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Nitrogen and Phosphorus Self-Doped Carbon Supported Palladium as Highly Efficient Electrocatalysts for Formic Acid Oxidation

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Exploring new Pd-based catalysts with both high activity and CO resistance for formic acid oxidation remains of great importance of direct formic acid fuel cell (DFAFC) technology. Here, a nitrogen and phosphorus self-doped carbon have been facilely synthesized by a direct pyrolysis of aminophosphonic acid resin (APAR) which was employed as the N, P and C sources. The synthesized N, P self-doped carbon at different temperatures (NPC-T, T=850, 900, 950, 1000 °C) were used as supports for the preparation of Pd/NPC-T electrocatalysts by microwave-assisted glycol reduction method. All prepared catalysts show better catalytic performance than commercial Pd/C counterparts towards formic acid electro-oxidation (FAEO). Among them, Pd/NPC-900 demonstrates optimal electrocatalytic activity with an enhancing factor of 1.98 than commercial Pd/C catalyst. Moreover, the Pd/NPC-T catalysts present excellent stability, highly tolerant to CO poisoning and faster charge-transfer kinetics of FAEO. The superior catalytic performance of the Pd/NPC-T catalysts are attributed to the doping of nitrogen and phosphorus, which modified the electronic structure of Pd particles and accelerated the removal of CO intermediates.

Keywords: N, P self-doped carbon; Pd electrocatalyst; Formic acid oxidation; Microwave-assisted reduction

1. INTRODUCTION

DFAFC has been considered as a promising energy conversion device due to its outstanding performance, such as low operation temperature, high power density, high open circuit potential and less environment pollution [1,2]. Electrocatalysts are the key factors that determine the efficiency of fuel cells. Noble metals Pt and Pd have been widely researched as DFAFC catalysts due to their excellent electrocatalytic properties [3-6]. It has been reported that Pd based catalysts exhibits superior electrocatalytic activity for formic acid oxidation compared to Pt based catalysts, because the direct pathway is mainly preformed through Pd based catalysts [7,8]. However, the stability of Pd catalysts is poor because of the accumulated CO-like intermediates on its surface and the agglomeration of Pd nanoparticles in the catalytic process. Therefore, it is of great significance to improve the activity and stability of Pd catalysts toward FAEO.

To improve the catalytic activity and stability, a variety of carbon materials with good conductivity and special structure, such as carbon blacks [9], carbon nanotubes [10] and graphene [11], have been developed as supports for Pd particles. Doping heteroatoms (N, P, S, B) into carbon supports could modify its electronic structure and further promote the electrocatalytic performance of Pd because of the increased dispersion and enhanced metal-support interactions [12-15]. Our previous work successfully prepared nitrogen-doped carbon (MMT-CN_x) through high-temperature pyrolysis of polyaniline in the presence of montmorillonite as nitrogen-doped carbon support [16]. Phosphorusdoped carbon support has also been synthesized by annealing the triphenylphosphine with Vulcan XC-72 carbon [17]. After loading Pd, both catalysts show enhanced FAEO performances compared with Pd/C. In addition, compared to single heteroatom doping, the physicochemical properties of two different elements co-doped carbon materials can be regulated broadly because of the synergistic effects between the different heteroatoms [18-20]. The unique electronic structure of these dual-doped carbon materials enable them suitable for various electrocatalytic reactions. Zan et al. [21] designed hierarchically porous carbon with phytic acid (PA) as phosphorus source, dicyandiamide (DCDA) as nitrogen source dual-doped catalyst, which shows a superior ORR performance. Wang et al. [22] prepared a N, P self-doped biocarbon (NPBC) through a directly pyrolysis of spirulina. The as-obtained NPBC delivers bifunctional activity to catalyze both oxygen reduction and oxygen evolution reactions. Heteroatoms in these dual-doped carbon carriers can provide sufficient anchoring sites for metal pd precursors, play an important role in their nucleation and growth processes, and improve the electronic structure on the surface of formed pd nanoparticles. Lou et al. [23] synthesized the N, P dual-doped carbon fiber supported Pd catalyst using a variety of different sources of nitrogen and phosphorus for FAEO. The characterization results indicate that dual-doped catalyst possess better performance than the single doped catalysts owing to the the synergistic effect of N and P with Pd catalyst.

