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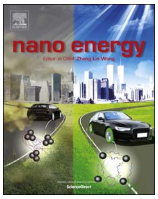

Nanostructured palladium catalyst poisoning depressed by cobalt phosphide in the electro-oxidation of formic acid for fuel cells

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ABSTRACT

Nanostructured palladium is considered as the best catalyst materials for direct formic acid fuel cells but catalyst poisoning suffering from the intermediates seriously reduces catalytic activity and stability, thus further hinders the commercial application of fuel cells technology. Herein, we report the tricky Pd catalyst poisoning problem could be greatly depressed by cobalt phosphide (CoP) material during formic acid oxidation, so an extremely active and stable Pd catalyst with very low Pd loading (5 wt%) is realized. The high anti-poisoning ability was evidenced by a significantly faster kinetics study and less poisoning intermediates adsorbed on its surface compared with Pd/C catalyst. When integrated into a real fuel cells model, a power density of 150 mW cm^{-2} catalyzed by this Pd-CoP/C catalyst (5 wt%, Pd) was comparable to that of the commercial Pd/C catalyst (20 wt%, Pd) indicating a very promising application in the electrochemical energy devices. This work opens an avenue to overcome the universal catalyst poisoning issue and pushes Pd catalyst system much stronger for commercial application in fuel cells technology.

1. Introduction

Using liquid formic acid (a promising hydrogen carrier) solution as fuel, direct formic acid fuel cells (DFAFCs) can effectively avoid the issues of hydrogen gas storage and transportation [1–3]. When combined with the electrocatalytic reduction of CO_2 using wind or solar energy to produce formic acid, a sustainable energy cycle can be realized, which is very important for the balance of greenhouse gases [4–7]. Normally, Pt or Pd noble metals are used to maintain high performance of DFAFCs, and it is recognized Pd has much higher anti-poisoning ability than Pt, thus lots of research by modifying or alloy with other materials have been done on Pd [8–13]. However, the universal catalyst poisoning problem resulting from the accumulated poisoning intermediates is concomitant on all the newly developed Pd catalysts. The high noble metal loading as high as 20 wt% and the serious instability/dissolution of the current Pd catalysts have significantly hindered the commercialization of such kind of fuel cells technology [14–20]. Thus, for the widespread commercialization, it is urgent to develop robust and efficient catalysts materials with low noble meal loading but high anti-poisoning ability.

Keeping that goal in mind, scientists have tried many strategies by combining transition metal or metal oxide with Pd to overcome the catalyst poisoning problem [3,21]. Unfortunately, the instability of the promoter elements results in a rapid decay of catalytic performance. We have discovered that nickel phosphide is a robust catalytic promoter that greatly promotes the noble Pt or Pd catalyst activity in fuel cells [22–24], the impressive catalytic performance and the unknown promotion mechanism stimulate us to probe the new potential material in the phosphide family members. Fortunately, after trial and error, we found that cobalt phosphide (CoP) can greatly reduce Pd catalyst poisoning problem in direct formic acid fuel cells. Differing from previous work, the super stability and promotion effect explored by current advanced technologies were highlighted. A significant breakthrough was achieved that an extremely active and stable Pd catalyst with very low Pd loading (5 wt%) was realized for direct formic acid fuel cells. The higher anti-poisoning ability was evidenced

