J. Chem. Eng. Data **2010,** *55,* 2233–2237

Electrochemical Study on Palladium Acetate + *p*-Benzoquinone + Molybdovanadophosphate System by Cyclic Voltammetry

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Palladium compounds + *p*-benzoquinone (BQ) + molybdovanadophosphate are of great interest in many catalytic reactions. The electrochemical characteristics of the palladium acetate + BQ + molybdovanadophosphate system in acid aqueous solution are studied by cyclic voltammetry. The redox process of palladium species involves a two-electron reaction, which can be expressed as $Pd^{2+} + 2e \leftrightarrow Pd^0$. Since both BQ and molybdovanadophosphate can reoxidize Pd^0 to Pd^{2+}, an appropriate amount of BQ or molybdovanadophosphate can enhance the catalytic activity of Pd^{2+} and the oxidative reaction rate. However, excessive BQ or molybdovanadophosphate decreases the reaction rate. Since molybdovanadophosphate can reoxidize the reduced form of BQ, adding an appropriate amount of molybdovanadophosphate to the Pd^{2+} + BQ system enhances the catalytic activity of Pd^{2+}. The injection of oxygen to Pd^{2+} + BQ + molybdovanadophosphate system can increase the oxidative reaction rate of molybdovanadophosphate and ultimately enhance the activity of Pd^{2+}.

Introduction

The discovery of the Wacker type catalytic system (Pd^{2+} + $CuCl_2$ + O_2) in 1959 is very important in the homogeneous catalysis of organic synthesis.[1−3] In a Wacker system, the reactants, for example, olefins, alcohols, arenes, and so forth, can be oxidized by Pd^{2+} species, and the Pd^{2+} species is simultaneously reduced into Pd^0 species which can be reoxidized by Cu^{2+} species to regenerate Pd^{2+} species.[4] Finally, oxygen, due to its environmental friendliness, is used to regenerate Cu^{2+} species as the terminal oxidant. In this catalysis system, high concentration of chloride is required to render the oxidation of Pd^0 by Cu^{2+} thermodynamically possible and to avoid Pd^0 deposition.[5] Unfortunately, high levels of chloride results in strong corrosion of the reaction vessel and formation of chlorinated byproducts;[6] moreover, the percentage of chlorinated byproducts increases when the oxidation of higher olefins is attempted. Therefore, it is necessary to develop chloride-free oxidants to replace $CuCl_2$.

Matveev proposed that the Keggin type molybdovanadophosphate + Pd^{2+} catalyst system can work in the absence of or at very low concentration of chloride.[7] To achieve excellent yields and high selectivity, *p*-benzoquinone (BQ) or hydroquinone (H_2Q) is usually employed,[8] and thus a three-component redox system is developed. In this system, molybdovanadophosphate can smoothly oxidize H_2Q into BQ, and then BQ oxidizes Pd^0 into Pd^{2+} rapidly.[9]

So far, there has been already much research on the industrial application of the Pd^{2+} + molybdovanadophosphate + O_2 and Pd^{2+} + BQ + molybdovanadophosphate + O_2 systems. It is generally assumed that (π-allyl) palladium intermediate forms during the oxidation of olefins by the catalysis of $Pd(OAc)_2$ + BQ + molybdovanadophosphate + O_2, followed by activation of the intermediate by BQ coordination, nucleophilic substitution, and electron transfer for Pd^0 to coordinated BQ.[10−12]

Since Pd^{2+}/Pd^0, BQ/H_2Q, and molybdovanadophosphate/molybdovanadophosphate blue can form an electron-transfer chain[13] during the reaction, their oxidation and reduction behavior can be studied by electrochemical methods. Cyclic voltammetry is a popular technique in electrochemical studies especially to obtain information about the kinetics, mechanism, catalyst characterization, and intermediate product of reactions. The purpose of the present paper is thus to study the electrochemical characterization of the catalyst system.

Experimental Section

Materials. Sodium 9-molybdo-3-vanadophosphate ($Na_6[PMo_9V_3O_{40}]\cdot 34H_2O$, HPA) was prepared and purified according to the literature.[14,15] Palladium acetate, *p*-hydroquinone, BQ, potassium chloride, and sulfuric acid were of analytical grade.

