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# Electrocatalytic reduction of nitrite using Dawson-type tungstodiphosphate anions in aqueous solutions, adsorbed on a glassy carbon electrode and doped in polypyrrole film

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## Abstract

The electrochemical behavior of Dawson-type  $P_2W_{18}O_{62}^{6-}$  adsorbed on a glassy carbon electrode and doped in a polypyrrole film electrode was described. These modified electrodes all display catalytic activity for nitrite reduction, either in acid solutions or in  $pH > 4.0$  solutions.

*Keywords:* Tungstodiphosphate; Nitrite; Electrocatalysis; Polypyrrole film electrode

## 1. Introduction

The electroreduction of nitrite usually requires a large overpotential at most electrode surfaces, but various transition-metal complexes were proved to be efficient electrocatalysts for nitrite reduction [1–4]. The transition-metal usually acts as an active site to react with  $NO_2^-$  or  $HNO_2$  forming several reactive intermediates including metal nitrosyl complexes, etc. Some of them were radical ones which always cause degradation of the organic ligands that surround the active site of the catalysts through their oxidation. Therefore, more robust catalysts are desired.

A series of totally inorganic complexes, transition-metal-substituted heteropolytungstates, which are capable of delivering multiple elec-

trons to a substrate so as to avoid radical intermediate formation and thus are more inert toward oxidizing environments, were designed to catalyze the reduction of nitrite [5]. However, these catalysts are difficult to be incorporated on the electrode surface [6] and their application is limited. Recently, unsubstituted parent heteropolyanions and lanthanide heteropoly complexes were found to be a system of robust catalysts for electroreduction of nitrite, and all of them are easy to be incorporated on the electrode surface [7,8a,8b]. The mechanism for electrocatalytic reduction of nitrite with parent heteropolytungstates as catalysts is proposed [8b] which is different from that with transition-metal complexes as catalysts. Especially for heteropolytungstate compounds as catalysts, unique catalytic activities are presented. A different catalytic behavior was observed for  $P_2W_{18}O_{62}^{6-}$  in solutions of  $pH < 3.0$  and  $pH > 3.0$ , or in

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aqueous solution and incorporated on the electrode surface.

These differences are attributed to the electrochemical behavior of  $P_2W_{18}O_{62}^{6-}$  changing with environment. The conversion between the one- and two-electron redox waves usually occurs with solution conditions.

## 2. Experimental section

### 2.1. Materials

The parent unsubstituted heteropolytungstate  $\alpha\text{-K}_6P_2W_{18}O_{62} \cdot 14H_2O$  was prepared as described previously [9]. These compounds were recrystallized twice from water before use. Pyrrole was used after further purification. Doubly distilled water was used in all experiments. All other chemicals were reagent grade and used as received. Fresh  $NaNO_2$  and  $P_2W_{18}O_{62}^{6-}$  solutions were prepared daily. Buffer solutions for  $pH > 3.0$  consist of a 0.1 M solution of  $CH_3COOH/CH_3COONa$  mixtures, and for  $pH < 3.0$ , 0.1 M  $H_2SO_4/Na_2SO_4$  mixtures.

### 2.2. Apparatus and procedures

A combination of PARC Model 370 electrochemical system (Model 173 potentiostat, Model 175 universal programmer and Model 179 Digital Coulometer, U.S.A.) and a Model Series 60000 X–Y Recorder (Gould Electronics, manufactured in China) was used to record general cyclic voltammograms under argon in a conventional two-compartment cell with a glassy carbon ( $12.6 \text{ mm}^2$ ) working electrode, a platinum wire counter electrode and an  $Ag/AgCl$  reference electrode (saturated with potassium chloride).

The working electrodes were polished with  $0.3 \mu\text{m}$  alumina and washed by sonication for two minutes in doubly distilled water before use. A polypyrrole film doped with  $P_2W_{18}O_{62}^{6-}$  on a glassy carbon (GC) electrode was prepared as previously described [10].

The pretreatment of GC is necessary before  $P_2W_{18}O_{62}^{6-}$  is directly adsorbed on a GC electrode surface as described previously [11]. A GC electrode was anodized at the potential of +2.0 V for 30 s in 2 M  $H_2SO_4$  solution, and then transfer to 2 M  $H_2SO_4$  containing 10 mM  $P_2W_{18}O_{62}^{6-}$  for potential cycling.