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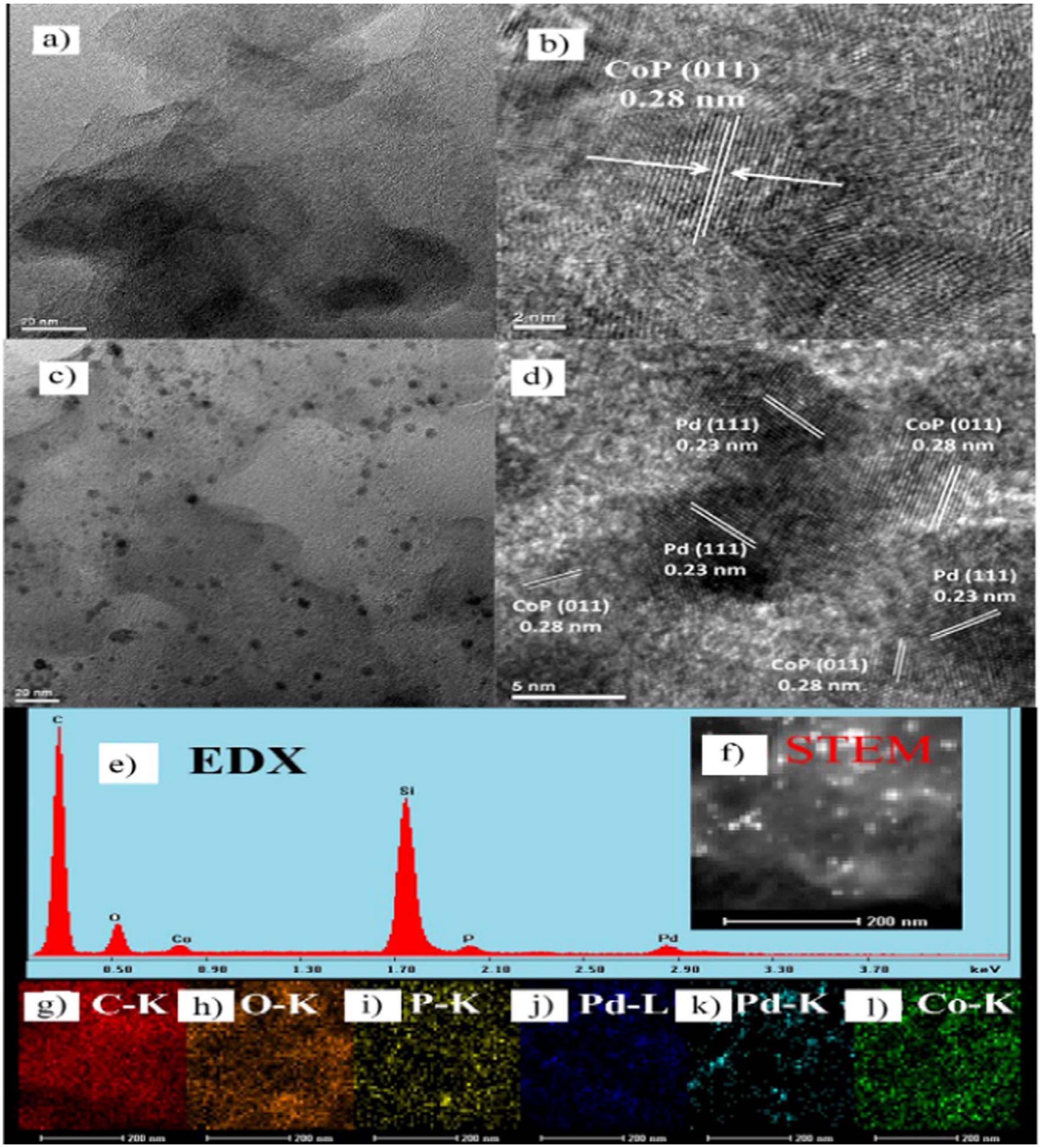

Fig. 1. (a) TEM (scale bar: 20 nm) and (b) HR-TEM (scale bar: 2 nm) images of CoP/C-30% sample. (c) TEM (scale bar: 20 nm) and (d) HR-TEM (scale bar: 5 nm) images of Pd-CoP/C-30% sample. (e) EDX, (f) STEM, (g–l) (scale bar: 200 nm) Elemental mapping images of the Pd-CoP/C-30% catalyst.

by a significantly faster kinetics process and less poisoning intermediates adsorbed on its surface when compared with state-of-the-art commercial Pd catalyst. As a result, a power density of 150 mW cm^{-2} achieved by Pd-CoP/C catalyst (5 wt%) was comparable to that of a commercial Pd/C catalyst (20 wt%, Pd), indicating very promising application in the electrochemical energy devices. This study establishes a novel protocol for extending the life-time of electrocatalyst subject to poisoning problem in fuel cells technology.