Apparatus and Procedure. Cyclic voltammetric measurements and electrolysis experiments were carried out by a Labnet UI5022 electrochemical analyzer (ShiRuiSi Co. Ltd., Zhengzhou, PR China). The platinum disk (2 mm diameter) was used as working electrode, saturated calomel electrode (SCE), and platinum foil (1.0 cm × 1.0 cm) were used as reference electrode and counter electrode, respectively. These electrodes were supplied by Aida Co. Ltd., Tianjin, PR China. Before each measurement, the working electrode surface was polished with 0.5 μm alumina powders, followed by ultrasonic washing in ethanol solutions (the volume ratio of ethanol to water was 1), hot nitric acid (the volume ratio of nitric acid to water was 1), and distilled water in turn for three times.

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10.1021/je900774d

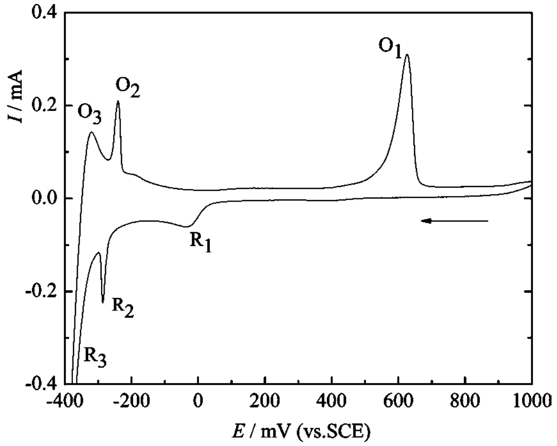

Figure 1. Cyclic voltammetric curve of $Pd(OAc)_2$.

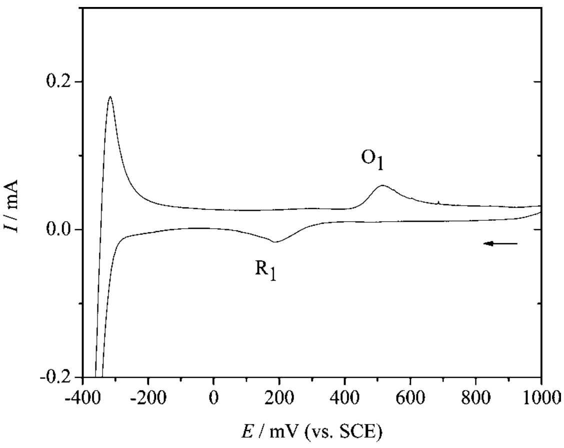

Figure 2. Cyclic voltammetric curve of BQ.

All electrochemical experiments were done at atmospheric pressure and room temperature. The electrolyte aqueous solution was deaerated with pure nitrogen gas for at least 20 min just prior to use, and during the measurements nitrogen gas was passed over the unstirred solutions. The concentration of $Pd(OAc)_2$ is 5 mM in the electrolyte solution. The measurements were done in 0.5 M KCl solution of pH 1 that was adjusted by the appropriate addition of H_2SO_4. The scan rate is 50 $mV \cdot s^{-1}$ if it is not specially stated.

Results and Discussion

Single-Component System. $Pd(OAc)_2$ Aqueous Solution. Figure 1 represents cyclic voltammetric curve in 5 mM $Pd(OAc)_2$ aqueous solution. There are three redox couples, among which peaks R_3 and O_3 attribute to the hydrogen adsorption and desorption reaction.

To determine how many electrons are involved in the reduction process at peak R_1 (−40.0 mV), an electrolysis experiment was performed. When depositing at −40.0 mV for 20 min, a thin film of black Pd^0 was found in the working electrode. Therefore, the reduction process at peak R_1 could involve two electrons with formation of Pd^0 which is adsorbed at the electrode surface, and the resulting Pd^0 would be oxidized at the reverse scan (at peak O_1).