In this work, a series of N, P self-doped carbon (NPC) supports were facilely prepared by onestep calcination of aminophosphonic acid resin at different temperature. The effects of N and P with subsequently loaded Pd were investigated and performance of the as-prepared catalysts were evaluated by physical characterization and electrochemical characterization.

2. EXPERIMENTAL DETAILS

2.1 Materials and Reagents

Aminophosphonic acid resin was purchased from Sunresin New Materials Co. Ltd. (Xi'an, China). PdCl₂ were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). 5wt.% Nafion solution was bought from Aldrich Chemical Co., USA. A commercial 20 wt.% Pd/C was used as contrast catalyst. All other reagents were of analytical grade and used without further purification. All aqueous solutions were prepared with ultrapure water (Resistivity \geq 18.2 Ω M·cm).

2.2 Preparation of NPC-T and Pd/NPC-T catalysts

The aminophosphonic acid resin was washed with deionized water before dried in a vacuum oven. To fabricate NPC, the treated resin was placed in a tube furnace and heated to a series of designated temperature (850, 900, 950, and 1000 °C) at a ramping rate of 3 °C min⁻¹ under a nitrogen atmosphere and held for 30 min. After cooling down to room temperature, the N and P self-doped carbon (NPC) was ground into powders and denoted as NPC-850, NPC-900, NPC-950, NPC-1000, respectively.

The Pd/NPC-T catalysts were synthesized through a microwave-assisted polyol process. Typically, 40 mg NPC powder was mixed with 1.88 ml of 0.05 M PdCl₂ solution and 40 ml ethylene glycol (EG) in a 100 ml flask. The suspension was then ultrasonically dispersed for 10 minutes. Afterwards, 1 mol L⁻¹ NaOH/EG solution was added to the suspension to adjust its PH value to 10 under magnetic stirring. After stirred for an additional 1 h, the mixture was heated in a microwave oven (Sineo Microwave Chemical Technology Co. Ltd.) at 600W with the pulse form 10 s-on/10 s-off cycle for 7 times. After the solution was cooled to room temperature, 0.2 mol L⁻¹ HCl solution was added to adjust its pH to 3 to promote the adsorption of the Pd nanoparticles onto the NPC support. Finally, the obtained Pd/NPC-T catalysts were filtered, washed and dried at 80 °C in a vacuum oven for 4 hours. The loading of Pd metal is 20 wt. % in all the samples.

2.3 Material characterizations

X-ray diffraction (XRD) patterns were performed on a Bruker D8 diffractometer (Germany), using Cu K α radiation (40 kV, 40 mA). Surface morphology of the catalysts were recorded on a scanning electron microscopy (SEM, JEOL, Japan). The particle size distribution and elemental mapping of the prepared catalysts were conducted on a JEM-2100F transmission electron microscope. X-ray photoelectron spectra (XPS) measurements were carried out on a Thermo ESCALAB 250XI spectrometer. A Thermo Fisher DXR spectrometer was taken to record Raman spectra of carbon supports.

2.4 Electrochemical measurements

All electrochemical measurements were accomplished on a CHI660E electrochemical workstation with a standard three-electrode cell system at room temperature. A platinum wire and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. To prepare working electrode, a glassy carbon electrode (GC, 3 mm in diameter) was firstly polished with Al_2O_3 powder, then ultrasonicated in ethanol and pure water for 1 minute, respectively. 5.0 mg catalyst was ultrasonically dispersed in 0.5 ml ethanol containing 0.5 wt% Nafion solution to obtain a suspension of the catalyst. About 4.0 µL of the above suspension was spread on the polished glassy carbon electrode. After drying naturally, the Pd loading of the electrode was ca. 8 µg.