All experiments were carried out at ambient temperature. Formal potentials were estimated as the average of the anodic and cathodic peak potentials which are quoted with respect to an  $Ag/AgCl$  reference electrode.

## 3. Results and discussion

### 3.1. Electrochemical behavior of $P_2W_{18}O_{62}^{6-}$ in aqueous solution before and after addition of $NO_2^-$

The polarographic and cyclic voltammetric behavior of  $P_2W_{18}O_{62}^{6-}$  was described previously [10,12–14].  $P_2W_{18}O_{62}^{6-}$  anions are stable in solution of  $pH < 6.5$ . The cyclic voltammograms of Fig. 1 show the different behavior of  $P_2W_{18}O_{62}^{6-}$  in 0.05 M  $H_2SO_4$  and pH 6.0 solutions. The voltammograms of  $P_2W_{18}O_{62}^{6-}$  at  $pH < 3.0$  consist of two reversible one-electron waves, followed by two reversible two-electron waves (Fig. 1A). However, at  $pH > 4.0$ , four reversible

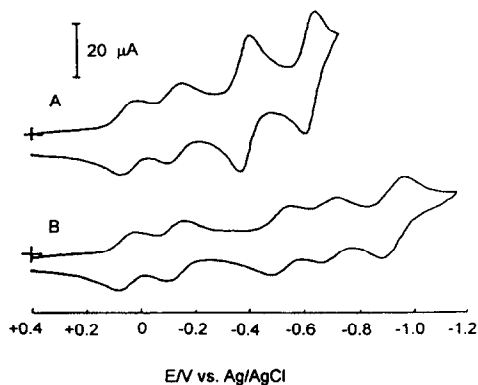


Fig. 1. Cyclic voltammograms of 1 mM  $P_2W_{18}O_{62}^{6-}$  (A) in 0.05 M  $H_2SO_4$ , (B) in solution of pH 6.0 at a glassy carbon electrode. Scan rate:  $20 \text{ mV s}^{-1}$ . Supporting electrolyte: 0.1 M  $Na_2SO_4$  and 0.1 M  $CH_3COOH + CH_3COONa$ .

one-electron waves followed by a two-electron wave appear (Fig. 1B). The plots in Fig. 2 give us the effect of pH on each peak potential. We can conclude that the two-electron redox process is accompanied by two protons, and pH has no effect on one-electron waves. This result is the same as that obtained by the polarographic method [12].

With addition of nitrite to a solution of  $P_2W_{18}O_{62}^{6-}$ , there are remarkable changes in the voltammetry of  $P_2W_{18}O_{62}^{6-}$  as shown in Fig. 3. At pH < 3.0 (Fig. 3A–E), the cathodic peak current of the first wave (most positive) is enhanced while its anodic counterpart is greatly diminished. The highest response appeared in 0.05 M  $H_2SO_4$  solutions (Fig. 3D). As the pH increases, the enhancement of the current at potentials corresponding to the  $P_2W_{18}O_{62}^{6-}/P_2W_{18}O_{62}^{7-}$  couple decreases (Fig. 3E and F). For example, at pH > 3.0, the addition of nitrite is virtually no effect on the more

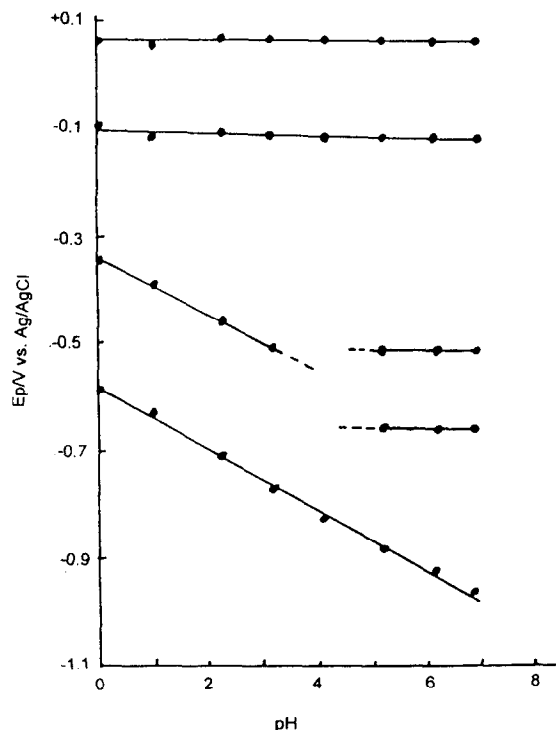


Fig. 2. Relationship between peak potential and pH. Supporting electrolyte as in Section 2.