The cyclic voltammetry was studied with the above Pd^0-coated platinum disk electrode as the working electrode in KCl + H_2SO_4 aqueous solution. The results show that peaks R_2 and O_2 appeared in the first cycle, whereas, because of the oxidation of Pd^0 coatings, they disappeared gradually in the following cycles. For comparison, cyclic voltammetry was recorded on platinum disk electrode in the same aqueous solution, and peaks R_2 and O_2 could not be observed. Therefore, it can be inferred that peaks R_2 and O_2 are attributed to the process of H adsorbed on Pd^0 and desorbed from Pd^0.

BQ Aqueous Solution. The peak potential separation is usually used as the criterion for electrochemical reversibility. The electrochemical reaction is reversible at a peak potential separation of 58/n mV (n is the number of electron transfer); it is irreversible when the separation is greater than 58/n mV.[16] Another criterion is the exchange current density (J_0),[17] and the electrochemical process is irreversible at a low value of J_0.

Cyclic voltammetric curve in 5 mM BQ aqueous solution is shown in Figure 2. As can be seen in Figure 2, reduction and oxidation peaks of BQ/H_2Q couple are located at 190.0 mV and 520.0 mV, respectively, and the peak potential separation is 310.0 mV, much higher than 27.5 mV (as BQ is reduced by a two-electron mechanism[18]). In addition, it was reported that J_0 in 5.5 mM BQ aqueous solution at pH of 1.1 is $7.8 \cdot 10^{-5}$ $mA \cdot cm^{-2}$.[19] Therefore, the BQ/H_2Q couple is irreversible on the platinum electrode.

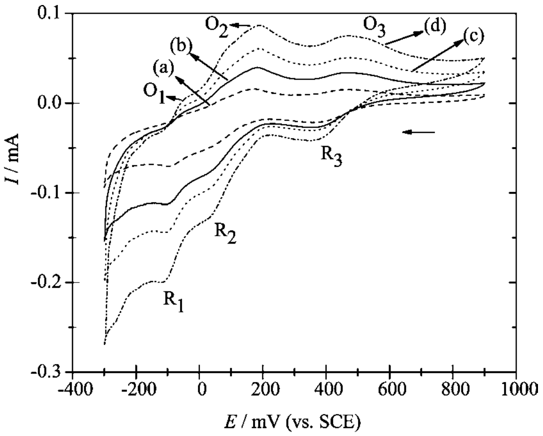

Figure 3. Cyclic voltammetric curves of HPA at various scan rates. (a) 25 $mV \cdot s^{-1}$, (b) 50 $mV \cdot s^{-1}$, (c) 80 $mV \cdot s^{-1}$, (d) 100 $mV \cdot s^{-1}$.

HPA Aqueous Solution. Villabrille et al.[20] studied the cyclic voltammetry of molybdophosphoric acid in an acidic medium. Three waves of Mo were observed, corresponding to the redox process of $Mo^0 \leftrightarrow Mo^{2+}$, $Mo^{2+} \leftrightarrow Mo^{4+}$, and $Mo^{4+} \leftrightarrow Mo^{6+}$, respectively. When a molybdenum atom is substituted by a vanadium atom in a molybdophosphoric acid molecule, only two waves of Mo remain, and a new couple appeared at a more positive potential, which should be attributed to the vanadium species.

A cyclic voltammetric curve in 5 mM HPA aqueous solution is shown in Figure 3. As can be seen in Figure 3, the R_1/O_1 couple would correspond to the redox process of $Mo^0 \leftrightarrow Mo^{2+}$, and the R_2/O_2 couple is attributed to the redox processes of $Mo^{2+} \leftrightarrow Mo^{4+}$ and $Mo^{4+} \leftrightarrow Mo^{6+}$. Since the vanadium atom has a great impact on the nearest peak of Mo, two peaks of Mo close to the vanadium atom superpose each other. The R_3/O_3 couple, at a more positive potential, is attributed to the redox processes of vanadium species.

