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Palladium dispersed in three-dimensional polyaniline networks as the catalyst for hydrogen peroxide electro-reduction in acidic medium

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A novel Pd/polyaniline/CFC electrode is prepared by electroless deposition of palladium (Pd) onto three-dimensional polyaniline networks. The polyaniline matrix on carbon fiber cloth (CFC) in reduction state is electro-synthesized by cyclic voltammetry with lower vertex potential of -0.4 V vs. Ag/AgCl. The particle size of Pd coated on polyaniline chains is gradiently distributed. The as-prepared Pd/polyaniline/CFC electrode is characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). Hydrogen peroxide (H$_2$O$_2$) electro-reduction reaction in H$_2$SO$_4$ solutions on the Pd/polyaniline/CFC electrode is investigated by cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). Results reveal that the electrode exhibited high catalytic activity and excellent stability in the strong oxidizing solution of H$_2$O$_2$ and H$_2$SO$_4$. Polyaniline itself shows electro-catalytic activity towards H$_2$O$_2$ to some extent involving chemical-electrochemical (C-E) coupling mechanism.

1. Introduction

Fuel cell (FC), distinguished from other rechargeable secondary power, such as Li ion battery and supercapacitor$^{1-3}$, is a kind of power source that can constantly generate electricity$^{4-7}$. FCs convert chemical energy efficiently into electrical energy without the limitation of Carnot cycle. Hydrogen, methane and alcohols are the three main fuel resources for FCs. Compared with the abundant resources of anode fuel, there is only one kind of universal oxidant, that is, oxygen. Oxygen can be extracted directly from air, however, its electro-reduction activity depends very closely on platinum catalyst. The gas needs extra humidifying apparatus and high-strength pumping to achieve good FC performance. For the past few years, hydrogen peroxide (H$_2$O$_2$) was used as the oxidant for metal semi-fuel cell$^8$, direct borohydride$^9$, direct hydrogen peroxide$^{10}$ and hydrazine$^{11}$ fuel cell. Using H$_2$O$_2$ instead of O$_2$ will make FC system more compact, and especially helps FCs work in the oxygen-free underwater and outer space. Catalysts with high specific surface area supply more active sites for H$_2$O$_2$ electro-reduction$^{12, 13}$. Commercial Pd/C and Pt/C catalysts are obtained by chemically reducing Pd or Pt on carbon black to maintain their nano-particle morphology. Others favored graphene which has the thickness of a few nanometers, and then dispersed noble metal particles on it for better catalytic applications. Polyaniline, synthesized by simple process, generally has various nanoscale structures, such as particle, fiber, tube and sphere$^{14-17}$. Lamy et al.$^{18}$ prepared polyaniline on glassy carbon stationary electrode by cyclic voltammetric technique, afterwards, potentiostatically electrodeposited platinum on polyaniline film to design a Pt/polyaniline electrode for oxygen reduction reaction. The supply of electrodeposition potential for depositing Pt would change the redox states and impair the electrical conductivity of polyaniline, invalidating the composite electrode. Stejskal et al.$^{19}$ adopted silver nitrate as oxidant to oxidize aniline to polyaniline, and in the meantime silver ions were reduced to silver coated on polyaniline. Li and the co-workers$^{20}$ synthesized Au/polyaniline through mutual redox of aniline vapor and HAuCl$_4$ aqueous solution for the oxidation and sensing of ascorbic. The ways that using noble metal compounds as oxidant to chemically make noble metal/polyaniline electrode need extra processes, like mixing noble metal/polyaniline powder with binder, coating on a support for testing, etc. The binder would lower the conductivity of electrode and, for long duration tests, the electrode powders may fall off from the support in the aqueous electrolyte$^{21-23}$. Electro-synthesized polyaniline assisted by CV technique has different redox states and conductivity by selecting potential range of CV$^{24, 25}$. Fig. 1 illustrates the common three redox states of polyaniline. Emeraldine has the highest conductivity while leucomeraldine and pernigraniline are electrically isolated$^{26}$. If as-prepared polyaniline on a support...
is in reduction state, and can thermodynamically reduce noble metal complex ions, a binder-free noble metal/polyaniline electrode would be successfully achieved. Moreover, the oxidation of polyaniline cannot go too far and thus, the mutual redox between formed polyaniline and noble metal compounds has less severe influence on the electrode conductivity. In this work, Pd was electrolessly deposited on polyaniline fibrils by the reduction-state polyaniline itself. The Pd/polyaniline/CFC electrode was introduced to catalyze H₂O₂ electro-reduction because of the synergistic properties of high-surface-area polyaniline doping-dedoping in H₂SO₄ and Pd electro-reduction towards H₂O₂. The obtained electrode owns unique three-dimensional network structure, which enables easy access of the fuel and product into or out from the catalytic active sites. Results indicated that the Pd/polyaniline/CFC electrode for H₂O₂ electro-reduction exhibited high catalytic activity and excellent stability.

