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Pd nanoparticles supported on Mg-Al-CO_3 layered double hydroxide as an effective catalyst for methanol electro-oxidation

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Abstract: Pd/C and Pd/Mg-Al-CO_3 LDH (Pd/LDH) catalysts were prepared and their catalytic performances for methanol electro-oxidation in the alkaline solution were investigated in this work. The result of cyclic voltammograms proves that Pd/LDH has a much higher specific activity than Pd/C. CO stripping results indicate that Mg-Al-CO_3 LDH could facilitate the oxidative removal of adsorbed CO and improve the CO poison resistance of Pd/LDH catalysts. The chronoamperograms also indicate Pd/LDH has a better stability. All the results imply that Pd/LDH is very promising for probable application in DMFC field. Furthermore, the insight for the increase of the specific activity is discussed in this work.

Keywords: Palladium nanoparticles; Layered double hydroxide; Electro-catalyst; Methanol electro-oxidation

1. Introduction

Direct methanol fuel cells (DMFCs) are attractive as portable power sources primarily owing to their low operating temperature, high energy conversion efficiency, low pollutant emission, low cost and ease of storage [1]. Currently, platinum (Pt) and its alloys are the best electrocatalysts for methanol oxidation but they suffer from high cost, limited reserve and serious poisoning by the strong adsorption of oxidation intermediates, such as CO [2]. Up to date, palladium (Pd), with a similar crystal structure as well as electronic properties as Pt, is a promising alternative to Pt-based electrocatalysts due to its relatively lower cost, good catalytic activity in alkaline media and higher resistance to CO poisoning towards methanol electro-oxidation [2-4]. Although a number of Pd-based catalysts, such as Pd-C and Pd-oxides, have been developed for enhancing the methanol oxidation activity [5-8], it remains challenging to develop excellent catalysts with high electrocatalytic activities which are feasible for practical applications.

Layered double hydroxides (LDHs), also known as anionic clays, are a family of layered materials consisting of positively charged brucite-type octahedral layers where the charge-balancing anions and water molecules occupy the interlayer space [9-12]. In recent years, LDHs have attracted growing interest for applications in numerous fields owing to their desirable properties, such as good anion-exchange ability, high thermal stability, and good catalytic activity. For example, Mg-Al-CO_3 LDH was manifested as a hydroxide ion conductor due to its anion-exchange ability. An alkaline-type direct ethanol fuel cell (DEFC), using this kind of LDHs as the

electrolyte and aqueous solution of ethanol and potassium hydroxide as a source of fuel, exhibits excellent electrochemical performance from room temperature to 80℃: open circuit voltage of 0.87 V and electric power of more than 65 W cm^{-2} were obtained [9]. Methanol or ethanol electro-oxidation process is a hydroxide ion related reaction and Mg-Al-CO_3 LDH is a hydroxide ion conductor. Therefore, it will be interesting to see if the incorporation of Pd particles into LDH is a good way to fabricate a new effective catalyst for DMFCs.

Herein, we utilized the hydroxide conductor (Mg-Al-CO_3 LDH) and carbon black (XC-72, Gashub), as support materials, synthesized Pd/Mg-Al-CO_3 LDH and Pd/C catalysts and investigated the electrocatalytic activity of the as-prepared catalysts for methanol oxidation. Furthermore, the insight for the increase of the specific activity was also discussed in this work.

2. Experimental

2.1 Preparation of Mg-Al-CO_3 LDH

In a typical synthesis, co-precipitated Mg-Al-CO_3 LDH was synthesized by simultaneous dropwise addition of 30 mL of 1.0 M $Mg(NO_3)_2$ and 30 mL of 0.5 M $Al(NO_3)_3$ solutions to 100 mL of 1.5 M Na_2CO_3 solution during constant stirring. The pH was adjusted to ~10 by addition of NaOH solution. Then the vessel was transferred to water bath kept at 65℃ for 6 hours. Finally the precipitate was filtered, washed with deionized water, and dried in air at 80℃.

2.2 Preparation of catalysts

To synthesize the electrocatalysts, 100 mg support materials including carbon black and Mg-Al-CO_3 LDH were added into 75 mL deionized water and ultra-sonicated for 8 min, respectively. Then 41.7 mg $PdCl_2$ and 103.7 mg sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) were added into above suspensions. Afterwards, excess amount of 0.01 M $NaBH_4$ aqueous solution (freshly prepared) was added dropwise, followed by stirring for 6 hours at room temperature. Finally, the suspensions were filtered and washed several times with deionized water, and the remaining solids were dried at 60℃ overnight. The catalysts were harvested and denoted as Pd/C and Pd/LDH, respectively. The theoretical content of Pd is 20 wt%.

2.3 Characterization of catalysts

Structure and morphology of the catalysts were investigated by X-ray diffraction (XRD, Smartlab (9 kw), Cu Kα) and transmission electron microscopy (TEM, JEM-2100, 200 kV). The elemental analysis was performed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, IRIS Intrepid Ⅱ XSP (ThermoFisher)). The nature of surface species of catalysts was investigated by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi).

