

# Electrochemical Degradation of Phenol by MnO<sub>2</sub>-Pd/C Gas-Diffusion Electrode

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**Abstract:** MnO<sub>2</sub>/C and Pd/C catalysts used for the MnO<sub>2</sub>- Pd/C gas-diffusion cathodes were prepared by redox, and characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS). The electrochemical degradation of phenol was surveyed in a diaphragm electrolysis system and a connected electrolysis system, feeding with air, making the most of four kinds of self-made gas-diffusion cathodes. It turns out the MnO<sub>2</sub>- Pd/C cathodes was better than other cathodes, and the degradation efficiency reached 96.95% and 99.3% in two kinds of electrolysis systems, respectively, after reaction for 100min.

**Keywords:** Electrochemical, MnO<sub>2</sub>- Pd/C, Phenol

## 1. Introduction

Numerous industries, like oil refineries and coke, chemical, and plastic plants, more often than not, are the fountainhead of phenolic pollutants[1]. Phenol is one kind of toxic organic compounds, and difficult to be treated by biological action, the most important point is acute toxic in spite of the low concentration.[2]. Hence, high-efficiency and appropriate treatment is demanded urgently. Photochemical degradation, chemical oxidation, wet oxidation, and electrochemical oxidation are of particular interest, [3].[4]among these existing processes, due to without secondary pollution, electrochemical oxidation have attracted much attention.under the action of strong oxidants, produced on the electrode surface by the electrochemical reaction organic, pollutants can be mineralized by electrochemical treatment; therefore, electrode material is the key to improve electrochemical efficiency. Zoltowski[5] discovered catalytic activity of MnO<sub>2</sub> to accelerate reduction of O<sub>2</sub> in 1973. Catalytic activity of precious metal had been received a large amount of attention for a long time. The electrochemical degradation of 4-chlorophenol over Pd/C catalyst prepared by hydrogen reduction method was surveyed in a diaphragm electrolysis device using the Pd/C gas-diffusion electrode as a cathode.[6] Results display that Pd/C gas-diffusion cathode can reduce dechlorinate 4-chlorophenols not only by adding hydrogen, but also by adding air to accelerate oxygen dielectron reduction of hydrogen peroxide(H<sub>2</sub>O<sub>2</sub>).

This paper reports the degradation of phenol in a terylene 747 diaphragm cell and in a connected cell, a Ti/IrO<sub>2</sub>/RuO<sub>2</sub> anode, and self-made gas-diffusion cathodes. MnO<sub>2</sub>/C catalyst and Pd/C catalyst used for MnO<sub>2</sub>/C, Pd/C, and MnO<sub>2</sub>- Pd/C gas-diffusion electrode was prepared and satisfactory characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS). Additionally, A combined process of reduction and oxidation is an efficacious and amicable means of the treatment of organic contaminants. Phenol was oxidized and degraded both in a diaphragm electrolysis system and a connected electrolysis system. The selection of electrolysis system depended on industrial condition. Finally, four different self-made gas-diffusion cathodes were compared in the light of the electrochemical degradation of phenol.

## 2. Experimental

### 2.1. Preparation of MnO<sub>2</sub>/C Catalyst

MnO<sub>2</sub>/C catalyst was prepared by reaction of activated carbon and KMnO<sub>4</sub> solution. Activated

carbon powder was pretreated by 50 $\mu$ m sieved. The mixture of 5g activated carbon powder and 100mL deionized water was treated by ultrasonicator for 20min. A 50mL 0.1mol/L KMnO<sub>4</sub> solution was poured into activated carbon solution which was stirred vigorously at the temperature of 80 $^{\circ}$ C for 80min. the mixture was filtered, washed and dried, then heated at 350 $^{\circ}$ C for 2 hours.