2. Experimental

2.1. Preparation of the polyaniline/CFC and Pd/polyaniline/CFC electrodes

Aniline monomers were in-situ electro-polymerized on CFC by cyclic voltammetry in 1.0 mol L⁻¹ sulfuric acid and 0.1 mol L⁻¹ aniline (obtained from Aladdin Industrial Inc.) with a volume of 40 mL. Prior to use, the CFC (purchased from Shanghai Hesen Electric Inc.) was soaked in acetone for 20 minutes, washed copiously and preserved in milli-Q water (18.2 MΩ cm) successively. CFC was fixed between a pair of home-made titanium frame with an area of 1.0 × 1.0 cm exposed to the electrolyte. A platinum sheet (2.0 × 1.0 cm) and a saturated Ag/AgCl electrode (0.1981 V vs. SHE) were used as counter electrode and reference electrode, respectively. All potentials in this work were referred to this reference electrode except where noted. The electro-deposition solution was deoxygenated by bubbling ultrahigh purity N₂ for 10 min and maintained under N₂ atmosphere during polymerization. The CV polymerization was performed for 16 cycles with potential range of -0.4 V ~ 1 V at 50 mV s⁻¹.

To accomplish the electrolessly precipitated Pd/polyaniline/CFC modified electrode, the as-prepared polyaniline/CFC electrode was firstly washed by milli-Q water for several times in order to remove the aniline monomer and oligomer, and then immediately transferred to the Pd complex ions (Pd(II)) solution under open circuit condition within the shortest possible lapse (typically 10 s). The Pd(II) solution is composed of 1.0 mmol L⁻¹ PdCl₂ (Sinopharm Chemical Reagent Co., Ltd) and 20 mmol L⁻¹ HClO₄. The mutual redox between Pd(II) and polyaniline was lasted for 2 hours. All experiments were carried out at ambient temperature (20°C ± 1°C).

2.2. Characterization of polyaniline / CFC and Pd / polyaniline / CFC electrodes

The morphologies of polyaniline/CFC and Pd/polyaniline/CFC electrodes were examined by a scanning electron microscope (SEM, JEOL JSM-6480). The structure was analyzed using an X-ray diffractometer (XRD, Rigaku TTR III) with Cu Kα radiation (λ=0.1514178 nm). The relevant groups of polyaniline before and after mutual redox with Pd(II) were investigated with Fourier transform infrared spectroscopy (FTIR, Equinos55, Bruker) using the potassium bromide pellet technique. The active materials of polyaniline and Pd, together with CFC were grinded into powder for FTIR characterizations.

2.3. Electrochemical measurements

Electrochemical measurements were performed in a conventional three-electrode or two-electrode electrochemical cell using a computerized potentiostat (Autolab PGSTAT302, Eco Chemie) controlled by GPES software. The open circuit potentials (E_oc) were monitored in a two-electrode system of Pd(II) solution with saturated Ag/AgCl electrode as reference electrode. For comparison, the E_oc of polyaniline electrode immersed in PdCl₂-free solution was also recorded. The equilibrium potentials of polyaniline/CFC electrode in 20 mmol L⁻¹ HClO₄ and CFC electrode in Pd(II) solution were measured by potentiodynamic polarization at a scan rate of 1 mV s⁻¹. Electrochemical tests of cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronocoulometry (CA) and electrochemical impedance spectroscopy (EIS) for H₂O₂ electro-reduction were performed in a typical three-electrode electrochemical cell. The obtained polyaniline/CFC or Pd/polyaniline/CFC electrode, platinum foil and a saturated Ag/AgCl electrode were employed as working electrode, counter electrode and reference electrode, respectively. The EIS tests were operated after an equilibrium time of 600 s at fixed potential. The frequency region was 100 kHz ~ 10 mHz with 5 mV potential amplitude.