2. Results and discussion

The CoP/C was firstly synthesized by a solid phase reaction, where the cheap reagents of $CoCl_2$ and NaH_2PO_2 were employed. Pd was deposited onto CoP/C by a microwave assisted ethylene glycol reduction method. In order to track the optimal loading of CoP in the hybrid catalyst, a series of CoP loading from 10–50% in the Pd-CoP/C catalyst were prepared and characterized by different technologies (see the Supporting information for details). X-ray diffraction (XRD) technology was used to probe the crystal structure. An orthorhombic crystal structure of CoP on the carbon was observed in the typical XRD patterns; after Pd was deposited on the CoP/C surface, the typical face-centered cubic structure of Pd can be observed on all the samples (see Fig. S1 for details).

Take Pd-CoP/C-30% catalyst as an example, typical transmission electron microscopy (TEM) images of the catalyst and the background of CoP/C-30% support are shown in Fig. 1. For CoP/C support, besides the amorphous carbon, no obvious particles could be assigned to CoP in the low resolution TEM image (Fig. 1a); but they are visible on high resolution TEM images (HR-TEM) (Fig. 1b). When Pd was deposited on the surface, nanoparticles assigned to Pd can be seen clearly (Fig. 1c). For the HR-TEM image, a close contact of CoP and Pd was observed, and the lattice fringe of Pd and CoP could be seen by further magnification (Fig. 1d). The TEM images for other Pd catalyst are shown in Fig. S2. Similar particle sizes, shapes and size distributions