## 2.2. Preparation of Pd/C catalyst

Pd/C catalyst was prepared by the formaldehyde reduction means. Activated carbon powder used for the purpose of carrier of catalyst, refluxed with 10% nitric acid solution for 2 hours, washed to neutral with distilled water, and dried overnight in the temperature of 100 $^{\circ}$ C. Palladium chloride was dissolved in a concentrated muriatic acid solution and then thinned using 15mL of water. PdCl<sub>2</sub> solution was dropped into the activated carbon solution stirred violently in the temperature of 80 $^{\circ}$ C. The reaction was kept for 2 hours, and then cooled to 40 $^{\circ}$ C. Pd/C was compounded with 36% formaldehyde solution, stirred for 30 min, and 30% NaOH solution was added to make the PH value of mixture between 8 and 9. The mixture was filtered, washed and dried. Complete the above steps as required, Pd/C catalyst with a Pd load of 1.0 wt.% was acquired.[7]

## 2.3. Preparation of Electrode

Four kinds of self-made gas-diffusion cathodes were prepared respectively, including MnO<sub>2</sub>/C electrode, Pd/C electrode, MnO<sub>2</sub>- Pd/C electrode and C electrode. Stainless steel screen (40 mesh) was supporter of electrode, 10% PTFE was binder and anhydrous ethanol was dispersant. The mixture of 1.8g catalyst, 6.0g 10% PTFE and 10mL anhydrous ethanol was blended in 60–70 $^{\circ}$ C bath of water. Furthermore, The mixture was stacked onto a stainless steel screen, and hotpressed for 1min. the electrode was obtained. Activated carbon powder replaced of 1.8g catalyst in the C cathode, and the mixture of 0.36g Pd/C catalyst and 1.44g MnO<sub>2</sub>/C catalyst instead of 1.8g catalyst in the MnO<sub>2</sub>- Pd/C electrode.

## 2.4. Procedures

Electrochemical degradation of phenol was carried out in a terylene diaphragm cell of 100mL and in a connected cell of 100mL separately. The anode was a Ti/IrO<sub>2</sub>/RuO<sub>2</sub> net of 16 cm<sup>2</sup>. There is, in addition, one point to make, The cathode is a 16 square centimeter catalyst electrode. A laboratory DC power with current–voltage monitor to supplied electric power. The conditions of experiment were as below: distance between electrodes: 3 cm, current density: 39 mA/cm<sup>2</sup>, level of initial phenol: 100 mg/l, initial pH value: 6.8, electrolyte (Na<sub>2</sub>SO<sub>4</sub>) consistence: 0.1 mol/L. ; in advance feeding gas was 10 min and kept in the reaction process so as to keep dissolved gas saturation.

## 2.5. Analytical Methods

The Pd and MnO<sub>2</sub> particle morphology and size distributions were measured by transmission electron microscope (TEM: JEM-2100, microscope working under the condition of 200 kV accelerating voltage), Before the TEM observation, the MnO<sub>2</sub>/C catalyst and Pd/C catalyst were dispersed in anhydrous ethanol ultrasonically for 10min. The surface composition of MnO<sub>2</sub>/C catalyst and Pd/C catalyst were analysed by the means of X-ray photoelectron spectroscopy. (XPS: model PH15700 ESCA, Physical Electronics USA), Based on the binding energy of C1s, the numerical value of which is 284.6 eV, the date of XPS were standardization, All binding energies within an accuracy of  $\pm 0.1$ eV.

Phenol was determined in the way of electrolysis by UV-Visual Spectrophotometer with 4-aminoantipyrine (AAP) as the colorant. (UV-Vis spectrophotometer: model T6, produced by Beijing Purkinje General Instrument Co.LTD, China) at 510nm. The removal efficiency was calculated as follows:

$$X\% = (C_0 - C_t) / C_0 \times 100\% \quad (1)$$

Where C<sub>0</sub> and C<sub>t</sub> are the original and ultimate consistence of phenol.