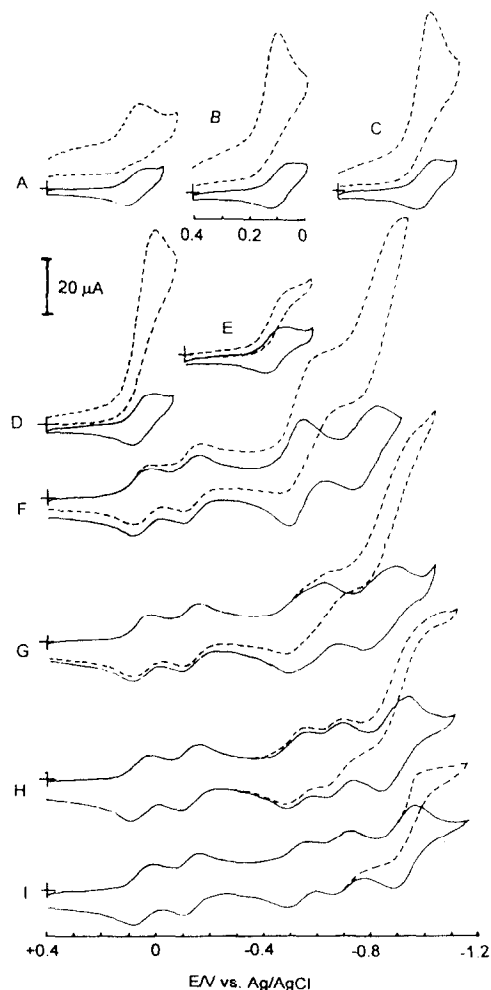


Fig. 3. Cyclic voltammograms of 1 mM  $P_2W_{18}O_{62}^{6-}$  before (—) and after (---) addition of 4 mM  $NO_2^-$  at a glassy carbon electrode in solution of (A) 2 M  $H_2SO_4$ , (B) 1 M  $H_2SO_4$ , (C) 0.5 M  $H_2SO_4$ , (D) 0.05 M  $H_2SO_4$  + 0.1 M  $Na_2SO_4$ , (E) pH = 2.0, (F) pH 3.0, (G) pH 4.0, (H) pH 5.0, (I) pH 6.0. Scan rate:  $20 \text{ mV s}^{-1}$ . Supporting electrolyte as in Section 2.

positive four cathodic waves (Fig. 3G–I). However, the fifth cathodic wave that appears at the most negative potential is significantly enhanced (Fig. 3G–I) so that the reduction of nitrite appears to be catalyzed by the multiply, but not the singly reduced form of tungstodiphosphates at pH > 3.0 solutions.

Fig. 4A shows that the current is increased with stepwise addition of nitrite. However, the current is not linearly dependent on the nitrite concentration (Fig. 4B). But in pH > 3.0 solu-