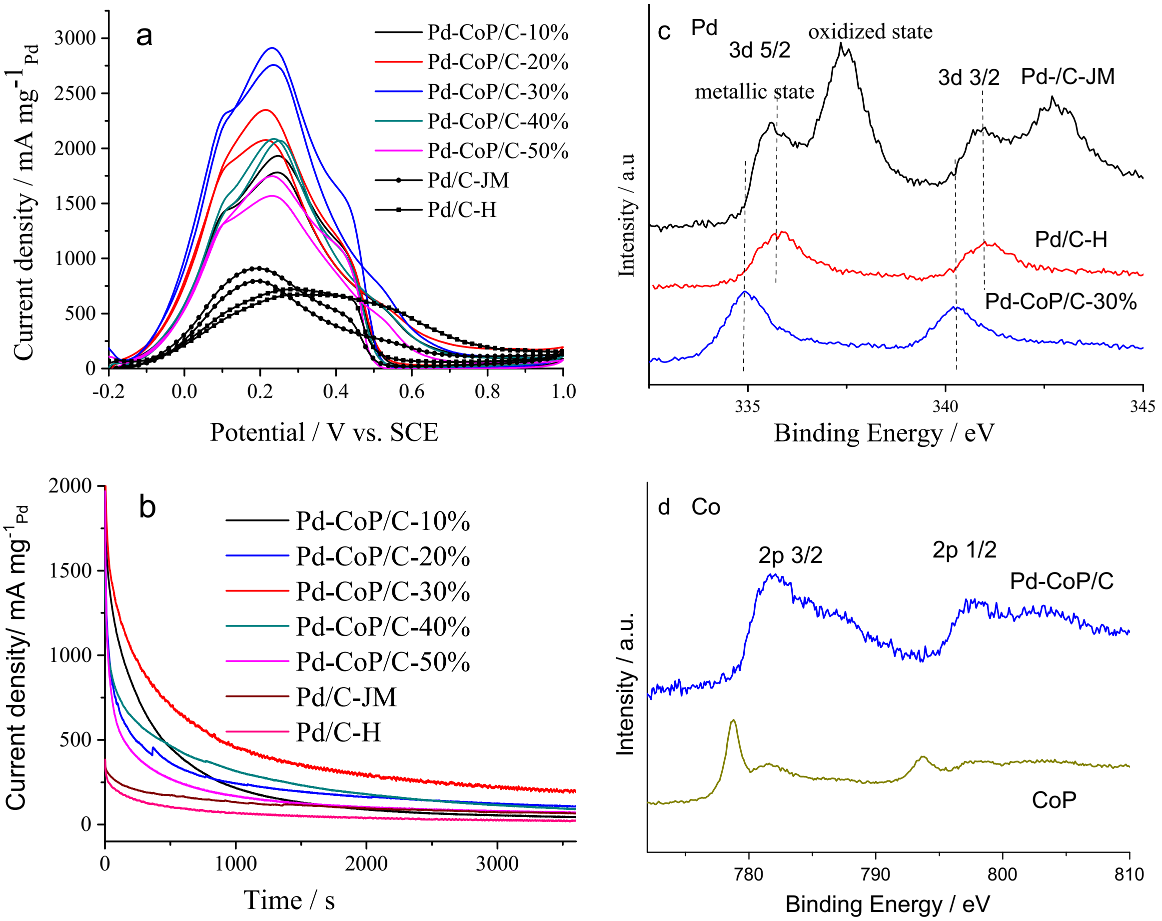

Fig. 2. (a) Cyclic voltammograms of various Pd catalysts (Scan rate: 50 mV s^{-1}), (b) CA curves for different Pd-based catalysts at 0.2 V for 3600 s in N_2-saturated 0.5 M H_2SO_4 solution containing 0.5 M HCOOH. (c) XPS spectra of Pd 3d region for various Pd catalysts, (d) XPS spectra of Co 2p region for Pd-CoP/C catalyst and CoP.

are observed, which excluded the morphology and/or particle size effect on the activity differences with different CoP loadings [25].

Energy-dispersive X-ray spectroscopy (EDX) and element mapping was done on a randomly selected area, and a typical result is shown in Fig. 1e–l. The elements of Pd, Co and P are clearly visible, and the content of Pd and Co is 4.98 wt% and 18.75 wt%, respectively, which agree well with the nominal contents. The composition of all catalyst materials was further probed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) technology, and the composition of all the samples agrees well with the nominal contents (Table S1a).

Before the electrochemical catalytic performance evaluation, physical stability tests on CoP/C (30%) in acid conditions was performed, which was kept soaking in 0.5 M H_2SO_4 for different times (i.e., 1 h, 6 h, 12 h and 24 h) and then the content of Co and P dissolved in the solution was detected with ICP-AES. The results (Table S1b) indicated CoP/C has a very nice chemical stability. It can be seen that even after 24 h, the dissolved Co and P were just ~0.09%, which can be negligible.

The as-prepared catalyst was drop-cast onto a glassy carbon electrode for electrochemical measurements. Typical Pd behaviors were observed in the background of 0.5 M H_2SO_4 solution (Fig. S3) [26,27]. The influence of CoP loading on the catalytic activity of Pd-CoP/C catalyst towards formic acid oxidation was compared by cyclic voltammetry (Fig. 2a). The optimal loading is 30 wt% of CoP on carbon by judging the peak current. The enhanced activity of Pd-CoP/C-30% catalyst for formic acid oxidation was further confirmed by comparing with the home-made Pd/C-H catalyst and state-of-the-art commercial Pd/C-JM catalyst. Specifically, the mass activity of Pd-CoP/C-30% is 2757 mA mg$^{-1}_{Pd}$, which is ca. 3.5 times that of the commercial Pd/C-JM catalyst (Pd, 20 wt%). The catalytic stability is evaluated by the chronoamperometry measurements (Fig. 2b), and the highest stable current after 1 h was found on the Pd-CoP/C-30% catalyst. Specific activity was generally employed to compare the intrinsic activity of the catalysts. The more accurate electrochemical surface area (ECSA) obtained by CO stripping (Fig. S4 and Table S2) was used to evaluate the specific activity, and it was found that Pd-CoP/C-30% catalyst still displayed the best performance among all the Pd-based catalysts (Fig. S5 and Table S3).