3. Results and discussion

Fig. 2 shows the cyclic voltammograms for the polymerization of polyaniline on CFC. The first cycle shows an onset oxidation potential of aniline at approximately 0.8 V. The anodic and cathodic current response continuously increased, indicating the regular growth of polyaniline through the formation of a redox couple. The peaks during the potential range referred to various redox states of polyaniline, representing simultaneous electro-polymerization and doping/dedoping process. In the former literature, the lower vertex potential of CV for electro-
polymerization was mostly \(-0.16\) V vs. Ag/AgCl (converted from the SCE scale in the references) or higher. For the sake of reduction state polyaniline (labeled as PAN\(_{\text{ox}}\)), a more negative vertex potential of \(-0.4\) V was set in this study. For the sake of reduction state polyaniline (labeled as PAN\(_{\text{re}}\)), a more negative vertex potential of \(-0.4\) V was set in this study. During the CV polymerization from \(-0.4\) V to the higher vertex of 1.0 V, the color of polyaniline turning darker and darker from light green to black. The resulting polyaniline coated on CFC appeared a light green color. Before modification with Pd, the reaction feasibility of PAN\(_{\text{re}}\) oxidation and Pd(II) reduction was confirmed by their own equilibrium potentials. The two reactions are listed at below:

\[
PAN_{\text{re}} - x e^- \rightleftharpoons PAN_{\text{ox}} - x ClO_4^- \tag{1}
\]

\[
x/2 Pd(II) + x e^- \rightleftharpoons x/2 Pd(0) \tag{2}
\]

In Eqs. (1), PAN\(_{\text{ox}}\) refers to the oxidation state of PAN\(_{\text{re}}\) after losing \(x\) electrons. Fig. 3a shows the Tafel plots derived from potentiodynamic polarization curves. Polyaniline/CFC electrode was immersed in perchloric acid solution, involving the proton doping/dedoping and simultaneous redox reaction as the potential swept (Eqs. (1)). CFC electrode was tested in perchloric acid and PdCl\(_2\) solution, involving Pd(II)/Pd(0) redox reaction (Eqs. (2)). Based on the linear fittings of experimental data in Fig. 3a, the equilibrium potentials were 0.03 V for Eqs. (1) and 0.53 V for Eqs. (2). The oxidation reaction had a more negative equilibrium potential than reduction reaction, proving that Pd can be electrolessly deposited on the polyaniline synthesized in this work thermodynamically (as explained in the right of Fig. 1). The \(E_{\text{oc}}\)-\(t\) curves of polyaniline/CFC electrode in 20 mmol L\(^{-1}\) HClO\(_4\) with and without 1.0 mmol L\(^{-1}\) PdCl\(_2\) were demonstrated in figure 3b. The open circuit potential\((E_{\text{oc}})\) in PdCl\(_2\)-free solution shows a slightly upward tendency from 0.17 V at 0 s to 0.18 V at 7200 s, due to the weak oxidizability of dilute HClO\(_4\) at room temperature. \(E_{\text{oc}}\) in PdCl\(_2\)-free solution was nearly unchanged, while that in PdCl\(_2\) solution gradually rose up from 0.15 V at 0 s to 0.35 V at 2000 s. After that, the open circuit potential with time was kept in parallel with that in PdCl\(_2\)-free solution. This platform illustrated that after 2000s the mutual redox of Pd(II) and PAN\(_{\text{re}}\) finished. The long duration time of 2000 s and the slow rising between 0 s and 2000 s for the chemical redox reaction suggested that, there was probably a gradient diffusion of Pd(II) ions inside the polyaniline matrix where more active sites were available for the reduction of Pd(II) to Pd(0)\(^+(27)\).