CO stripping tests were conducted with the following procedure: CO was adsorbed on the catalysts at a potential of 0.2 V in the 0.5 M H₂SO₄ solution for 30 min. High pure N₂ was slowly bubbled for 20 min to remove the excess CO in the electrolyte. Then the stripping voltammograms were recorded at 50 mV s⁻¹ between -0.2 V to 1 V. Cyclic voltammograms (CV) and Chronoamperometry (CA) measurements of catalysts were performed in a 0.5 M HCOOH/H₂SO₄ solution, where oxygen was purged by pure N₂. The potential of CV experiments were set from -0.2 V to 0.8 V and scan rate were 50 mV s⁻¹. CA experiments were conducted at a fixed potential of 0.1 V for 1 hour. Electrochemical impedance spectroscopy (EIS) experiments were executed in a frequency range from 10⁵ to 0.1 Hz at the open potential. All potentials in the electrochemical experiments were given versus reference electrode.



3. RESULTS AND DISCUSSION

Figure 1. XRD patterns of Pd/NPC-850 (a), Pd/NPC-900 (b), Pd/NPC-950 (c) and Pd/NPC-1000 (d) catalysts.

The crystalline structure of Pd/NPC-T catalysts was studied by X-ray diffraction (XRD). As shown in Figure 1, a broad peak at around 23° (2 θ) in each sample is corresponding to the (002) plane of carbon, indicating the carbon materials present a low degree of graphite structure. Meanwhile, five

peaks at $2\theta = 40.0^{\circ}$, 46.6° , 68.0° , 82.0° and 86.6° are consistent with (111), (200), (220), (311) and (222) lattice planes of Pd (JCPDS card No. 46-1043) respectively, suggesting that metal Pd with face-centered cubic (fcc) structure has been successfully synthesized through ethylene glycol reduction. According to the Pd (111) peak, mean crystalline size of Pd in Pd/NPC-850, Pd/NPC-900, Pd/NPC-950, Pd/NPC-1000 catalysts were calculated as 4.53 nm, 3.31 nm, 3.51 nm and 4.13 nm, respectively, using Scherrer formula [24].



Figure 2. SEM spectra of Pd/NPC-850 (a), Pd/NPC-900 (b), Pd/NPC-950 (c) and Pd/NPC-1000 (d) catalysts.



Figure 3. Typical TEM images and corresponding particle size distribution histograms and HRTEM images of Pd/NPC-850 (a1, a2 and a3), Pd/NPC-900 (b1, b2 and b3), Pd/NPC-950 (c1, c2 and c3) and Pd/NPC-1000 (d1, d2 and d3).

The morphology of the as-synthesized Pd/NPC-T catalysts was characterized by scanning electron microscopy (SEM). As shown in Figure 2a-d, the Pd/NPC-T catalysts are irregular nanoparticles, NPC-T exhibits the densely distributed microsized pores on the surfaces and in the interior. Figure 3a1-d1 show the typical TEM images of the Pd/NPC-850, Pd/NPC-900, Pd/NPC-950, Pd/NPC-1000 catalysts. As seen, the Pd NPs on Pd/NPC-850, Pd/NPC-950 and Pd/NPC-1000 catalysts are found to have a slight agglomeration compared with Pd/NPC-900. Figure 3a2-d2 display the corresponding particle size distribution histograms. According to the histograms, the mean particle sizes of the Pd/NPC-850, Pd/NPC-900, Pd/NPC-950, Pd/NPC-1000 catalysts were observed as 5.7, 3.45, 4.37 and 5.46 nm, respectively, which was consistent with the crystalline size sequence calculated from the XRD technique. The high-resolution transmission electron microscope (HRTEM) was utilized to characterize the fine structure of the Pd/NPC-T catalysts further. As shown in Figure 3a3-d3, the Pd NPs exhibit clear lattice fringes, indicating good crystallinity. The lattice distance of the Pd/NPC-850, Pd/NPC-900, Pd/NPC-950, Pd/NPC-1000 catalysts were measured as 0.226, 0.235, 0.235 and 0.233 nm, respectively, which were assigned to the Pd (111) crystal plane (0.225 nm). To confirm that N and P were successfully doped in the samples, the elemental mapping of N, O, P and Pd in Pd/NPC-900 was carried out, which is displayed in Figure 4. It demonstrates the N, O, P and Pd are homogeneous distributed on the surfaces of Pd/NPC-900, confirming successful fabrication of Pd/NPC-T catalysts. This one-pot pyrolysis strategy using APAR as low-cost carbon, nitrogen and phosphorus source significantly simplifies the preparation procedures of N, P co-doped carbon support. Furthermore, microwave-assisted polyol method accelerated reducing of Pd precursor. Consequently, the assynthesized Pd/NPC-T catalysts may be considered as cost-effective electrocatalysts for formic acid oxidation.