The electrochemical measurements were conducted on an electrochemical workstation system (CHI760D, Chenhua, Shanghai, China) with a three-electrode cell using Pt foil and HgO/Hg electrode as the counter and reference electrodes, respectively. The working electrode was prepared by dropping 5 μL of the electrocatalyst ink onto glassy carbon electrode (GCE). The ink was prepared by ultrasonically mixing 5 mg electrocatalyst sample in 2 mL of ethanol for 8 min. Then

2μL of Nafion solution was dropped on top to fix the electrocatalysts. All potentials in this work were given versus HgO/Hg electrode. Cyclic voltammetry (CV)was performed in a 1.0 M KOH+1.0 M methanol solution, where oxygen was removed by purging N_2 for 15 min. The CV experiments were conducted at a sweep rate of 50 mV s^{-1}, with potentials ranging from −0.8 V to 0.3 V. Electrochemial impedance spectrums (EIS) were measured at -0.2 V from 100 KHz to 0.01 Hz and the perturbing AC amplitude was 5 mV. CO stripping experiments were performed as follows: after purging the solution with N_2 for 20 min, gaseous CO was bubbled for 15 min to form CO adlayer on catalysts while maintaining potential at -0.8 V. Then excess CO in solution was purged with N_2 for 20 min and CO stripping voltammetry was recorded in 1 M KOH solution at 50 mV s^{-1}. The chronoamperometry (CA) was conducted at -0.15 V for 3600 s.

3. Results and discussion

3.1 Structural and compositional analysis

XRD patterns of the Pd/C and Pd/LDH catalysts are shown in Fig. 1(a). There are five diffraction peaks corresponding to (111), (200), (220), (311) and (222) planes of Pd at ca. 40.1, 46.6, 68.1, 82.1 and 86.6°, respectively [13-15]. The diffraction peak at ca. 25° in the pattern of Pd/C belongs to the characteristic peak of carbon [15]. For Pd/LDH catalyst, other peaks except that associated with metallic Pd are well matched with the characteristic peaks of Mg-Al-CO_3 LDH [9]. According to Debye-Scherrer equation, the diameters of Pd particles on Pd/C and Pd/LDH are

11.54 and 7.89 nm, respectively. Fig. 1 (f) presents the morphology of Mg-Al-CO_3 LDH and it is apparent to see the nanosheet structure of this as-prepared sample. Therefore, Mg-Al-CO_3 LDH can be used as a catalyst support material. Fig. 1(b)-(e) show the TEM images and particle size distributions of the as-prepared catalysts. It can be seen that metal nanoparticles are dispersed uniformly on the support materials. The uniform distribution may be attributed to: 1) the support material sheets could provide more locations for the reduction reaction; 2) sodium citrate plays an anti-precipitation effect to manipulate the particle size and 3) sodium citrate also could inhibit the aggregation of the metal particles and make Pd distribute uniformly on the support materials. The average sizes of Pd particles in Pd/C and Pd/LDH catalysts analyzed from TEM images are 8.86 and 5.96 nm, respectively, which are smaller than those obtained from Debye-Scherrer equation. Additionally, according to ICP-AES analysis results, the real mass percentages of Pd in Pd/C and Pd/LDH catalysts are 18.83 and 17.68%, respectively.

XPS was further employed to examine the surface electron structure of the as-prepared samples. Pd3d core level spectra of Pd/C and Pd/LDH catalysts were presented in Fig. 2 (a) and (b) and were fitted by two pairs of overlapping Lorentzian curves [14-15]. In Pd3d XPS spectra for Pd/C, the more intense peaks (335.87 and 340.2 eV) were assigned to metallic palladium, Pd(0). The other set of doublets (336.7 and 341.9 eV) can be attributed to the Pd(□) chemical state on PdO or $Pd(OH)_2$. Pd3d XPS spectra on the as-prepared Pd/LDH catalyst, shown in Fig. 2(b), are also constructed by two sets of doublets which are associated with metallic Pd(0)

and Pd(□). However, the relative intensity of metallic Pd(0) in Pd/LDH is 73.38%, higher than 51.24% obtained from Pd/C. Table 1 lists the relative intensity of Pd(0) and Pd(□) of the as-prepared catalysts. The results indicate that Mg-Al LDH can increase the content of Pd(0) in Pd/LDH catalyst. As shown in Fig. 2 (c) and (d), there is no obvious change of chemical state for Mg and Al in Pd/LDH and Mg-Al LDH. Therefore, it suggests that Mg-Al LDH may act as a catalyst to enhance Pd(□) reduction process.

3.2 Electrochemical properties of Pd/Mg-Al-CO_3 LDH catalyst

It is known that the activity of a catalyst is not only controlled by its catalytic properties but also by the geometrical properties, and the electrochemical surface area (*ESA*) of the catalysts can be calculated using Pd oxide reduction voltammetry by following equation:

$$ESA = \frac{S_R}{v \times Q_{Pd} \times m_c}$$

where S_R is the Pd oxide reduction peak area in voltammetry; v is the scan rate; Q_{Pd} is the charge needed for the reduction of single layer of oxide on Pd, which is 0.000405 C cm^{-2} and m_c is the loading amount of catalyst.

According to the background cyclic voltammograms of Pd/C and Pd/LDH in 1 M KOH solution at a scan rate of 50 mV s^{-1}, shown in Fig. 3(a), ESAs of Pd/C and Pd/LDH were 28.03 and 29.01 m^2 g^{-1}, respectively. Therefore, there is no apparent difference in *ESAs* of the as-prepared catalysts.

The cyclic voltammograms of methanol oxidation on these two catalysts are shown in Fig. 3 (b). The magnitude of the peak current on the forward scanning direction

indicates the electrocatalytic activity of the electrocatalyst for methanol oxidation [12]. The forward peak current density of the Pd/LDH is higher than that of Pd/C and the result suggests the electrocatalytic activity of Pd/LDH is much higher than that of Pd/C. Furthermore, the higher anodic current on Pd/LDH indicates the presence of LDH can improve the electrocatalytic activity of Pd/LDH for methanol oxidation.