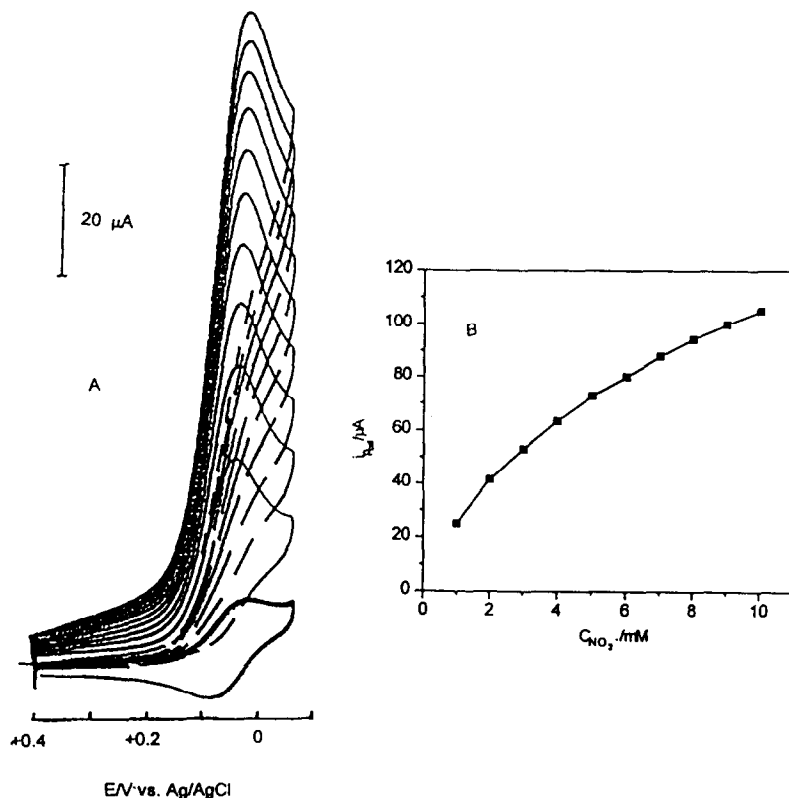


Fig. 4. (A) Cyclic voltammograms of 1 mM  $P_2W_{18}O_{62}^{6-}$  after addition of nitrite: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 mM (from lower to higher) at a glassy carbon electrode. (B) Relationship between catalytic current and nitrite concentration.

tions, the catalytic current increasing with step-wise addition of nitrite is proportional to the nitrite concentration as shown in Fig. 5.

### 3.2. Electrochemical behavior of $P_2W_{18}O_{62}^{6-}$ adsorbed on a GC electrode before and after addition of nitrite

Although good catalytic activity for nitrite reduction was achieved in aqueous solution, the catalysts only modified on an electrode surface are suitable to be extensively applied. Therefore, the modified electrode with  $P_2W_{18}O_{62}^{6-}$  directly adsorbed on an electrode surface was prepared. Fig. 6 gives us cyclic voltammograms of  $P_2W_{18}O_{62}^{6-}$  adsorbed on a GC electrode surface. Four couples of redox waves appeared (Fig. 6A) as in Fig. 1A for a just finished modified electrode. However, the first wave is not as high as the second one, one day later, the

first wave disappeared, only three couples of waves left (Fig. 6B) corresponding to two-electron, two-proton redox processes. However, there are two couples of one-electron redox waves and two couples of two-electron redox waves for  $P_2W_{18}O_{62}^{6-}$  in homogeneous solutions under the same conditions (2 M  $H_2SO_4$ ), namely, two one-electron redox waves were easily changed to one two-electron redox wave for  $P_2W_{18}O_{62}^{6-}$  adsorbed on the electrode. However, this film is easy to be destroyed by decreasing acidity and increasing pH even within the stable pH range of  $P_2W_{18}O_{62}^{6-}$ . Therefore, it is difficult to investigate the electrocatalytic reduction of nitrite on such modified electrode in solutions of  $pH > 3.0$ , so 2 M  $H_2SO_4$  was used in the following experiments.

Although the electrochemical behavior of  $P_2W_{18}O_{62}^{6-}$  adsorbed on a GC electrode is different from that in homogeneous solutions, elec-

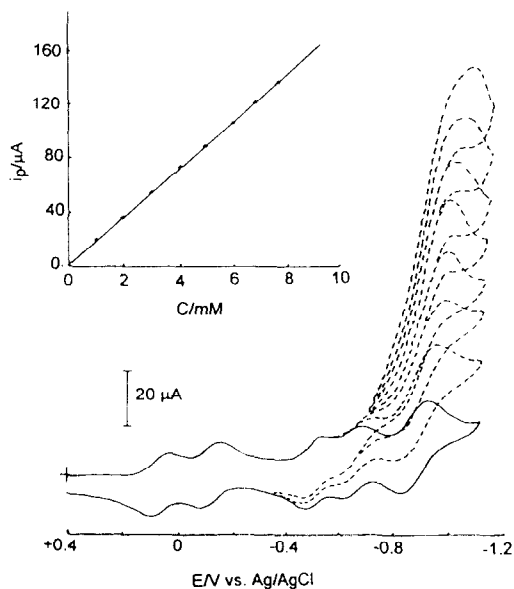


Fig. 5. Cyclic voltammograms of 1 mM  $P_2W_{18}O_{62}^{6-}$  in pH 5.0 solution before (—) and after (---) addition of nitrite 1, 2, 3, 4, 5, 6, 7 mM (dotted line, from lower to higher). Scan rate:  $20 \text{ mV s}^{-1}$ . Inset graph: Relationship between catalytic current and nitrite concentration.