### 3. Results and Discussion

#### 3.1. Characterization of MnO<sub>2</sub>/C catalyst and Pd/C Catalyst

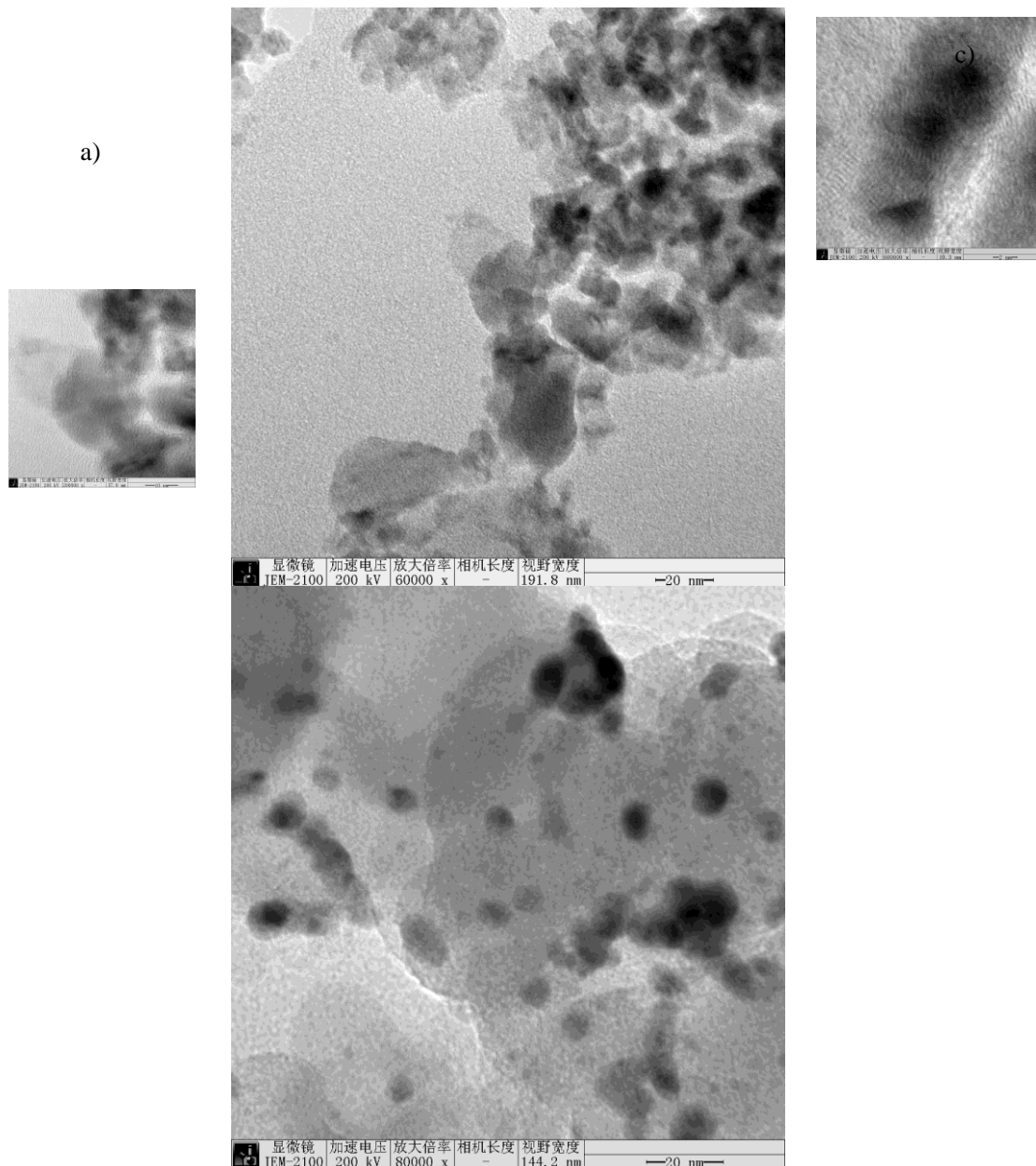


Figure 1: TEM pattern of MnO<sub>2</sub>/C catalyst (a) and Pd/C catalyst (c).

Figure 1 shows the TEM pattern of MnO<sub>2</sub>/C catalyst (a) and Pd/C catalyst (b), the distribution of whose metal granules size was surveyed as well. Figure 1 a) and c) clearly shows MnO<sub>2</sub> and Pd are dispersed on the activated carbon supports. The mean granule sizes of of MnO<sub>2</sub>/C and Pd/C catalyst were 25 and 5 nm, respectively.