Figure 4. Elemental mapping of N, O, P and Pd in Pd/NPC-900.



Figure 5. XPS spectra of survey spectra (a), P 2p (b), Pd 3d (c), N 1s (d) and the percentage of different N species (e).

Table 1. The atomic content of C, N, O, P and Pd elements in Pd/NPC-850, Pd/NPC-900, Pd/NPC-950 and Pd/NPC-1000 catalysts obtained from XPS.

Catalysts	C (at%)	N (at%)	O (at%)	P (at%)	Pd (at%)
Pd/NPC-850	68.55	3.14	24.2	1.2	2.91
Pd/NPC-900	69.21	2.95	23.35	1.52	2.97
Pd/NPC-950	71.17	2.79	21.95	1.45	2.64
Pd/NPC-1000	69.72	2.72	23.37	1.36	2.83

XPS was employed to analyze the elemental compositions and bond information of prepared catalysts. The XPS survey spectra of the catalysts (Figure 5a) shows several element peaks of C 1s, N 1s, O 1s, P 2p and Pd 3d, the corresponding element content are summarized in Table 1. The P 2p spectrum of Pd/NPC-T catalysts (Figure 5b) can be deconvoluted into two peaks. The binding energy (BE) of P 2p spectra for each catalyst is listed in Table 2. The peak at 132.61 eV in Pd/NPC-900 indicates the formation of P-C bond [25,26], while as the peak at 133.57 eV is assigned to P-O bond, which may exist in the form of CH₃OP(OH)₂ [27]. The amount of oxygen-containing functional groups could be largely increased with the doping of P [28], which is beneficial for the removal of CO intermediates, therefore enhancing the anti-poisoning of the catalysts. Compared to the BE of pure P (130.4 eV) [29], the peaks of P-C bond of the Pd/NPC-T catalysts at 132.71 eV (T=850 °C), 132.61 eV (T=900 °C), 132.76 eV (T=950 °C) and 133.41 eV (T=1000 °C) are positively shifted 2.31 eV, 2.21 eV, 2.36 eV and 3.01 eV respectively. The positively charged phosphorus accepts electrons from the palladium species, which results in an increase of the 2p electron density of P atom and leads to a negative shift of binding energies of P [17,23]. Pd/NPC-900 has the lowest binding energy of P 2p among the catalysts, confirming the stronger interaction between Pd and P-containing active sites in Pd/NPC-900 than other catalysts. The BE of Pd 3d for each catalyst is listed in Table 3. As described in Figure 5c, the Pd 3d signals of the Pd/NPC-T catalysts can be deconvolved into two components, assigned to Pd⁰ and Pd²⁺ species. The 3d binding energy of Pd⁰ of Pd/NPC-900 at 335.58eV ($3d_{5/2}$) and 340.83eV ($3d_{3/2}$) doesn't show more positively shift than other catalysts. This result may due to the high electron-donating ability of N in the catalysts, which lead to an increase of the 3d electron density of Pd [30,31]. These oppositely electron transfers behavior in Pd-P and Pd-N ultimately lead to a positively shift of binding energies of Pd 3d in our catalysts. The positively shifted binding energies of Pd is hard to bind the COOH intermediates [32]. Thereby, HCOOH is easy to be oxidized through the direct pathway. The highresolution N 1s spectrum of the Pd/NPC-T catalysts are showing in Figure 5d. The N 1s peak of the Pd/NPC-T catalysts can be deconvoluted into four peaks, corresponding to pyridinic-N, pyrrolic-N, graphitic-N, and oxidized-N [33,34]. It was reported that the pyridinic-N and the pyrrolic-N species could act as anchors for Pd nanoparticles [35-37].

