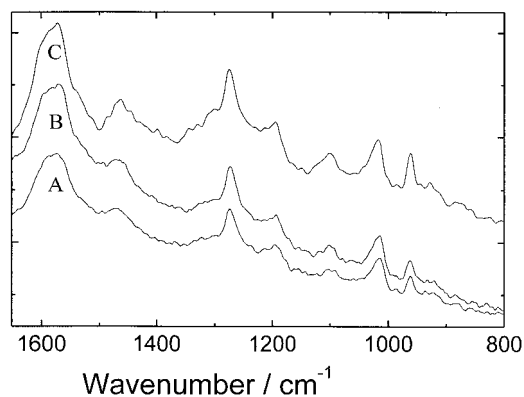
related to the C=C stretching vibration, is always considered characteristic of the effective conjugation length of conducting polymers. The redshift of this peak implies a longer conjugation length, whereas the blueshift of this peak implies a shorter conjugation length. However, even if the PFu film is cycled in an aqueous solution 100 times, this peak shifts little. It seems that although the electrochemical activity is totally lost, most of the conjugation structures in PFu remain undestroyed. This may be because the overoxidation takes place only at the electrochemically active sites, which may be positively charged sites (polaron) in the chain, and not all the furan rings are attacked by water molecules. Because PFu shows a strong localization at the site of the electronic perturbation (i.e., the delocalization of the electrons along the polymer backbone is restricted to several furan rings), the introduction of carbonyl groups to the electrochemically active sites does not bring so many changes to the effective conjugation length.

CONCLUSIONS

The electrochemical activity of PFu is partly lost in dried MeCN solutions and is totally lost in aqueous solutions. FTIR shows that it is controlled by two different degradation mechanisms: crosslinking in MeCN solutions and nucleophilic attack in aqueous solutions. Raman spectra show that most of the conjugated structures in PFu remain undestroyed even when PFu is cycled in an aqueous solution 100 times. This may indicate that only positively charged sites in polymer chains are attacked during the electrochemical process.

Figure 5 Fourier transform Raman spectra of (A) as-prepared PFu, (B) PFu cycled in MeCN/H$_2$O (20:1 v/v) 100 times, and (C) PFu cycled in an aqueous solution 100 times.

References

1. Skotheim, T. A. Handbook of Conducting Polymers; New York, 1986; p 501.

2. Sotzing, G. A.; Briglin, S. M.; Grubbs, R. H.; Lewis, N. S. Anal Chem 2000, 72, 3181.
3. Bartlettl, P. N.; Birkin, P. R. Synth Met 1993, 61, 15.
4. Shinohara, H.; Aizawa, M.; Shirakawa, H. J Chem Soc Chem Commun 1986, 87.
5. Mirmohseni, A.; Oladegaragoze, A. Synth Met 2000, 114, 105.
6. Buckley, L. J.; Eashov, M. Synth Met 1996, 78, 1.
7. Pud, A. A. Synth Met 1994, 66, 1.
8. Christensen, P. A.; Hamnett, A. Electrochim Acta 1991, 36, 1263.
9. Qian, R.; Qiu, J.; Yan, B. Synth Met 1986, 14, 81.
10. Beck, F.; Braun, P.; Oberst, M. J Phys Chem 1987, 91, 967.
11. Beck, F.; Barsch, U.; Michaelis, R. J Electroanal Chem 1993, 351, 169.
12. Novak, P.; Rasch, B.; Vielstich, W. J Electrochem Soc 1991, 138, 3300.
13. Zotti, G.; Schiavon, G.; Berlin, A. Synth Met 1989, 28, 183.
14. Ghosh, S.; Bowmaker, G. A.; Cooney, R. P.; Seakins, J. M. Synth Met 1998, 95, 63.
15. Bukowska, J.; Jakowska, K. Synth Met 1990, 35, 143.
16. Wang, S.; Tanaka, K.; Yamabe, T. Synth Met 1989, 32, 141.
17. Harada, H.; Fuchigami, T.; Nonaka, T. J Electroanal Chem 1991, 303, 139.
18. Kobayashi, T.; Yoneyama, H.; Tamura, H. J Electroanal Chem 1984, 161, 419.
19. Kitani, A.; Kaya, M.; Yoshikawa, K.; Sasaki, K. Synth Met 1987, 18, 341.
20. Yang, H.; Bard, A. J. J Electroanal Chem 1992, 339, 423.
21. Wan, X.; Yan, F.; Jin, S.; Liu, X.; Xue, G. Chem Mater 1999, 11, 2400.
22. Walter, M.; Ramaley, L. Anal Chem 1973, 45, 165.
23. Atkinson, R. S.; Bullock, E. Can J Chem 1963, 41, 625.