Mizuno et al.[21] suggested that vanadium exists as VO_2^+ in an acidic solution (pH ≤ 2). Kozhevnikov[9] reported that VO_2^+ cations are split out from oxidized HPA in an acidic solution at pH ~ 1, and VO^{2+} cations are still easier split out from reduced HPA. Therefore, the VO_2^+/VO^{2+} couple exists in the aqueous solution of HPA during cyclic voltammetric measurements. It was earlier established by kinetic methods that the VO_2^+/VO^{2+} couple is exclusively responsible for oxidative properties of

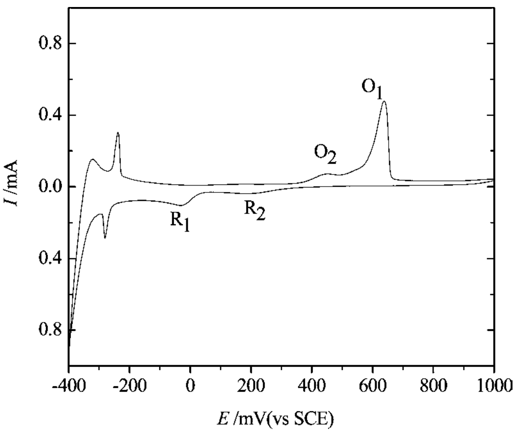

Figure 4. Cyclic voltammetric curve of $Pd(OAc)_2$ + BQ aqueous solution (the mole ratio of $Pd(OAc)_2$ to BQ is 1:1).

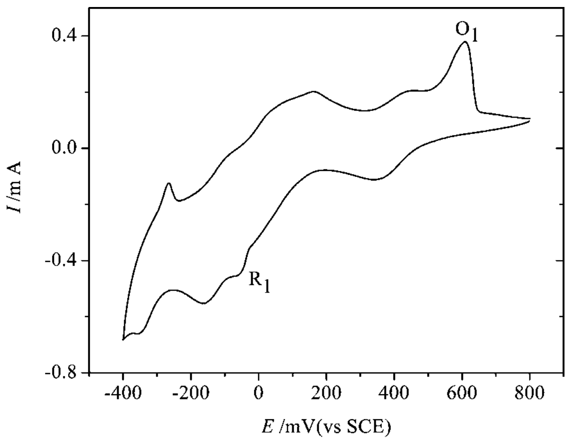

Figure 5. Cyclic voltammetric curve of $Pd(OAc)_2$ + HPA aqueous solution (the mole ratio of $Pd(OAc)_2$ to HPA is 1:1).

HPA. Therefore, the vanadium species exists in the form of the VO_2^+/VO^{2+} couple, whose reduction and oxidation potential occurs at 390 mV and 480 mV, respectively. The peak potential separation of the VO_2^+/VO^{2+} couple is estimated to be 80 mV, and the redox peaks of the VO_2^+/VO^{2+} couple roughly remain unchanged at various scan rates. According, HPA is reduced by a one-electron mechanism, and the redox process is quasi-reversible.[22,23]

Two-Component System. $Pd(OAc)_2$ + BQ System. Grennberg et al.[24] studied aerobic allylic oxidation of cyclohexene catalyzed by palladium + BQ + molybdovanadophosphoric acid. The results showed that BQ enhanced the oxidation reaction, the highest rate occurred at a 1:1.4 mole ratio of $Pd(OAc)_2$ to BQ, and doubling the BQ amount led to a slightly lower rate. Also An et al.[8] have reported that increasing the amount of BQ beyond twice of $Pd(OAc)_2$ does not significantly promote the reaction further.

To study the effect of adding BQ in $Pd(OAc)_2$ aqueous solution on catalytic activity, cyclic voltammetric behavior was studied in $Pd(OAc)_2$ + BQ aqueous solution.

Figure 4 gives a typical cyclic voltammetric curve of $Pd(OAc)_2$ + BQ aqueous solution (the mole ratio of $Pd(OAc)_2$ to BQ is 1:1). Peaks R_1/O_1 and R_2/O_2 are attributed to Pd^{2+}/Pd^0 and BQ/H_2Q couples, respectively. The peak potential of BQ in this mixture solution is almost the same as the peak potential in single BQ solution, which does not superpose with the potential of Pd^{2+}/Pd^0 couple. Other peaks have already been interpreted in a single-component system of $Pd(OAc)_2$ aqueous solution. Table 1 shows peak potential and current at various mole ratios of $Pd(OAc)_2$ to BQ. E_{pa} and E_{pc} are the oxidation and reduction peak potential of Pd^{2+}/Pd^0, and I_{pa} and I_{pc} are the oxidation and reduction peak current, respectively.