Figs. 4a-c are the SEM micrographs of polyaniline and Pd/polyaniline composite supported on CFC. In Fig. 4a, the polyaniline synthesized by CV showed typically loose and fibrillary structure\(^{25, 28, 33, 34}\). The fibril diameter was \(\sim 150\) nm on average. Many monofilament fibers cross-linked from each other to form the networks. Fig. 4b and c demonstrate the SEM images of Pd/polyaniline composite in low and high magnification. The much longer fibers in Figure 4b with a diameter of \(\sim 9\) µm were carbon fibers. Based on previous reports\(^{33, 34}\), the white spots, distinguished from darker CFC and polyaniline, were Pd centers. Zooming in the Pd/polyaniline/CFC, as shown in Fig. 4c, the Pd dispersion in polyaniline networks was inhomogeneous. Furthermore, the size of Pd particles was not uniform and even appeared to be...
Fig. 4 SEM images of polyaniline before (a) and after (b and c) modification of Pd; (d) FTIR spectrums of polyaniline/CFC and Pd/polyaniline/CFC.

gradient distribution. A, B and C spots were where polyaniline faced to the Pd(II) solution from outside to inside. In the A spot, the Pd deposits nearly in-situ wrapped the polyaniline fibrils. In the B spot, the agglomeration of Pd occurred with clusters of particles on polyaniline fibrils. Pd particle at B spot had a size of 120 ~ 200 nm in diameter. Penetrating in the polyaniline networks to C spot, the Pd particle dotted sporadically on polyaniline fibrils had much smaller diameter of 50 ~ 80 nm. As Pd(II) ions diffused into polyaniline matrix for reduction, the concentration gradient would form from A to C spot, which undoubtedly made the size of Pd particle gradiently distribute. Fig. 4d shows the FTIR spectrums of polyaniline before and after modification with Pd, respectively. The band of 3418 cm\(^{-1}\) represented N\(_2\)H\(^+\) stretching mode\(^{35}\). The bands at 1383, 1301 and 1241 cm\(^{-1}\) were attributed to C\(_6\)N stretching vibrations in QBQ, QBB, BBQ and BBB(Q denotes quinoid ring, B denotes benzenoid ring)\(^{36, 37}\). In the region of 1138 cm\(^{-1}\), \(\text{N}\equiv\text{N}\) stretching mode was observed. Out-of-plane deformations of C-H on 1,4-disubstituted benzenoid rings were located in the region of 833 cm\(^{-1}\).\(^{38}\) The two main bands of 1619 and 1498 cm\(^{-1}\) were respectively assigned to \(\text{C}==\text{C}\) stretching vibrations in quinoid and benzenoid rings. It can be seen that the peak at 1619 cm\(^{-1}\) of Pd/polyaniline/CFC became stronger while that at 1498 cm\(^{-1}\) was weaker compared with the peaks of polyaniline/CFC. It was elucidated that after modification of Pd, polyaniline was oxidized from PAN\(_{red}\) to PAN\(_{ox}\) with more quinoid and less benzenoid units.

XRD was introduced to confirm the existence of crystalline Pd. In Fig. 5a, the CFC displayed three broad peaks centered at about 23°, 43° and 80°, which can be attributed to carbon. The characteristic peaks of polyaniline probably overlapped with that of CFC and thus, polyaniline cannot be identified in XRD profiles. After the polyaniline/CFC was modified by Pd, there were five diffraction peaks at 40°, 47°, 68°, 82° and 87°, corresponding well to the (111), (200) and (220), (311) and (222) planes of Pd, respectively, according to the standard crystallographic spectrum of Pd (JCPDS card No. 46-1043).