EIS was further applied to analyze the electrocatalytic performance of Pd/C and Pd/LDH. Fig. 4 (a) represents the EIS plots of Pd/C and Pd/LDH at -0.2V in 1.0 M KOH+1.0 M methanol solution and the data was analyzed by the electric equivalent circuit shown in Fig. 4(b). In the electric equivalent circuit, R_s is the sum of resistance of electrolyte, electrode material and the contact resistance at the interface of the active material/current collector; C represents the double layer capacitance; R_t is the charge transfer resistance; R_c is the resistance of intermediate adlayer and L is the inductance induced by the intermediate. The values of R_s, C, R_t, R_c and L were calculated from the CNLS fitting of the experimental impedance spectra and their resulting values are listed in Table 2.

According to the fitting results in Table 2, it is apparent to see the resistances for Pd/LDH, no matter R_t or R_c, are smaller than that for Pd/C. Therefore, Pd/LDH shows a better performance in methanol electro-oxidation process than Pd/C. Furthermore, Pd/LDH has smaller double layer capacitance (C) and inductance (L) generated by the intermediate than Pd/C catalyst. It indicates that less amount of intermediate in the methanol electro-oxidation process adsorbed on Pd/LDH surface. Pd/LDH may have a better CO poisoning resistance than Pd/C.

To further evaluate the resistance to the CO_{ads} poisoning of each catalyst, the CO stripping voltammograms were recorded, as shown in Fig. 5. It is clear that the onset potential of CO oxidation on Pd/LDH catalyst is more negative than that on Pd/C catalyst, indicating that Mg-Al-CO_3 LDH facilitates the removal of CO out of the surface of the Pd/LDH catalyst owing to the potential adsorption and conduction of OH^-. Furthermore, due to the catalytic effect, Mg-Al-CO_3 LDH could activate water at lower potentials than Pd. The activated water could oxidize the adsorbed CO and liberated Pd active sites [15-16]. This result helped to explain the higher activity of Pd/LDH catalyst for the oxidation of methanol.

The above analytic results confirm that Pd/LDH composite has a better electrocatalytic activity for methanol oxidation in KOH. The probable reason for this trend is summarized as follows: 1) content increase of metallic state palladium in the Pd/LDH catalyst, which is well known that the more content of metallic state in catalysts, the better catalytic performance; 2) as a hydroxide ion conductor, Mg-Al-CO_3 LDH could deliver OH^- and increase the concentration of OH^- around Pd particle surface, as shown in scheme 1.

The better CO poisoning resistance of Pd/LDH also can be explained as follows: the surface adsorbed hydroxyl of Mg-Al-CO_3 LDH may remove the adsorbed carbonyl on the surface of Pd, and then dissociation–adsorption of methanol proceeds quickly. The reaction can be written as Equation.1~3.

$$LDH + OH^- \rightarrow LDH - OH_{ads} + e^- \quad (1)$$

$$Pd - (CH_3OH_{ads}) + 4OH^- \rightarrow Pd - CO_{ads} + 4H_2O + 4e^- \quad (2)$$

$$Pd - CO_{ads} + LDH - OH_{ads} + OH^- \rightarrow Pd + LDH + CO_2 + H_2O + e^- \quad (3)$$

Mg-Al-CO_3 LDH would increase the concentration of OH_{ads} species on the catalyst surface, and these OH_{ads} can react with CO-like intermediate species to produce CO_2 or water soluble products, releasing the active sites on Pd for further electrochemical reaction [12]. Furthermore, the other reason for CO tolerance improvement is the so-called wetness effect of Mg-Al-CO_3 LDH on the primary Pd-OH oxide spillover, which is considered decisive for CO oxidation [17-18], as shown in the following equation (4).

$$Pd - CO + 2Pd - OH \rightarrow CO_2 + H_2O + 3Pd \quad (4)$$

The long-term stability of Pd/C and Pd/LDH catalysts for the oxidation of methanol at a potential of -0.15 V were also investigated and the chronoamperometry curves are shown in Fig.6. Due to the formation of some Pd oxides/hydroxides and adsorbed intermediates in the alcohol electro-oxidation reaction, all these catalysts show a current decay before a steady current status was attained [9, 15]. As expected, the current density of Pd/LDH was larger than that of Pd/C in methanol solution. In addition, in the beginning, the current for Pd/LDH declined more slowly than that for Pd/C. This also proves that Pd/LDH has better electrochemical catalytic stability for the oxidation of methanol than Pd/C.

4. Conclusions

Pd/C and Pd/Mg-Al-CO_3 LDH catalysts were prepared and their catalytic performance for methanol electro-oxidation was compared. Cyclic voltammograms in

the alkaline solution showed the much higher specific activity of Pd/LDH than that of Pd/C. The increase of the specific activity could be attributed to the OH^- conductivity of Mg-Al-CO_3 LDH and the content increase of metallic Pd. According to CO stripping results, it is found that Mg-Al-CO_3 LDH facilitates the oxidative removal of adsorbed CO. The chronoamperograms indicated that Pd/LDH has a better stability. All the results imply that Pd/LDH is very promising for probable application in DMFC field. Furthermore, Mg-Al-CO_3 LDH may act two important roles in the Pd/LDH catalyst: 1) catalyst for Pd(□) reduction, 2) facilitating hydroxide ion conduction.