As can be seen in Table 1, the addition of BQ in $Pd(OAc)_2$ aqueous solution increases the oxidation peak current of the Pd^{2+}/Pd^0 couple. This indicates that BQ can promote the oxidation reaction of Pd^0, and this is beneficial to render the activity of Pd^{2+} in a catalytic system. However, excessive BQ results in the decrease of the reduction peak current, indicating that the addition amount of BQ should be precisely adjusted to increase the catalytic activity of Pd^{2+} in practical application. These results are consistent with refs 8 and 24. The mechanism of the effect of BQ on Pd^{2+} regeneration still needs further study.

$Pd(OAc)_2$ + HPA System. Lee et al.[25] studied the oxidative coupling of methyl benzoate with palladium + heteropolyacid catalysts and suggested that the methyl benzoate conversion increased initially with increasing heteropolyacid amount but slightly decreased once its quantity went above about 0.1 mmol for 0.08 mmol of $Pd(OAc)_2$. To determine the effect of the mole ratios of Pd^{2+} to heteropolyacid on the reaction rate, cyclic voltammetric curves of $Pd(OAc)_2$ + HPA aqueous solution were measured.

Figure 5 shows a typical cyclic voltammetric curve of $Pd(OAc)_2$ + HPA aqueous solution (the mole ratio of $Pd(OAc)_2$ to HPA is 1:1). As can be seen in Figure 5, one of the reduction peaks of Mo may superpose with the reduction peak of palladium (R_1); however, it does not superpose with the oxidation peak of palladium (O_1) (other couples are attributed to HPA). Therefore, the variation of the oxidation peak of palladium with the mole ratios of $Pd(OAc)_2$ to HPA is studied.

Table 2 lists the oxidation peak potential and current of palladium species in $Pd(OAc)_2$ + HPA aqueous solution at various mole ratios of $Pd(OAc)_2$ to HPA. It can be seen that

Table 2. Oxidation Peak Potential and Current of Palladium Species in $Pd(OAc)_2$ + HPA Aqueous Solution at Various Mole Ratios of $Pd(OAc)_2$ to HPA

	Pd^0/Pd^{2+}	
	E_{pa}/mV	I_{pa}/mA
$Pd(OAc)_2$	620.0 ± 2.0	0.249 ± 0.003
$Pd(OAc)_2$:HPA = 1:0.1	630.0 ± 2.0	0.296 ± 0.003
$Pd(OAc)_2$:HPA = 1:0.5	630.0 ± 2.0	0.285 ± 0.003
$Pd(OAc)_2$:HPA = 1:1	630.0 ± 2.0	0.264 ± 0.003
$Pd(OAc)_2$:HPA = 1:3	620.0 ± 2.0	0.230 ± 0.003
$Pd(OAc)_2$:HPA = 1:5	610.0 ± 2.0	0.176 ± 0.003

Table 1. Peak Potential and Current in $Pd(OAc)_2$ + BQ Aqueous Solution at Various Mole Ratios of $Pd(OAc)_2$ to BQ

	Pd^0/Pd^{2+}		Pd^{2+}/Pd^0	
	E_{pa}/mV	I_{pa}/mA	E_{pc}/mV	I_{pc}/mA
$Pd(OAc)_2$	620.0 ± 2.0	0.249 ± 0.003	−40.0 ± 1.0	−0.049 ± 0.001
$Pd(OAc)_2$:BQ = 1:1	640.0 ± 2.0	0.369 ± 0.003	−30.0 ± 0.8	−0.073 ±0.002
$Pd(OAc)_2$:BQ = 1:2	640.0 ± 2.0	0.281 ± 0.003	−50.0 ± 1.2	−0.070 ±0.002
$Pd(OAc)_2$:BQ = 1:3	640.0 ± 2.0	0.240 ± 0.003	−60.0 ± 1.2	−0.050 ±0.001
$Pd(OAc)_2$:BQ = 1:5	640.0 ± 2.0	0.212 ± 0.003	−50.0 ± 1.2	−0.049 ±0.001