Catalysts	Species	Binding Energy	BE Shift (eV)
DJ/NDC 950	P-C	132.71	2.31
Pu/INPC-830	P-O	133.74	3.34
	P-C	132.61	2.21
Pd/NPC-900	P-O	133.57	3.17
DJ/NDC 050	P-C	132.76	2.36
Pu/INPC-930	P-O	134	3.6
DJ/NDC 1000	P-C	133.41	3.01
Pu/NPC-1000	P-O	134.45	4.05

Table 2. Binding Energy (BE) and its shift of P 2p spectra of Pd/NPC-850, Pd/NPC-900, Pd/NPC-950and Pd/NPC-1000 catalysts.

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Therefore, pyridinic-N and pyrrolic-N may significantly affect the dispersion of Pd nanoparticles in the catalyst. Figure 5e shows the percentage of pyridinic-N and pyrrolic-N in Pd/NPC-900 is the highest among the four catalysts, which promote a higher dispersion of Pd NPs. Consequently, fine and uniformly dispersed Pd NPs are obtained, which is confirmed by the TEM results.

Table 3. Binding Energy (BE) and its shift of Pd 3d spectra of Pd/NPC-850, Pd/NPC-900, Pd/NPC-950 and Pd/NPC-1000 catalysts.

Catalysts	Species	Binding Energy	BE Shift (eV)
DJ/NDC 950	$Pd^{0}3d_{3/2}$	340.78	0.48
Fu/INFC-030	$Pd^{0}3d_{5/2}$	335.49	-0.01
	$Pd^{0}3d_{3/2}$	340.83	0.53
Pu/INPC-900	$Pd^{0}3d_{5/2}$	335.58	0.08
DJ/NDC 050	$Pd^{0}3d_{3/2}$	340.89	0.59
Pu/INPC-930	$Pd^{0}3d_{5/2}$	335.62	0.12
D1/NDC 1000	$Pd^{0}3d_{3/2}$	340.89	0.59
Pu/NPC-1000	$Pd^{0}3d_{5/2}$	335.6	0.1
$BE(Pd^{0}3d_{3/2})=340.3 \text{ eV}$	$BE(Pd^{0}3d_{5/2})=335.5 \text{ eV}$		



Figure 6. Raman spectra of NPC-850, NPC-900, NPC-950 and NPC-1000 supports.

Figure 6 depicts Raman spectra of NPC-T samples. It can be seen that all samples exhibit two remarkable peaks at about 1360 cm⁻¹ and 1600 cm⁻¹, corresponding to D-band (disorder sp³ carbon) and G-band (graphite sp² carbon), respectively. The intensity ratio of D-band to G-band I_D/I_G is a significant parameter to quantify the defect level in the graphitic structure. The value of I_D/I_G for Pd/NPC-T catalysts are calculated to be 0.97, 0.98, 0.99 and 1.06, respectively. The slightly increase of I_D/I_G with the increasing pyrolysis temperature indicates that higher heating temperature benefits to improve the disordered degree of the NPC.



Figure 7. CO-stripping curves of Pd/NPC-850 (a), Pd/NPC-900 (b), Pd/NPC-950 (c), Pd/NPC-1000 (d) and commercial Pd/C (e) catalysts in 0.5 M H₂SO₄ solution at a scan rate of 50 mV s⁻¹.

CO-stripping experiments were executed to evaluate the anti-poisoning performances of the Pd/NPC-T and commercial Pd/C catalysts to the CO_{ads}, as demonstrated in Figure 7a-e. The peak of the first cycle at around 0.8V is caused by the oxidation of CO_{ads} on the catalyst surface. No peak was found in the second cycle confirms that CO_{ads} was completely oxidized in the first sweep. The CO_{ads} oxidation peak of Pd/NPC-T and commercial Pd/C catalysts emerges at 777, 774, 716, 744 and 810 mV, respectively. Obviously, more negative peak potentials are found in Pd/NPC-T catalysts as compared with commercial Pd/C catalyst, which may attribute to the doping of N and P. As discussed in XPS section, the oxygen-containing functional groups derived from P doping are benefit for CO intermediates oxidation. Moreover, oxophilic C-N defects generated by the nitrogen in the graphitic plane could