Thus the optimal catalyst of Pd-CoP/C-30% was taken for further in depth study by comparing with home-made and state-of-the-art commercial Pd/C catalyst in below. XPS was employed to probe the promotion effect of CoP from the origin of electronic effect. The commercial Pd/C-JM catalyst and home-made Pd/C catalyst were used as reference here (Fig. 2c). Similar to literature [28], Pd oxide was observed on the commercial Pd/C-JM catalyst, while metallic state of Pd was mainly present in the home prepared Pd/C and Pd-CoP/C catalysts. The peak positions of metallic Pd [29] for Pd/C-H and Pd/C-JM locate at ca. 335.7 and 341.0 eV respectively for Pd $3d_{5/2}$ and $3d_{3/2}$. Due to different physical properties of commercial and home-made catalysts resulting from different preparation methods, it is more valid to probe the electronic effect by comparing the two home-made catalysts. Important to note is that peak position of Pd-CoP catalyst is shifted significantly, by about 0.7 eV, to lower binding energy when compared to Pd/C catalyst as shows in Fig. 2c. Meanwhile, a definite peak position shift of Co 2p and P 2p to higher binding energy was observed compared with Co or P elements of CoP (Fig. 2d for Co 2p and Fig. S6 for P 2p). This shift is a sign of an interaction between CoP support and Pd nanoparticles resulting from a partial electron transfer from CoP to Pd surface. Similar shift was reported on several Pd