Table 3. Peak Potential and Current of H_2Q in H_2Q + HPA Aqueous Solution at Various Mole Ratios of H_2Q + HPA

	E_{pa}/mV	I_{pa}/mA	E_{pc}/mV	I_{pc}/mA
H_2Q	500.0 ± 1.8	0.063 ± 0.002	230.0 ± 1.1	−0.039 ± 0.001
H_2Q:HPA = 1:1	500.0 ± 1.8	0.070 ± 0.002	220.0 ± 1.1	−0.040 ± 0.001
H_2Q:HPA = 1:3	520.0 ± 1.8	0.072 ± 0.002	400.0 ± 1.1	−0.042 ± 0.001
H_2Q:HPA = 1:5	490.0 ± 1.8	0.088 ± 0.002	340.0 ± 1.1	−0.155 ± 0.001

Table 4. Peak Current and Potential of the VO_2^+/VO^{2+} Couple in the HPA and HPA + O_2 Systems

	E_{pa}/mV	I_{pa}/mA	E_{pc}/mV	I_{pc}/mA
HPA	490.0 ± 1.8	0.008 ± 0.001	380.0 ± 1.2	−0.018 ± 0.001
HPA + O_2	500.0 ± 1.8	0.009 ± 0.001	370.0 ± 1.2	−0.023 ± 0.001

the addition of HPA can enhance the oxidation peak current of Pd^{2+} compared to the single-component system of Pd^{2+}, indicating that HPA can enhance the oxidization rate of the palladium species to Pd^{2+} as the reaction $Pd^0 + HPA \rightarrow Pd^{2+} + H_XHPA$ (the reduced form of HPA). However, when the mole ratio of Pd $(OAc)_2$ to HPA exceeds 1:1, the reduction peak current of Pd^{2+} decreases.

H_2Q + HPA System. In the Pd^{2+} + BQ + molybdovanadophosphate catalysis system, BQ is reduced into H_2Q in the course of the regeneration of Pd^{2+}, and then it is regenerated by oxidizing with HPA. Thus, it is important to study the effect of the mole ratio of HPA to H_2Q on the oxidation rate of H_2Q.

The peak potential and current of H_2Q in H_2Q + HPA aqueous solution at various mole ratios are shown in Table 3. E_{pa} and E_{pc} are the oxidation and reduction peak potentials of BQ + H_2Q, and I_{pa} and I_{pc} are the oxidation and reduction peak currents, respectively.

It can be seen from Table 3 that the oxidation peak current increases with increasing HPA amount, which indicates that increasing the HPA amount can enhance the oxidation rate of H_2Q.

HPA + O_2 System. In the Pd^{2+} + molybdovanadophosphate or Pd^{2+} + BQ + molybdovanadophosphate catalysis system, oxygen is used as the ultimate oxidant to regenerate HPA. Because of the existence of oxygen, reduced HPA can be oxidized much easier, which is also confirmed by cyclic voltammetric study (Table 4). E_{pa} and E_{pc} are the oxidation and reduction peak potentials of VO_2^+/VO^{2+}, and I_{pa} and I_{pc} are the oxidation and reduction peak currents, respectively. Table 4 shows that the oxidation peak current of the VO_2^+/VO^{2+} couple increases with the addition of oxygen; namely, oxygen enhances the regeneration rate of HPA.

Multicomponent System. Pd^{2+} + BQ + HPA System. Grennberg et al.[24] reported that the percentage of molybdovanadophosphoric acid had a significant effect on the catalytic activity of palladium + BQ + molybdovanadophosphoric acid. When the mole ratio of Pd^{2+} to BQ was 1:1.4, the highest yield of product can be achieved as the mole ratio of Pd^{2+} to HPA was 1:0.02, and doubling the amount of HPA decreased the yield of product.