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Figure caption

Fig.1 (a) XRD patterns of Pd/C and Pd/LDH (inset: XRD pattern of Mg-Al-CO_3 LDH); (b) TEM image of Pd/C; (c) Diameter distribution of Pd Particles on Pd/C; (d) TEM image of Pd/LDH; (e) Diameter distribution of Pd Particles on Pd/LDH and (f) TEM image of Mg-Al-CO_3 LDH

Fig. 2 (a) XPS spectra of Pd of Pd/C; (b) XPS spectra of Pd of Pd/LDH; (c) XPS spectra of Mg of Mg-Al LDH and Pd/LDH; (d) XPS spectra of Al of Mg-Al LDH and Pd/LDH

Fig. 3 The cyclic voltammograms of Pd/C and Pd/LDH in 1.0 M KOH (a) and in 1.0 M KOH+1.0 M methanol solution (b)

Fig. 4 EIS plots of Pd/C and Pd/LDH at different potentials (a, b) and equivalent electrical circuit in 1.0 M KOH+1.0 M methanol solution

Fig. 5 CO stripping curves on Pd/C (a) and Pd/LDH (b) catalysts recorded in 1 M KOH solution

Scheme 1 Function of Mg-Al-CO_3 LDH in the methanol electro-oxidation at Pd particle surface

Fig.6 Chronoamperograms of Pd/C and Pd/LDH in 1.0 M KOH+1.0 M methanol at operation potential of -0.15 V at 25℃

Fig. 1 (a)

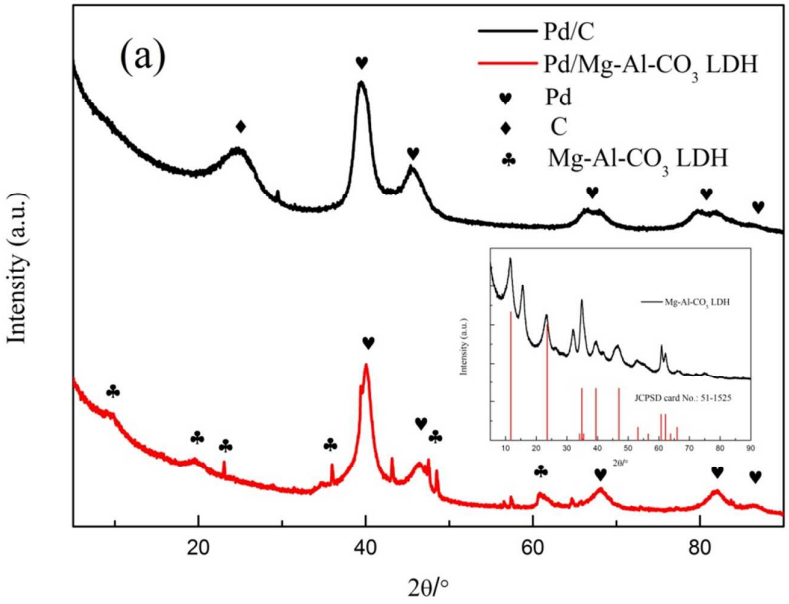


Fig. 1 (b)

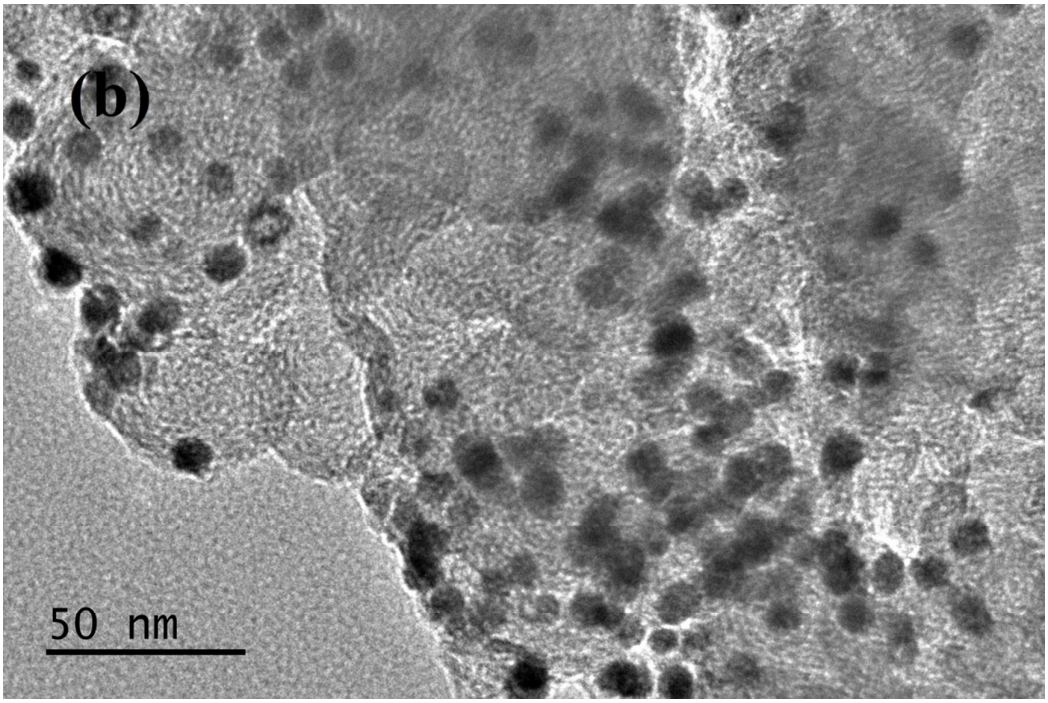


Fig. 1(c)