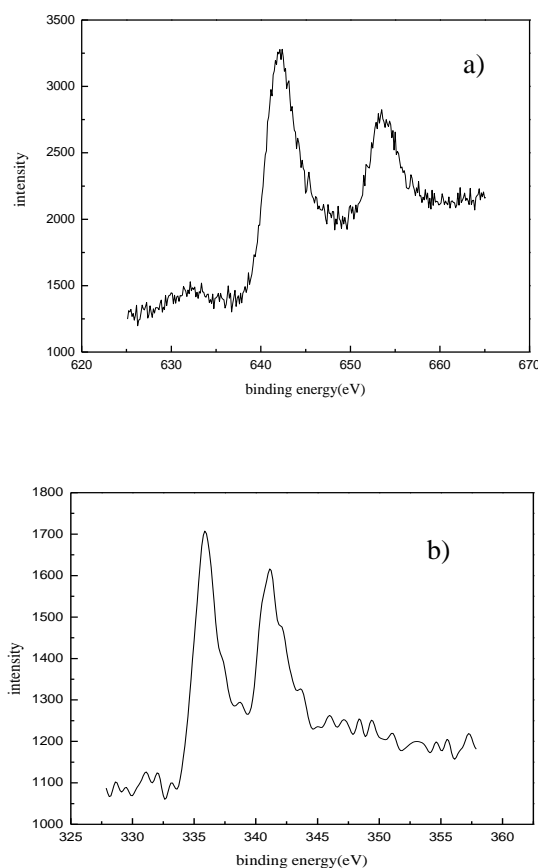


Figure 2: XPS pattern of MnO<sub>2</sub>/C catalyst (a) and Pd/C catalyst (b).

Figure 2a) displays the XPS profiles of MnO<sub>2</sub>/C catalyst, owing to spin-orbit coupling, the Mn 2p levels are split into 2p<sub>1/2</sub> and 2p<sub>3/2</sub> parts. The detected peak at bond energy of 642 eV corresponds to Mn 2p<sub>3/2</sub>, which indicates that Mn element in MnO<sub>2</sub>/C catalyst exists as Mn<sup>4+</sup>. furthermore, The binding energy of 654 eV can be attributed to Mn 2p<sub>1/2</sub>, which can be further used as evidence of the unique existence of Mn<sup>4+</sup>. [8] Hence, MnO<sub>2</sub> was successfully obtained. The content of MnO<sub>2</sub> granules from the surface of MnO<sub>2</sub>/C catalyst came up to 20.06%.

Figure 2b) displays chemical states of surface atoms in the Pd/C catalysts. We can see from the Figure 2b that the binding energies of Pd3d in the reduced catalyst are 335.1 and 336.2 eV, which resemble that data in former observations [9] attributed to Pd and Pd (II), respectively. The content of Pd granules on the surface of Pd/C catalyst came up to 1.12%.

### 3.2. Study on the Removal of Phenol

The effect of four kinds of self-made gas-diffusion cathodes and the different electrolysis systems was investigated. The absorbance of phenol was measured based on UV- Vis Spectrophotometer at 510nm.

The Fig.3 shows the efficiency of degradation of phenol of four kinds self-made gas-diffusion cathodes, including removal efficiency of phenol in the cathodic compartment, anodic compartment and average with different cathodes in diaphragm electrolysis system after reaction for 100min. In Fig.3, the efficiency of degrading phenol in MnO<sub>2</sub>-Pd/C gas-diffusion electrode system was superior to that in other electrode systems, the efficiency of degrading phenol in the MnO<sub>2</sub>/C and Pd/C gas-diffusion electrode system was superior to that in C electrode system, and the efficiency of degrading phenol in the MnO<sub>2</sub>/C and Pd/C gas-diffusion electrode system was approximate not only in the cathodic compartment but also in the anodic compartment, which indicated MnO<sub>2</sub>-Pd/C gas-diffusion electrode owns higher catalytic activity. Pd of surface of Pd/C catalysts was prone to become Pd(II) to reduce catalytic activity. MnO<sub>2</sub> was not uniform at the surface of MnO<sub>2</sub>/C catalysts

to exert all the catalytic activity. MnO<sub>2</sub>-Pd/C gas-diffusion electrode could make up for these shortcomings.