Table 5 presents the oxidation peak potential and current of Pd^{2+} in Pd^{2+} + BQ + HPA aqueous solution at various mole ratios. As can be seen in Table 5, rgw oxidation peak current of Pd^{2+} increases with the addition of a small amount of HPA to the Pd^{2+} + BQ system. The reason is that HPA can reoxidize H_2Q to BQ, and regeneration of BQ promotes the oxidation reaction of palladium species. However, when an excessive amount of HPA is added, the current decreases, and the peak potential becomes more negative, which indicates that excessive HPA decreases the reaction rate and oxidation capacity of Pd^{2+}. This result is consistent with Grennberg's.

Table 5. Oxidation Peak Potential and Current in Pd^{2+} + BQ + HPA Aqueous Solution at Various Mole Ratios

	Pd^0/Pd^{2+}	
	E_{pa}/mV	I_{pa}/mA
Pd^{2+}:BQ = 1:2	640.0 ± 2.0	0.281 ± 0.003
Pd^{2+}:BQ:HPA = 1:2:0.1	640.0 ± 2.0	0.345 ± 0.004
Pd^{2+}:BQ:HPA = 1:2:0.5	630.0 ± 2.0	0.242 ± 0.003
Pd^{2+}:BQ:HPA = 1:2:1	630.0 ± 2.0	0.215 ± 0.003
Pd^{2+}:BQ:HPA = 1:2:3	620.0 ± 2.0	0.195 ± 0.002
Pd^{2+}:BQ:HPA = 1:2:5	560.0 ± 2.0	0.055 ± 0.001

Table 6. Oxidation Peak Potential and Current in Pd^{2+} + BQ + HPA and Pd^{2+} + BQ + HPA + O_2 Systems

	Pd^0/Pd^{2+}	
	E_{pa}/mV	I_{pa}/mA
Pd^{2+} + BQ + HPA	620.0 ± 2.0	0.195 ± 0.002
Pd^{2+} + BQ + HPA + O_2	630.0 ± 2.0	0.269 ± 0.003

Pd^{2+} + BQ + HPA + O_2 System. In the Pd^{2+} + BQ + HPA system, oxygen is used as the ultimate oxidant, so it is necessary to study the effect of oxygen on the Pd^{2+} + BQ + HPA system.

Cyclic voltammetric characteristics of Pd^{2+} + BQ + HPA and Pd^{2+} + BQ + HPA + O_2 systems were compared in Table 6. Since oxygen evolution potential at 928.8 mV (vs SCE) does not fall in the scanning potential range of approximately 400 mV to 800 mV, there is no need to worry about the effect of oxygen evolution on the palladium species. Table 6 shows that the oxidation peak current of palladium species greatly increases when injecting oxygen, and this indicates that oxygen is helpful in increasing the catalytic activity. The reason for this is that the existence of oxygen increases the oxidation capacity of HPA and ultimately enhances the activity of Pd^{2+}.

Conclusions

Cyclic voltammetric and electrolysis experimental results show that the redox process of palladium acetate involves two electrons, which can be expressed as $Pd^{2+} + 2e \leftrightarrow Pd^0$. HPA is proved to be a one-electron oxidant, and the redox process is quasi-reversible. Since BQ or HPA can reoxidize Pd^0 to Pd^{2+}, an appropriate amount of BQ or HPA can enhance the catalytic activity of Pd^{2+} and the oxidative reaction rate for Pd^{2+} + BQ and Pd^{2+} + HPA systems. However, excessive BQ or HPA will decrease the reaction rate. Adding the appropriate amount of HPA to the Pd^{2+} + BQ system enhances the catalytic activity of Pd^{2+}, as HPA can reoxidize H_2Q to BQ. The injection of oxygen to Pd^{2+} + BQ + HPA system increases the oxidative reaction rate of HPA and ultimately enhances the activity of Pd^{2+}.

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Received for review September 24, 2009. Accepted December 1, 2009. This work was supported by National Natural Sciences Foundation of China (Grant No. 20776013) and Beijing Natural Science Foundation (Grant No. 2102034).

JE900774D