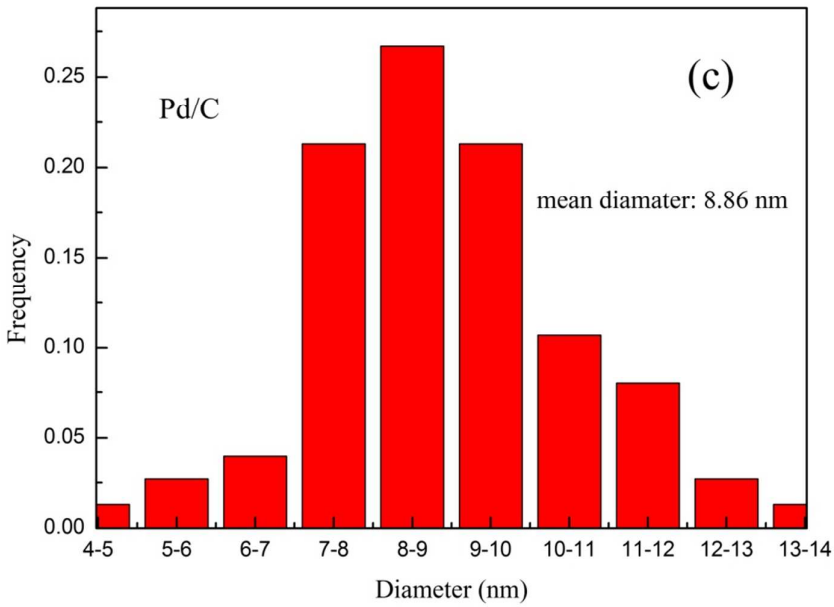
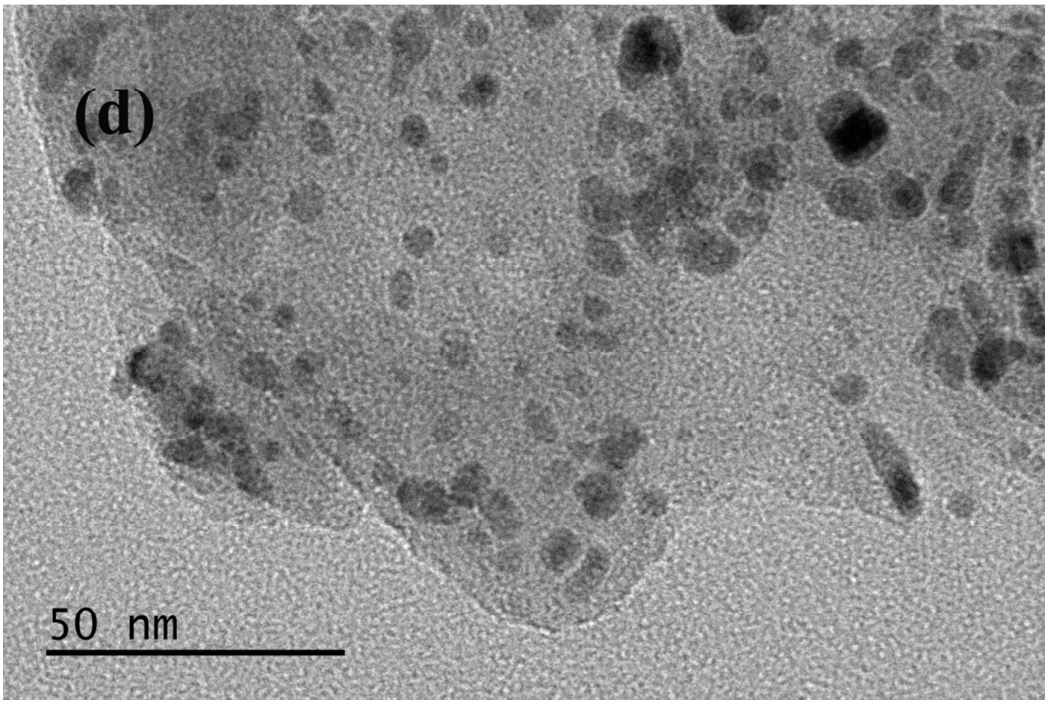


Fig. 1 (d)



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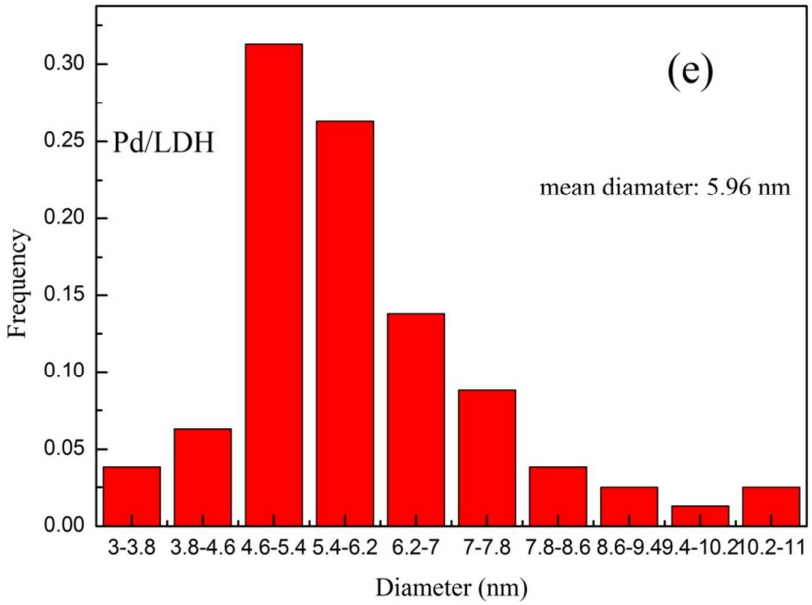


Fig. 1(f)