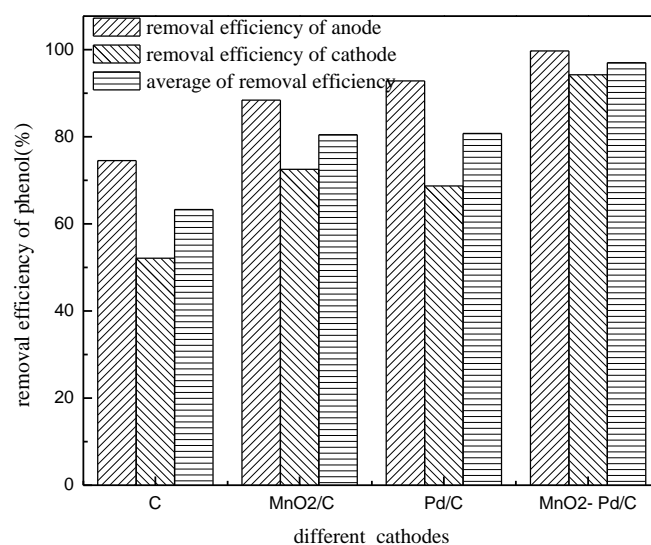


Figure 3: The effect of four different self-made gas-diffusion cathodes

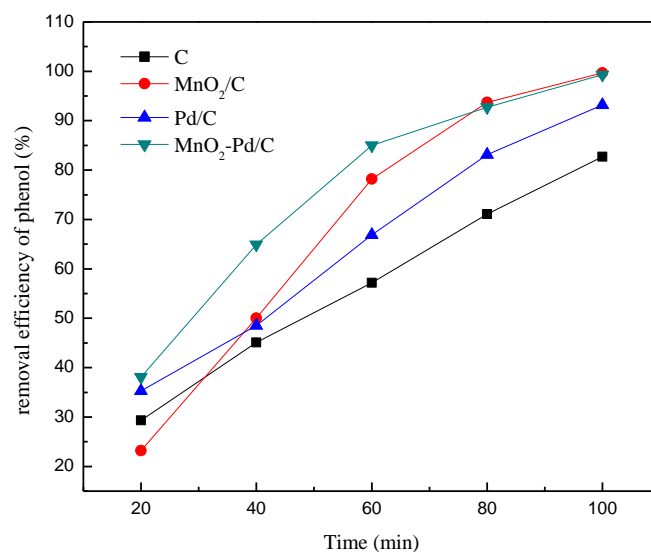


Figure 4: Removal of phenol in the connected electrolysis system

Fig. 4 shows the efficiency of degrading phenol with electrolysis time in the connected electrolysis system using four diverse gas-diffusion electrode systems, respectively. In Fig. 4, the efficiency of degrading phenol rising with electrolysis time in connected electrolysis system using four kinds gas-diffusion electrodes; in the initial 40 min, the removal efficiency of phenol of MnO<sub>2</sub>-Pd/C gas-diffusion electrode was superior to others, particularly electrode of C, which can be attributed to the same reason in diaphragm electrolysis system.

#### 4. Conclusions

A new MnO<sub>2</sub>-Pd/C gas-diffusion cathode was prepared and its ability of phenol degradation in

aqueous solution has been utilized. In MnO<sub>2</sub>/C catalyst, MnO<sub>2</sub> particles with more than 25nm were dispersed in the activated carbon in the state of amorphous structure; The content of MnO<sub>2</sub> on the surface of MnO<sub>2</sub>/C catalyst was up to 20.06 at.% ; In Pd/C catalyst, Pd granules which have an average size of 5.0 nm were dispersed to a considerable extent in the activated carbon; The content of Pd on the surface of Pd/C catalyst came up to 1.12 at.% . In diaphragm electrolysis system, the removal efficiency of phenol with MnO<sub>2</sub>-Pd/C gas-diffusion electrode reached about 94.2% when the time reaches 100 min in the cathodic compartment; the average of removal efficiency reached about 96.95%. in the connected electrolysis system, the removal efficiency of phenol with MnO<sub>2</sub>-Pd/C gas-diffusion electrode reached about 99.3% after 100min, particularly higher removal efficiency than others after 40min. Consequently, The removal effect of MnO<sub>2</sub>-Pd/C gas-diffusion cathode on phenol was superior to that of the C, MnO<sub>2</sub>/C, Pd/C gas-diffusion cathode.

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