troreduction of nitrite can also be catalyzed by  $P_2W_{18}O_{62}^{6-}$  adsorbed on a GC electrode in acid solutions, and different catalytic behavior was presented as shown in Fig. 7. Only low response appears for nitrite at the potential of  $-0.3$  to  $-0.4 \text{ V}$  on a bare glassy carbon electrode (Fig. 7A) whereas the enhanced current was observed on a GC electrode modified with  $P_2W_{18}O_{62}^{6-}$  so that the reduction of nitrite appeared to be cat-

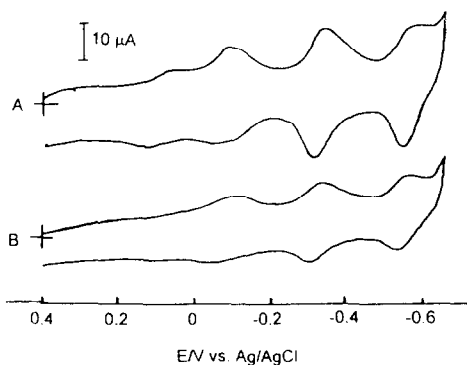


Fig. 6. Cyclic voltammograms of  $P_2W_{18}O_{62}^{6-}$  adsorbed on a pretreated glassy carbon electrode in  $2 \text{ M H}_2\text{SO}_4$  solution (A) just after modified (B) one day later. Scan rate:  $20 \text{ mV s}^{-1}$ .

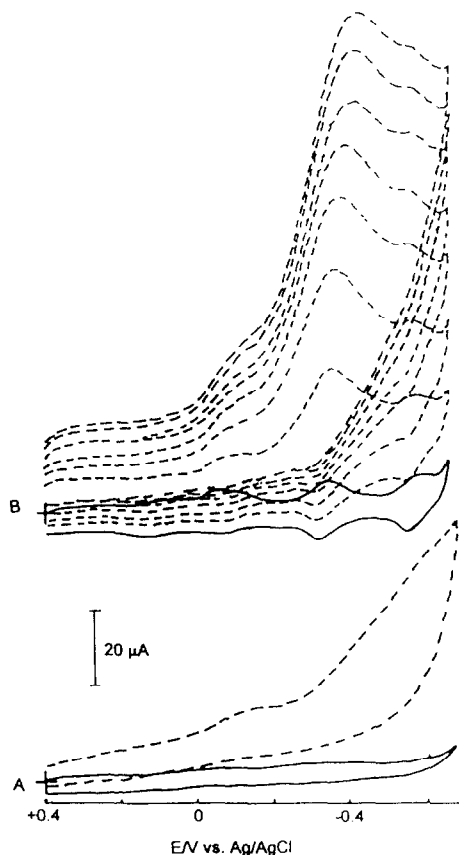


Fig. 7. Cyclic voltammograms of  $P_2W_{18}O_{62}^{6-}/\text{GC}$  in  $2 \text{ M H}_2\text{SO}_4$  before (—) and after (---) addition of nitrite (A) 4 mM, (B) 1, 2, 3, 4, 5, 6, 7 mM. Scan rate:  $20 \text{ mV s}^{-1}$ .

alyzed by the multiply reduced form of the tungstodiphosphates, four-electron reduced species  $H_4P_2W_{18}O_{62}^{6-}$ , not the singly reduced species as mentioned that in aqueous solution under the same conditions. Compared with Fig. 3A, the catalytic potential shifts negatively on a modified electrode, however, catalytic current is remarkably enhanced. These different catalytic behavior is all attributed to  $P_2W_{18}O_{62}^{6-}$  adsorbed on a electrode surface. On the one hand, the viscosity of solution ( $2 \text{ M H}_2\text{SO}_4$ ) which can affect simultaneously the diffusion coefficient of  $P_2W_{18}O_{62}^{6-}$  and  $\text{NO}_2^-$ , has no effect on the electrochemical behavior of  $P_2W_{18}O_{62}^{6-}$  incorporated on a GC electrode surface, on the other hand, such negative potential is helpful for  $\text{NO}_2^-$  reduction.

### 3.3. Electrochemical behavior of $P_2W_{18}O_{62}^{6-}$ doped in polypyrrole (PPy) film before and after addition of nitrite

The modified electrode with  $P_2W_{18}O_{62}^{6-}$  adsorbed on a GC electrode is not stable enough to be extensively used, therefore, the more robust modified electrode was desired and polypyrrole was believed to be a better film to dope  $P_2W_{18}O_{62}^{6-}$ . Fig. 8 shows cyclic voltammograms in different aqueous solutions. Three couples of two-electron, two-proton waves appeared in solutions of  $\text{pH} < 1.0$  (Fig. 8A), and two couples of one-electron waves, followed by two couples of two-electron, two-proton waves are presented in solutions of  $\text{pH} \geq 1.0$  (Fig. 8B). The behavior of the latter is similar to that of  $P_2W_{18}O_{62}^{6-}$  in acid solutions and that of the former is similar to that of  $P_2W_{18}O_{62}^{6-}$  adsorbed on a GC electrode in strong acid solutions.