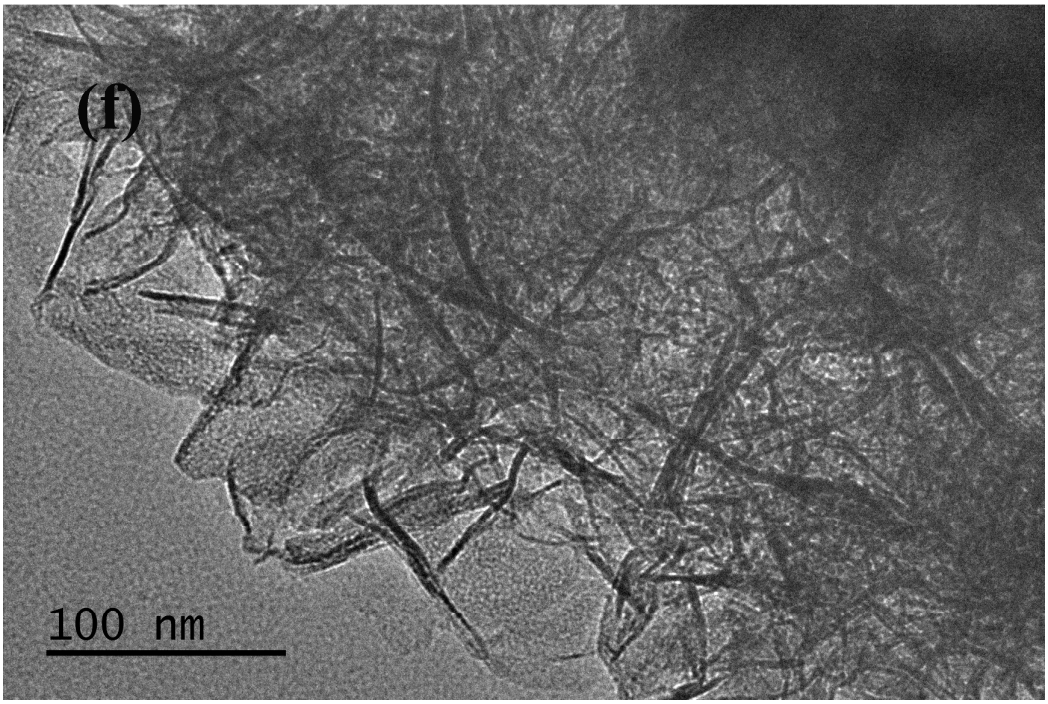
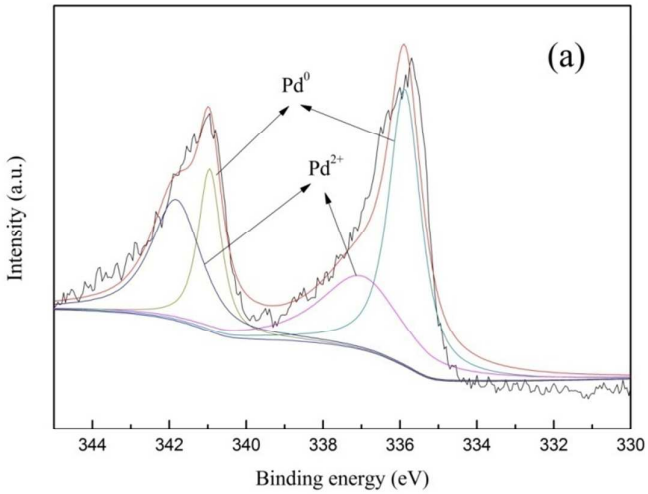


Fig. 2 (a)



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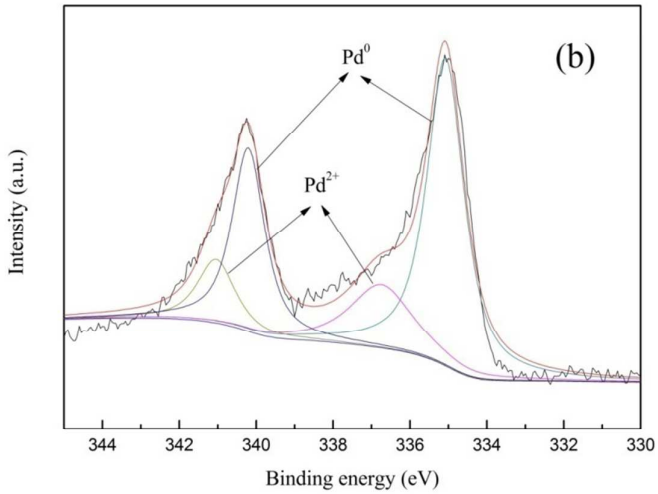
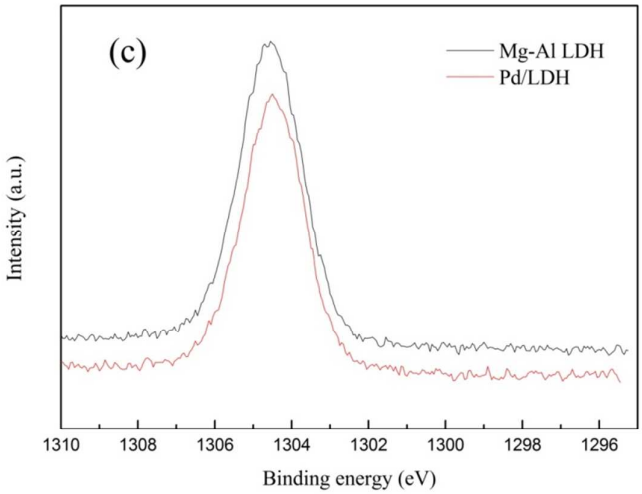


Fig. 2 (c)