These peaks indicated that Pd modified on polyaniline had a face-centered cubic (fcc) structure and presented as the metallic state. The FTIR and XRD patterns manifested that binder-free and self-catalytic reductive Pd/polyaniline/CFC electrode was successfully fabricated. Fig. 5b shows the cyclic voltammograms (CV) of the polyaniline/CFC and Pd/polyaniline/CFC electrode measured in 1.0 mol L\(^{-1}\) H\(_2\)SO\(_4\) at scan rate of 10 mV s\(^{-1}\), respectively. The CV curve of polyaniline/CFC exhibited two pair of redox peaks between –0.4 V and 1.0 V, due to the conversions of Emeraldine/lencomeraldine and lencomeraldine/pernigraniline. The CV of Pd/polyaniline/CFC displayed the absorption and/or evolution of hydrogen region from –0.1 V to –0.2 V and hydrogen desorption region at –0.08 V, which were the typical features of Pd\(^{39}\). Due to the metallic Pd oxidation and reduction reactions in H\(_2\)SO\(_4\)\(^{40}\), compared with polyaniline/CFC electrode, the current density of Pd/polyaniline/CFC between the potential ranges of 0.6–1.0 V and 0–0.8 V was larger. The CV of Pd/polyaniline/CFC emerged more couples of redox peaks than that of polyaniline/CFC, inferring that Pd modification could facilitate the successive conversions of more redox states of polyaniline.
The concentration of Pd electrode for H$_2$O$_2$ was 195 mA cm$^{-2}$, only 6 mA cm$^{-2}$ larger than that of 0.5 mol L$^{-1}$. Taking into account the fuel costs, 0.5 mol L$^{-1}$ was considered as the optimal concentration of H$_2$O$_2$.

The stability of polyaniline/CFC and Pd/polyaniline/CFC electrode in 1.0 mol L$^{-1}$ H$_2$SO$_4$ and 0.5 mol L$^{-1}$ H$_2$O$_2$ was tested by applying different polarization potentials. The current-time curves are depicted in Fig. 8. Starting from 0.4 V, the polarization potential was decreased to −0.2 V by three steps and held for 30 minutes at each potential. As seen, the lower the potential, the larger the reduction current density. The current densities were almost kept constant at 0.4 V (14 mA cm$^{-2}$) and 0.1 V (75 mA cm$^{-2}$). The current density at −0.2 V on Pd/polyaniline/CFC electrode delivered slight decrease from 166 mA cm$^{-2}$ at 3721 s to 157 mA cm$^{-2}$ at 5400 s during the 1800s testing time, which is likely resulted from the
consumption of $\text{H}_2\text{O}_2$ near the electrode surface. Polyaniline/CFC electrode was also tested in 1.0 mol L$^{-1}$ $\text{H}_2\text{SO}_4$ and 0.5 mol L$^{-1}$ $\text{H}_2\text{O}_2$ at 0.2 V. It demonstrated a low current density of ~3.0 mA cm$^{-2}$, nearly negligible compared with Pd/polyaniline/CFC electrode. The low current density was probably resulted from the reduction of polyaniline. Inset (left) of Fig. 8 is the SEM image of Pd/polyaniline/CFC electrode after chronoamperometric test. The morphologies of polyaniline fibrils and Pd particles were well retained. In conclusion, the Pd/polyaniline/CFC electrode exhibited excellent stability for $\text{H}_2\text{O}_2$ electro-reduction reaction because of the synergistic properties of high-surface-area polyaniline doping-dedoping in $\text{H}_2\text{SO}_4$ and Pd electro-reduction towards $\text{H}_2\text{O}_2$.