activate water and generate -OH_{ads} at lower potentials [38]. Both the oxygenated species generated from the doping of N and P would facilitate the removal of CO_{ads} on the Pd surface, thus enhance the CO poisoning tolerance of the Pd/NPC-T catalysts. The electrochemical surface area (ECSA) of each catalyst was calculated by the following equation, in which Q_{CO} represents the columbic charge of CO_{ads} oxidation, m denotes the mass of Pd on the working electrode, columbic charge required to oxidize the CO_{ads} of a monolayer is assumed as 420 µC cm⁻², according to the literature [39,40]

$$ECSA(m^2g^{-1}) = \frac{Q_{CO}(\mu C)}{420(\mu C \cdot cm^{-2})} \frac{100}{m(\mu g)}$$
(1)

The calculated ECSAs of Pd/NPC-T and commercial Pd/C catalysts are listed in Table 4.

Cyclic voltammetry experiments were used to investigate the catalytic activities of Pd/NPC-T and commercial Pd/C catalysts towards FAEO. As seen in Figure 8a, the peak mass activity of the as commercial Pd/C<Pd/NPC-1000<Pd/NPC-950<Pd/NPCcatalysts follows the sequence 850<Pd/NPC-900 catalyst. The mass activity on the Pd/NPC-850, Pd/NPC-900, Pd/NPC-950 and Pd/NPC-1000 catalyst is about 1.53, 1.98, 1.37 and 1.23 times of the commercial Pd/C catalyst, respectively. According to the calculated ECSA, the specific oxidative current of Pd/NPC-T and commercial Pd/C catalyst electrodes were determined as 15.3, 16.1, 13.2, 11.5 and 9.9 A m⁻², respectively, as shown in Figure 8b. The similar electrocatalysts reported in the literature are listed in Table 5 for comparison. The excellent activity exhibited by Pd/NPC-T catalysts may be attributed to the strong interactions between Pd and the N and P co-doped carbon supports which modifies the electronic structure of Pd. The activity difference among Pd/NPC-850, Pd/NPC-900, Pd/NPC-950 and Pd/NPC-1000 catalysts may partly ascribe to the various size and its distribution of Pd nanoparticles in the catalysts. Uniform dispersion are often more conducive to the enhancement of catalytic activity.



Figure 8. CV curves of Pd/NPC-850, Pd/NPC-900, Pd/NPC-950, Pd/NPC-1000 and commercial Pd/C catalysts in 0.5 M H₂SO₄ + 0.5 M HCOOH solution with a scan rate of 50 mV s⁻¹. The currents were normalized to the (a) mass currents and (b) specific currents.

To evaluate the stabilities of the different catalysts in FAEO, chronoamperometry technique was carried out. As shown in Figure 9, the current of all the catalysts reduced quickly at first due to the accumulation of poisoning intermediates which blocked the Pd sites and the agglomeration of Pd

nanoparticles during the FAEO process [41]. After long term test, Pd/NPC-T catalysts still showed the higher specific activity compared with commercial Pd/C for the oxidation of formic acid. The highest initial and termination currents are both presented on Pd/NPC-900 catalyst. The results may be mainly attributed to the doping of nitrogen and phosphorus, which generates -OH_{ads} for removal of CO_{ads} on the Pd surface and prevention from agglomeration of Pd nanoparticles through strong metal-support interaction.



Figure 9. Chronoamperometric curves of Pd/NPC-850, Pd/NPC-900, Pd/NPC-950, Pd/NPC-1000 and commercial Pd/C catalysts in 0.5 M H2SO4 + 0.5 M HCOOH solution at 0.1V.