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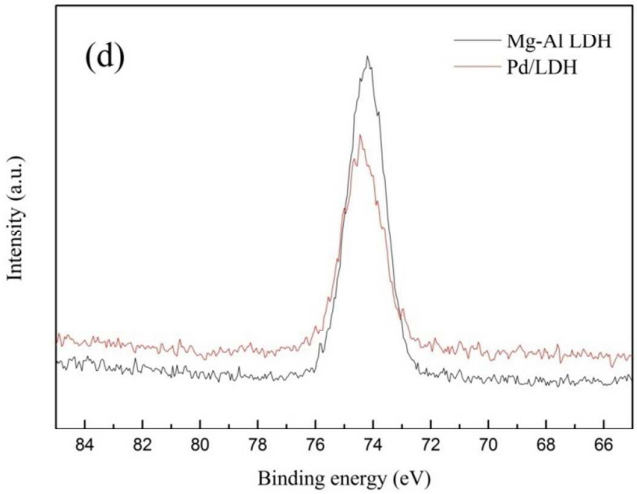


Fig. 3 (a)

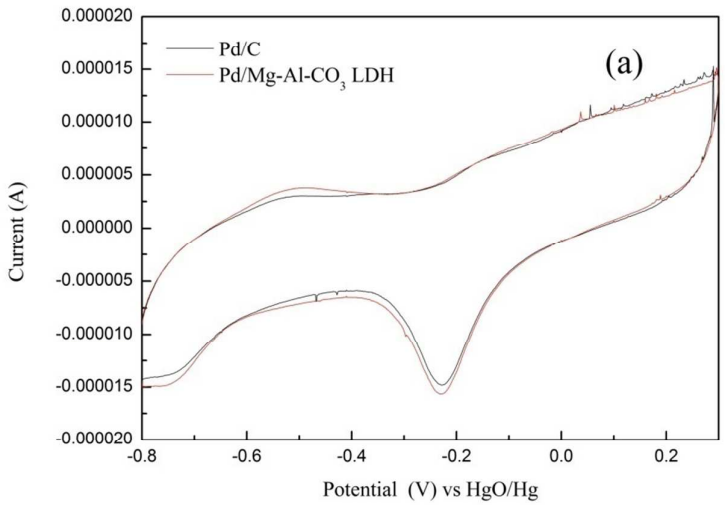


Fig. 3 (b)

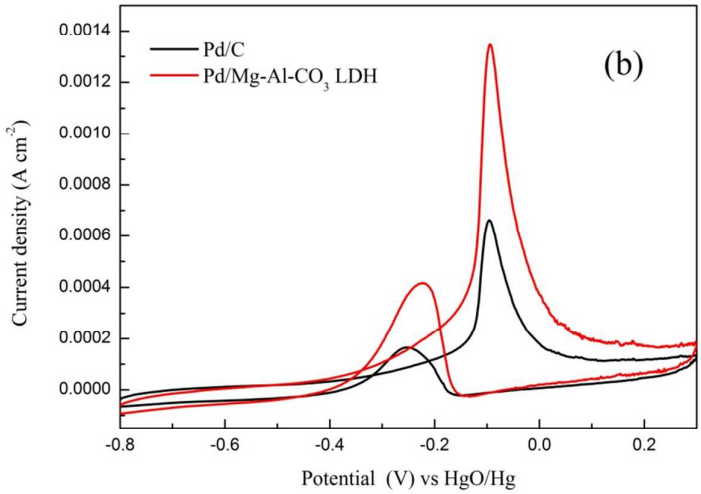


Fig. 4 (a)

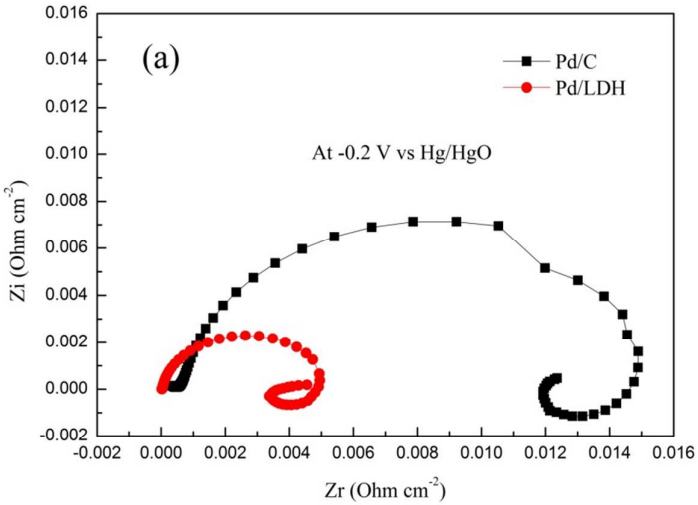


Fig. 4 (b)

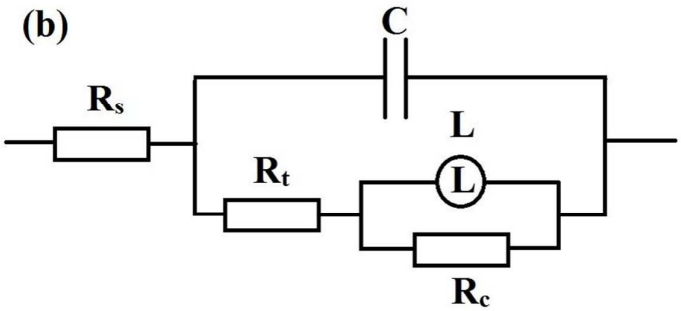


Fig. 5 (a)