Fig. 9a illustrates the Nyquist plots of Pd/polyaniline/CFC electrode at 0.1 V containing 1.0 mol L$^{-1}$ $\text{H}_2\text{SO}_4$ with and without 0.5 mol L$^{-1}$ $\text{H}_2\text{O}_2$, respectively. The electrochemical system was first polarized for 600 s at 0.1 V to achieve quasi-stable state. In the absence of $\text{H}_2\text{O}_2$, when only polyaniline was electro-reduced, one depressed semi-circle in the higher frequency region and a spike in lower frequency region appeared. After adding $\text{H}_2\text{O}_2$, there were two depressed semi-circles. One in the higher frequency region was ascribed to the electro-reduction reaction of polyaniline, since the frequency of first circle, 8.23 kHz, is very close to that without $\text{H}_2\text{O}_2$, 5.28 kHz$^{10, 42}$. The other circle with a frequency of 96.81 mHz was attributed to the $\text{H}_2\text{O}_2$ electro-reduction reaction on Pd with a diameter of 0.876 Ω ($R_{ct1}$). Inset of Fig. 9a is the equivalent circuit of both polyaniline electro-reduction and $\text{H}_2\text{O}_2$ electro-reduction on Pd. $\text{H}_2\text{O}_2$ electro-reduction ($R_{ct2}$) happened in parallel with polyaniline reduction ($R_{ct1}$). In comparison with the semi-circle without $\text{H}_2\text{O}_2$, the ohmic resistance ($R_0$) of that with $\text{H}_2\text{O}_2$ was smaller, this could be because of the increased solution and/or polyaniline conductivity after adding $\text{H}_2\text{O}_2$. The diameter of the semi-circle was charge transfer resistance ($R_{ct}$), which could be used to evaluate the electrochemical reaction rate. $R_{ct}$ of polyaniline (1.372 Ω) electro-reduction in $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}_2$ was smaller than that (2.342 Ω) only in $\text{H}_2\text{SO}_4$, implying the addition of $\text{H}_2\text{O}_2$ facilitated the polyaniline electro-reduction reaction. To further gain the understanding of interaction between polyaniline and $\text{H}_2\text{O}_2$, the CV synthesized polyaniline was solely tested in 1.0 mol L$^{-1}$ $\text{H}_2\text{SO}_4$ with and without 0.5 mol L$^{-1}$ $\text{H}_2\text{O}_2$. As shown in Fig. 9b, the OCP of polyaniline electrode changed from 0.31 V to 0.51 V. The positive shift of OCP implied that polyaniline was oxidized after adding $\text{H}_2\text{O}_2$. The amplitude of reduction current density was increased after adding $\text{H}_2\text{O}_2$. It was demonstrated that polyaniline itself showed electro-catalytic activity towards $\text{H}_2\text{O}_2$ to some extent. It could be speculated that $\text{H}_2\text{O}_2$ electrode-reduction on polyaniline proceeded in a way of chemical-electrochemical process (C-E process).

**Chemical process:**

\[
P\text{AN}_{ox} + \text{H}_2\text{O}_2 + 2\text{H}_2\text{SO}_4 \rightarrow P\text{AN}_{ox} \cdot 2\text{HSO}_4^- + 2\text{H}_2\text{O} \quad (3)
\]

**Electrochemical process:**

\[
P\text{AN}_{ox} \cdot 2\text{HSO}_4^- + 2e^- \rightarrow P\text{AN}_{ox} + 2\text{HSO}_4^- \quad (4)
\]

**Overall reaction**

\[
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O} \quad (3)+(4)
\]

Polyaniline was first chemical-oxidized to its oxidation state by $\text{H}_2\text{O}_2$ (chemical process), and then electrochemical-reduced to its reduction state by external potential driving force (electrochemical process). As a result, the overall reaction turned out that $\text{H}_2\text{O}_2$ was electro-reduced to $\text{H}_2\text{O}$ on the polyaniline electrode. The C-E coupling mechanism was commonly seen on the Cu and Pt electrodes for $\text{H}_2\text{O}_2$ electro-reduction or electro-oxidation$^{43-45}$ as well.

**4. Conclusions**

In conclusion, the binder-free Pd/polyaniline/CFC electrode was successfully prepared based on the equilibrium potential difference between Pd complex ions and CV synthesized polyaniline. The size of Pd particles coated on polyaniline networks gradiently distributed from the outside to inside. The modified Pd/polyaniline/CFC electrode demonstrated high catalytic activity and remarkable stability towards $\text{H}_2\text{O}_2$ electro-reduction in sulfuric acid even at relatively negative potentials.
Polyaniline solely exhibited electro-catalytic activity for H$_2$O$_2$ electro-reduction in a way of chemical-electrochemical coupling process.

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Notes and references


8 C. Shu, E. Wang, L. Jiang, Q. Tang and G. Sun, Studies on palladium coated titanium foams cathode for Mg-H$_2$O$_2$ fuel cells, J. Power Sources, 2012, 208, 159–164.