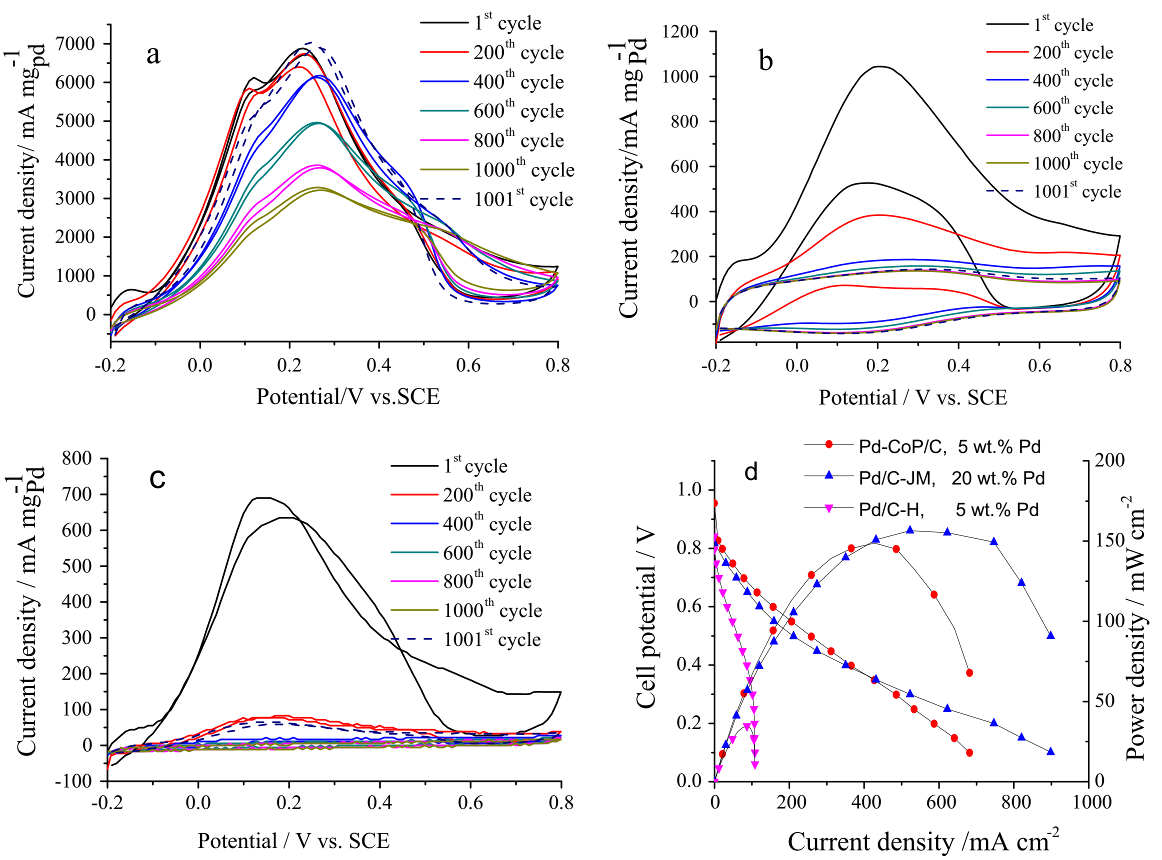

Fig. 3. Dynamic stability by accelerated stability test on Pd-CoP/C-30% (a), commercial Pd/C-JM (b), home-made Pd/C (c) catalysts in N_2-saturated 0.5 M H_2SO_4 solution containing 0.5 M HCOOH (Scan rate: 200 mV s^{-1}). Catalyst loading: 0.19 mg cm^{-2}. (d) Steady-state polarization and power-density curves for direct formic acid fuel cells employing Pd-CoP/C-30%, commercial Pd/C-JM and Pd/C-H as anode catalysts with 3 M formic acid fuel feeding at 30 °C. The flowing rate of formic acid was 2.0 mL min^{-1} and the flowing rate of O_2 was 200 mL min^{-1}.

catalyst systems [24,30,31], and it is thought this electronic interaction between CoP and Pd is favor in the electrocatalysis [32,33].

The dynamic stability is also very important for real application, and it was studied in an accelerated stability test (AST) by recording 1000 CV cycles at 200 mV s^{-1}. It can be observed that the current density was gradually reduced on Pd-CoP/C catalyst (Fig. 3a) probably due to slowly accumulating poisoning intermediates on Pd surface. While severely performance decay happened on the commercial and home-made Pd/C catalysts (Fig. 3b for commercial Pd/C and Fig. 3c for home-made Pd/C). The performance of Pd-CoP/C-30% catalyst could be recovered by nearly 100% of its initial activity (1001st cycle) after electrode was rinsed by ultrapure water and replaced with new electrolyte. Unfortunately, there was almost no activity recovered on the commercial and home-made Pd/C catalyst (1001st cycle), probably due to the strong poisoning intermediates accumulated on the active sites. With respect to this, similar results were also reported on Pd catalyst in direct formic acid fuel cells [34]. The possible reason was the poisoning species weakly absorbed on the Pd surface can be removed by washing, thus the activity of Pd catalyst could be regenerated. However, there is almost no activity recovered on both commercial and home-made Pd/C catalyst probably due to the poisoning effect resulting from the strong poisoning intermediates.

The real fuel cells performance of the proposed Pd-CoP/C catalysts was successfully evaluated on a home-made fuel cells to demonstrate the potential application. The steady-state polarization and power-density curves were compared in Fig. 3d. Generally, Pd loading of 20 wt % is considered as the low limit content in order to maintain an acceptable performances. However, even a 5 wt% of Pd in our Pd-CoP/C catalyst can give a comparable performance(150 mW cm^{-2}) to those catalyzed by 20 wt% of Pd with the state-of-the-art commercial Pd/C catalyst. Meanwhile, a very high stable discharge ability was achieved on Pd-CoP/C catalyst indicating very promising application (Fig. S7), while a large performance decay occurred in the initial 1 h on the commercial Pd/C catalyst. The strong promotion effect of CoP can be further verified by comparing the fuel cells performance with Pd/C-H catalyst, where a huge performance gap was observed. Due to the very low loading of Pd in the Pd/C-H catalyst, the performance was severely affacted by the the mass transfer process. The lower the loading of Pd, the less the active sites available, the lower the fuel cells performances. It is evident that the performnace improvement should come from the contribtution of CoP in the catalyst systme as the both home-made catalyst have the same Pd loading. The maximum power density of 500 mW mg_{Pd}^{-1} is achieved in the Pd-CoP/C catalyst, which is the highest performance for low temperature direct formic acid fuel cells at the current state of technology to our knowledge, and has never been reported in the literature . Specifically, its fuel cell performance is about 4 to 5 times as high as that of those catalyzed by other reference catalysts including the commercial Pd/C catalyst (see literature performance comparison in Table S4).The result is very significant as it can largely reduce the noble metal loading in fuel cells.