The electrocatalytic behavior for nitrite reduction can also be observed on such a modified electrode, however, catalytic behavior only

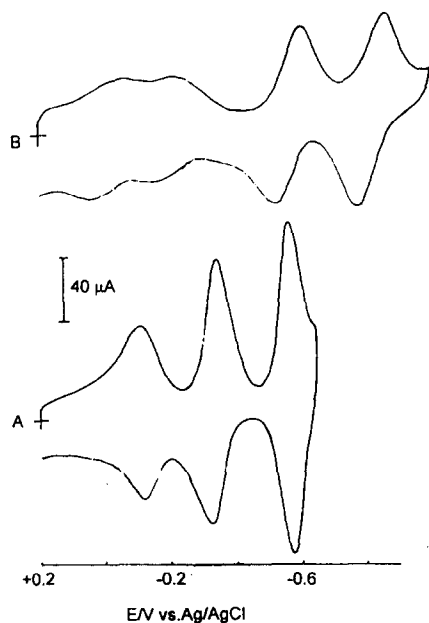


Fig. 8. Cyclic voltammograms of  $P_2W_{18}O_{62}^{6-}$  doped in polypyrrole film on a glassy carbon electrode (A) in 2 M  $H_2SO_4$ , (B) pH 5.0 solution. Scan rate:  $50 \text{ mV s}^{-1}$ . Supporting electrolyte as in Section 2.

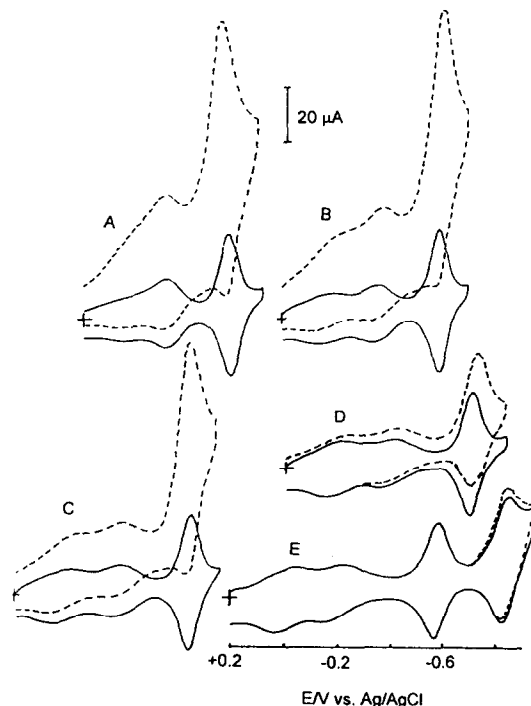


Fig. 9. Cyclic voltammograms of  $P_2W_{18}O_{62}^{6-}/PPy/GC$  before (—) and after (---) addition of nitrite 2 mM (A) in 1 M  $H_2SO_4$ , (B) 0.05 M  $H_2SO_4$  + 0.1 M  $Na_2SO_4$ , (C) pH 2.0 solution, (D) pH 3.0, (E) pH 4.0. Scan rate:  $20 \text{ mV s}^{-1}$ .

occurred in acid solutions of  $\text{pH} < 3.0$ . Four-electron reduced species, not one-electron reduced species as in aqueous solution catalyze the reduction of  $NO_2^-$ . The catalytic behavior on a  $P_2W_{18}O_{62}^{6-}/PPy$  is similar to that of  $P_2W_{18}O_{62}^{6-}$  adsorbed on a GC electrode, different from that of  $P_2W_{18}O_{62}^{6-}$  in aqueous solutions, especially catalytic current is not largely decreased with increasing sulfuric acid concentration (Fig. 9A–C). This indicates that the viscosity of solution has no effect on the behavior of  $P_2W_{18}O_{62}^{6-}/PPy$  but can affect the diffusion of nitrite. This is why the catalytic current is not increased with increasing sulfuric acid concentration but decreased with increasing pH of solution.