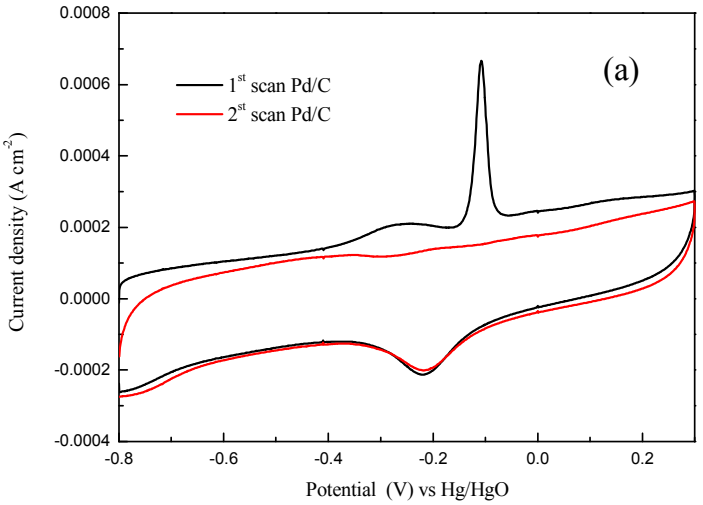
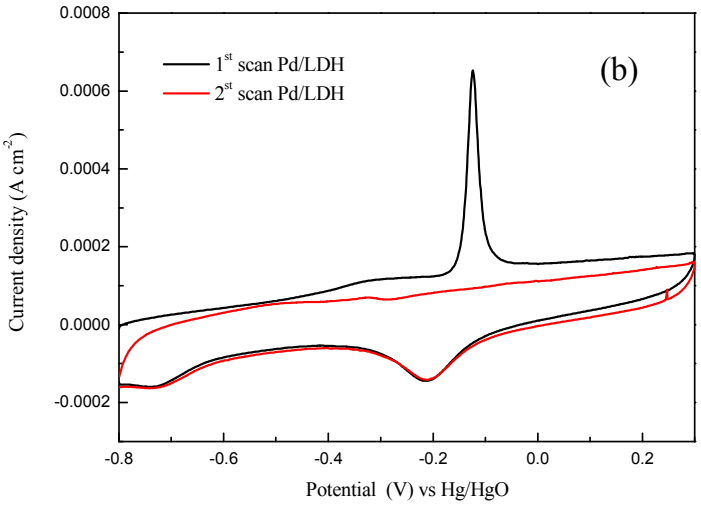


Fig. 5 (b)



Scheme 1

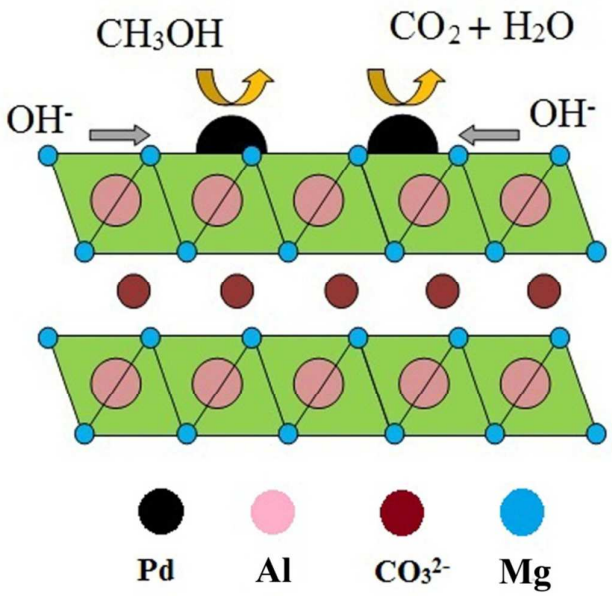


Fig.6

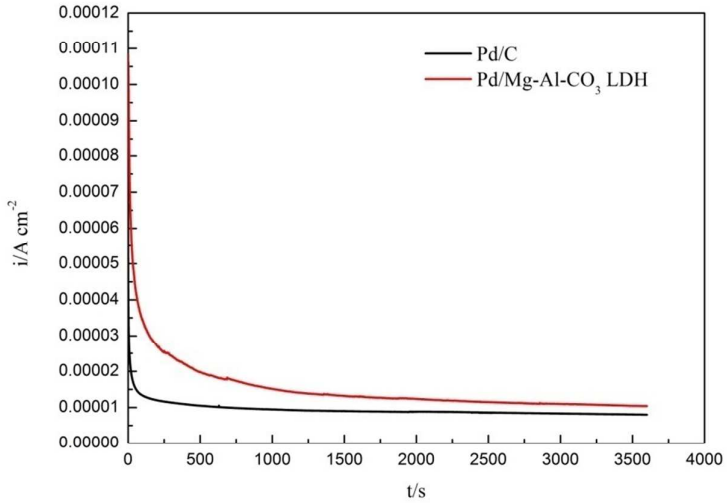


Table caption

Table 1 Binding energy (B.E.) and relative intensity of species from curve-fitted XPS spectra of Pd3d

Table 2 Fitting results of EIS (All the fitting data were normalized by *ESA*)

Table 1

Samples	B.E. of Pd $3D_{5/2}$ (eV)	B.E. of Pd $3D_{3/2}$ (eV)	Species	Relative intensity (%)
Pd/C	335.87	340.2	Pd(0)	51.24
	336.7	341.9	Pd(□)	48.76
Pd/LDH	335.7	341	Pd(0)	73.38
	336.51	342.1	Pd(□)	26.62

Table 2

	R_s (Ω cm^2)	C (F cm^{-2})	R_t(Ω cm^2)	R_c(Ω cm^2)	L (H cm^{-2})
Pd/C	5.53625E-4	9.48125E-9	0.01139	0.00227	0.00248
Pd/LDH	3.19302E-5	4.8924E-11	0.00364	4.30515E-4	0.00119