Kinetic studies then were done to probe the promotion mechanism. The typical dynamical behaviors of electrochemical impedance spectroscopy for all the evaluated catalysts at different potentials were compared and shown in Fig. S8. The charge transfer resistance at 0.3 V was compared by fitting the impedance data (Fig. S9 and Table S5). It can be seen that the lowest charge transfer resistance is obtained on the Pd-CoP/C catalyst, indicating this catalyst can catalyze the formic acid oxidation reaction with the highest reaction rate. The number of electrons transfer (nα) in the rate-determining step can reflect the catalytic process and mechanism. It was analyzed by

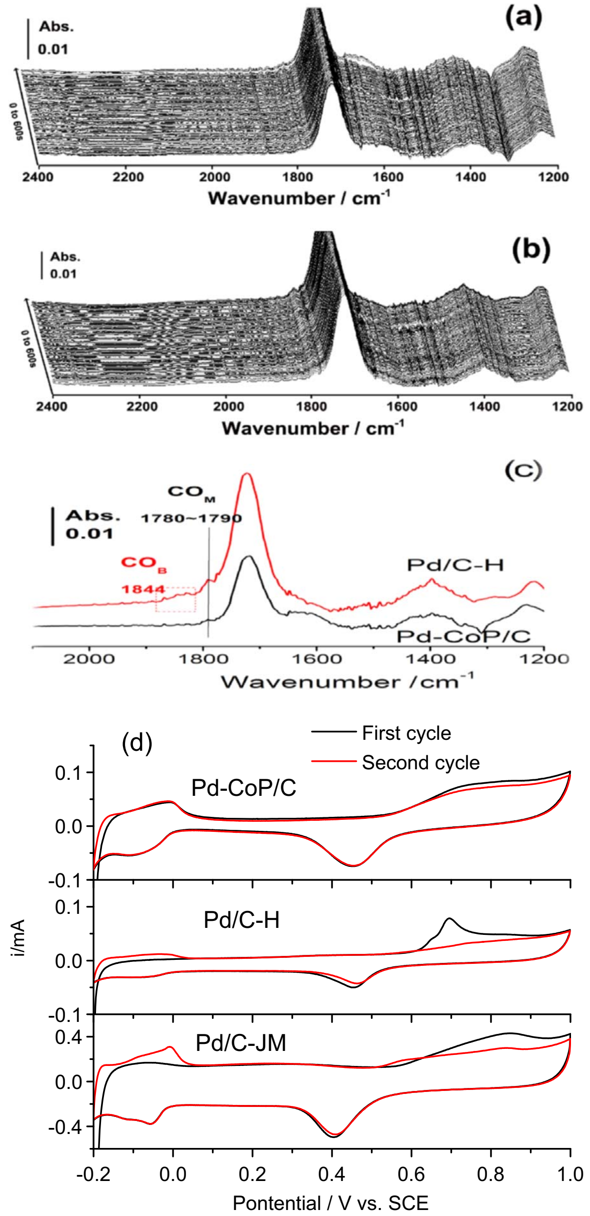

Fig. 4. Time-evolved ATR-IR spectra on the Pd-CoP/C (a) and Pd/C-H (b) catalysts coated Au/Si prism in 0.5 M H_2SO_4+3 M HCOOH at 0.2 V (vs. SCE). Reference spectrum was recorded in air before the electrolyte injection, and the acquisition time for each single-beam spectrum is 5 s (c) In situ EC-ATR-IR spectra recorded on different catalysts coated Au/Si prism after 600 s CA. (d) Cyclic voltammograms at 50 mV s^{-1} for different electrodes after 2 h chronoamperometry measurements at 0.2 V in 0.5 M H_2SO_4 solutions containing 0.5 M HCOOH.

recording the CVs at different scan rates and calculated to be ca. 1.99, 1.67 and 1.52 respectively for Pd-CoP/C, Pd/C-H and Pd/C-JM catalysts, if we assume that the charge transfer coefficient is 0.5 (Fig. S10 and see Supporting information for details). The nα is increased from 1.5 to 2.0 as one changes the catalysts from Pd/C-JM to Pd-CoP/C catalysts, that indicated formic acid electrooxidation on Pd-CoP/C takes place mainly via the direct path way which needs 2 electrons [35].