The EIS technique was conducted to examine the electrically conductive performances of the catalysts. Figure 10 presents the impedance plots of Pd/NPC-T and commercial Pd/C catalysts which composing of semicircles and linear parts. The impedance data can be fitted using an equivalent circuit, semicircle diameter is equal to the charge transfer resistance (R_{ct}) and linear parts are related to the Warburg impedance (W) of electroactive species diffusion [42]. The R_{ct} values of Pd/NPC-850, Pd/NPC-900, Pd/NPC-950, Pd/NPC-1000 and commercial Pd/C catalysts were determined as 56.4, 32.6, 92.5, 62.1 and 109.8 ohm, respectively. Compared with commercial Pd/C, the charge transfer resistance of Pd/NPC-T catalysts are obviously smaller, indicating easier formic acid oxidation proceed on the electrodes. The Pd/NPC-900 catalyst shows the smallest R_{ct} value, suggesting the fastest FAEO rate on its surface.



- **Figure 10.** Nyquist plots of Pd/NPC-850, Pd/NPC-900, Pd/NPC-950, Pd/NPC-1000 and commercial Pd/C catalysts in 0.5 M H2SO4 with 0.5 M HCOOH at open circuit potentials.
- **Table 4.** Electrochemical data for CO-stripping, cyclicvoltammetry and electrochemical impedance measurements of Pd/NPC-850, Pd/NPC-900, Pd/NPC-950, Pd/NPC-1000 and commercial Pd/C catalysts.

Catalysts	Pd/NPC-850	Pd/NPC-900	Pd/NPC-950	Pd/NPC-1000	commercial Pd/C
ECSA ($m^2 g^{-1}$)	48	59	49	51	48
Peak potential (mV)	777	774	716	744	810
Mass current (A/g)	734	948	652	588	477
Specific oxidation current (A m ⁻²)	15.3	16.1	13.2	11.5	9.9
Rct values (ohm)	56.4	32.6	92.5	62.1	109.8

Table 5. Summary of the literature data on ECSA and mass activity of formic acid oxidation obtained from similar electrocatalysts and comparison with this work.

catalyst	electrolyte solution	ECSA $(m^2 g^{-1})$	mass activity (A/g)	reference
Pd/PCNTs	0.5MHCOOH+0.5MH ₂ SO ₄	72	694	[13]
Pd/MMT-CN _x	$0.5MHCOOH+0.5MH_2SO_4$	22	763	[16]
Pd/P-C-800	$0.5MHCOOH+0.5MH_2SO_4$	40	775	[17]
Pd/NP-coal-CFs	$0.5MHCOOH+0.5MH_2SO_4$	87	536	[23]
Pd/N-C-400	0.25MHCOOH+0.5MKOH	160	525	[37]
Pd1Ni1/NG	1MHCOOH+0.5MH ₂ SO ₄	157	709	[43]
Pd/NC _x -TiO ₂	$0.5MHCOOH+0.5MH_2SO_4$	63.6	1070	[44]
Pd/NPC-900	$0.5MHCOOH+0.5MH_2SO_4$	59	948	this work

4. CONCLUSIONS

In summary, nitrogen and phosphorus self-doped carbon was obtained by one-step facile pyrolysis method at different temperature. Further, nano-Pd particles were loaded uniformly onto the NPC-T supports under microwave-assisted reduction. Among the as-obtained Pd/NPC-T catalysts, Pd/NPC-900 presents the smallest size of Pd nanoparticles with the most uniform dispersing as showing in TEM images. There are strong interactions between Pd NPs and N, P self-doped carbon in the prepared Pd/NPC-T catalysts. The lowest binding energy of P 2p of Pd/NPC-900 among the catalysts, confirming the strongest interaction between Pd and P-containing active sites due to the electron-donating of Pd species. More content of pyridinic-N and pyrrolic-N was found in Pd/NPC-900 which could act as anchors for Pd nanoparticles. The synergistic effect of nitrogen and phosphorus doping leads to the best electrochemical performance of Pd/NPC-900 among the prepared Pd/NPC-T catalysts. Its specific current of FAEO was around two times as that of commercial Pd/C catalyst. The Pd/NPC-T catalysts are more stable and have better tolerance of CO poisoning than commercial Pd/C catalyst from longtime electrochemical tests. The enhanced activity and stability of the prepared catalysts could be attributed to the modification of electronic structure of Pd under the synergistic effect of N and P. In addition, the oxygen-containing groups originated from nitrogen and phosphorus facilitate the removal of CO, thus improving the performance of the Pd/NPC-T catalysts.

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