Nitrite has no effect on the voltammetric behavior of  $P_2W_{18}O_{62}^{6-}/PPy$  in  $\text{pH} > 4.0$  solutions while nitrite can still be catalyzed on the fifth redox waves in homogeneous solutions. A little NO only produced on the first cathodic

wave on a  $P_2W_{18}O_{62}^{6-}/PPy$  electrode diffused away from the electrode surface before it can be further reduced by highly reduced species, however in aqueous solution, there are several ways to generate enough NO to be reduced further [8b].

### 3.4. Electrochemical behavior of $P_2W_{18}O_{62}^{6-}$ doped in overoxidized polypyrrole (OPPy) film before and after addition of nitrite

Recently, overoxidized polypyrrole film has received more attention [15,16], and was believed to be another cation-exchange polymer film besides Nafion which exhibits permselectivity against anions and excellent selectivity toward cations. However, the overoxidized polypyrrole film doped with  $P_2W_{18}O_{62}^{6-}$ , prepared from  $P_2W_{18}O_{62}^{6-}/PPy$  overoxidation not only did not exclude  $P_2W_{18}O_{62}^{6-}$  anions from the electrode surface, but also presented good catalytic activity for anion such as nitrite reduction.

Fig. 10 shows the  $P_2W_{18}O_{62}^{6-}/PPy$  overoxidized process. A high overoxidized peak appeared for the first cycling scan at the potential of about +1.0 V. For the second scan, two cathodic peak current are almost unchanged,

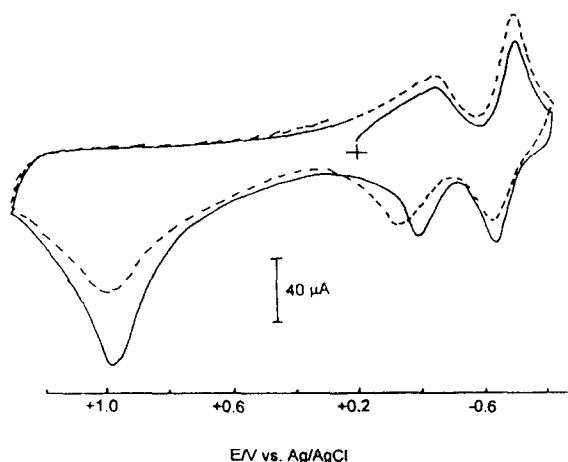


Fig. 10. Cyclic voltammograms of  $P_2W_{18}O_{62}^{6-}/PPy/GC$  for the first cycling (—) and the second cycling (---) in 0.5 M  $H_2SO_4$  solution. Scan rate:  $50\text{ mV s}^{-1}$ .

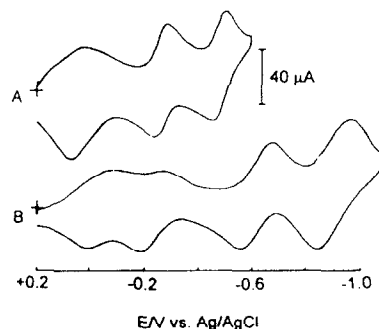


Fig. 11. Cyclic voltammograms of overoxidized polypyrrole film doped with  $P_2W_{18}O_{62}^{6-}$  (A) in 0.5 M  $H_2SO_4$  solution and (B) pH 5.0 solution. Scan rate:  $20\text{ mV s}^{-1}$ .

only the more positive anodic wave shifts positively. At the same time, the peak became broader and the overoxidized peak of PPy decreased. After six cyclic scans, the overoxidized peak disappeared completely and the voltammetric behavior of  $P_2W_{18}O_{62}^{6-}$  doped in overoxidized PPy are shown in Fig. 11. Three couples of two-electron, two-proton waves appeared in  $pH < 1.0$  solutions. Two couples of one-electron waves followed by two couples of two-electron, two-proton waves are presented in  $pH > 1.0$  solutions. The peak current is almost unchanged compared with that of  $P_2W_{18}O_{62}^{6-}/PPy$  electrode except that the separation of peak potential is higher than that of  $P_2W_{18}O_{62}^{6-}$  doped in PPy film. Fig. 12 shows us

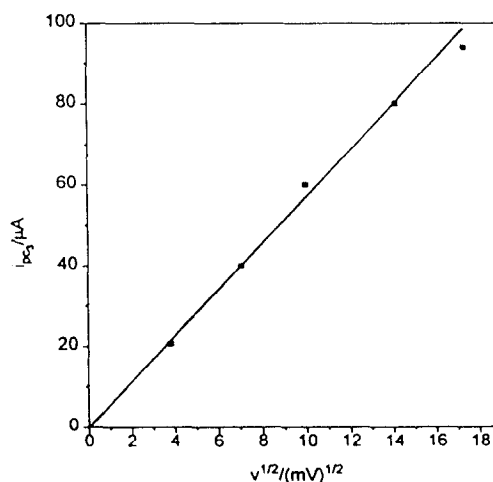


Fig. 12. Relationship between peak current and scan rate in pH 1.0 solution on a  $P_2W_{18}O_{62}^{6-}/OPPy/GC$  electrode.

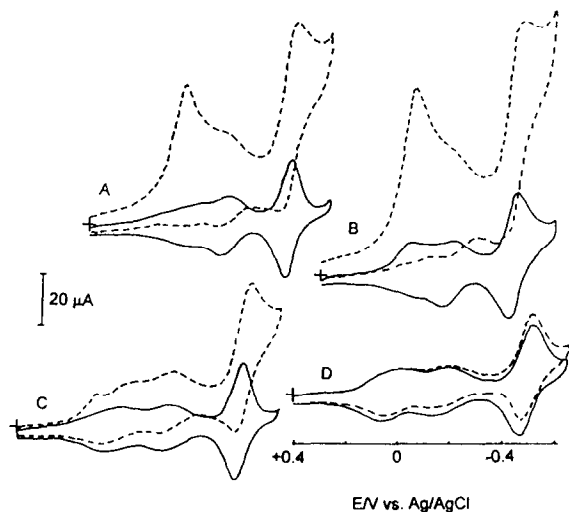


Fig. 13. Cyclic voltammograms of overoxidized  $P_2W_{18}O_{62}^{6-}/OPPy/GC$  before (—) and after (---) addition of 2 mM nitrite in (A) 1 M  $H_2SO_4$ , (B) 0.5 M  $H_2SO_4$ , (C) pH 2.0 solution, (D) pH 3.0 solution. Scan rate:  $20\text{ mV s}^{-1}$ .

that the peak current is proportional to the square root of scan rate, indicative of diffusion-controlled processes. This further confirms that OPPy film is ionic conductive, not electronic conductive.

The catalytic activity for nitrite also occurs on such a modified electrode in Fig. 13, and also four-electron reduced species react with  $NO_2^-$  in acid solutions.  $NO_2^-$  almost has no effect on  $P_2W_{18}O_{62}^{6-}/OPPy$  in  $pH > 3.0$  solutions. This phenomenon is the same as that of  $P_2W_{18}O_{62}^{6-}/PPy$ , but the sharp peak at the more positive potential in the more acid solution (Fig. 13A and B) in the presence of  $NO_2^-$  is not clear yet.

#### 4. Conclusion

$P_2W_{18}O_{62}^{6-}$  has good catalytic activity for nitrite reduction in homogeneous solutions. However, catalysis for nitrite reduction in acid solution can only occur when  $P_2W_{18}O_{62}^{6-}$  was restricted on the electrode surface, either directly adsorbed on an electrode or doped in PPy or OPPy.

A different electrochemical behavior was observed for  $P_2W_{18}O_{62}^{6-}$  in aqueous solutions and

on the modified electrode surface. Two-electron, two-proton waves are easier to appear for  $P_2W_{18}O_{62}^{6-}$  modified electrode under the same conditions. This may be attributed to the modified electrode similar to aprotic organic environment for  $P_2W_{18}O_{62}^{6-}$ .

The viscosity of solution can affect diffusion of both  $P_2W_{18}O_{62}^{6-}$  and  $NO_2^-$  in aqueous solutions. With increasing concentration of  $H_2SO_4$ , the viscosity is increased, thus the diffusion coefficients of  $P_2W_{18}O_{62}^{6-}$  and  $NO_2^-$  are decreased and therefore the catalytic current is reduced in homogeneous solutions. However, the viscosity of the solution has no effect on the electrochemical behavior of  $P_2W_{18}O_{62}^{6-}$  restricted on the electrode surface except that the diffusion of  $NO_2^-$  is still affected. Therefore, the catalytic current on the modified electrode has a higher response than that in homogeneous solutions under the same conditions, but is not largely increased with increasing concentration of  $H_2SO_4$ .

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