In order to further understand the promotion effect of CoP, we employed the advanced in situ electrochemical attenuated total reflection-infrared spectroscopic (EC-ATR-IR) technology to probe the poisoning intermediates during formic acid oxidation [36]. Fig. 4a and b shows the time-evolved ATR-IR spectra on Pd-CoP/C and Pd/C-H catalysts at 0.2 V (it was not done on Pd/C-JM catalyst due to different composition and optical signals). The major bands at 1720, 1400, and 1214 cm^{-1} can be ascribed to the $\nu_{C=O}$, $\delta_{COH}/\delta_{HCO}$, and ν_{C-O} vibrations of formic acid molecules, respectively. The 2345 cm^{-1} is attributed to the interfacial CO_2, for which the peak intensity gradually decreased after 60 s due to its diffusion to the electrolyte.

For both catalysts, the low-coverage and multi-bonded CO (CO_M) appear as a shoulder peak at ca. 1790 cm^{-1} to the strong 1720 cm^{-1} band of interfacial formic acid. Nevertheless, on Pd/C-H surface, the CO_M band is relatively stronger than that on the Pd-CoP/C surface. It was also noted that a very weak peak at ca. 1840 cm^{-1} attributed to the bridge-bonded CO (CO_B) occurred on Pd/C-H at open circuit potential following the above measurement, a more clear indication is shown in Fig. 4c. In combination with the accelerated stability test in Fig. 2, we speculated that the gradual performance decay on Pd-CoP catalyst may result from the multi-bonded CO, and the highly depressed bridge-bonded CO might guarantee the excellent activity.

Finally an electrochemical stripping voltammetry technology proposed by Pickup et al. [37] was employed to probe CO intermediates amount adsorbed on the electrode surface. The electrode after 2 h of chronoamperometry measurements at 0.2 V was performed and then the electrode was transferred to an electrochemical cell containing 0.5 M H_2SO_4 under the protection of nitrogen. A potential at 0.2 V (vs. SCE) was applied for 0.5 h to consume the residual formic acid, and cyclic voltammetry was then performed to probe the CO intermediates adsorbed on the electrode surface. In consistent with Pickup's reports [37], typical CO stripping voltammogram features were observed in Fig. 4d; a large CO oxidation peak was seen on Pd/C-H and Pd/C-JM catalysts, but only a minor CO oxidation peak on the Pd-CoP/C catalysts. The charge associated with the oxidation of the adsorbed CO was 20.58, 90.07, 123.67 mC mg^{-1} respectively for Pd-CoP/C, Pd/C-H and Pd/C-JM catalyst. The less CO formed on catalyst surface, the higher CO anti-poisoning ability. Taken the above results together, it can be concluded that CoP can greatly increase the anti-CO poisoning ability.

It is generally accepted that the electrooxidation of formic acid can proceed through two parallel pathways, the direct pathway and the indirect pathway [38]. In the direct pathway, formic acid is directly oxidized to CO_2 by 2 electrons reaction and no CO intermediate is formed. In the indirect pathway, formic acid is firstly oxidized to intermediate CO and then CO is oxidized to CO_2; the reaction rate is significantly affected by the strongly chemisorbed CO. According our above kinetic analysis and electrochemical-optical study, we confirmed that CoP can promote formic acid oxidation over Pd catalyst mainly via the direct pathway, thus greatly reduces the Pd catalyst poisoning problem in direct formic acid fuel cells. CoP recently was reported as an effective water splitting catalyst in terms of hydrogen evolution and oxygen evolution [39–42], the water activation ability probably also benefits the electrode process. On the one hand, the facile hydrogen adsorption and transfer on the CoP surface might accelerate the formic acid oxidation in a way similar to the hydrogen spill-over effect [43]. On the other hand, CoP is speculated to active the water to form oxygen containing species ($-OH_{ads}$) that can oxidize CO and other poisoning intermediates adsorbed at adjacent Pd sites through the so-called bifunctional mechanism [44,45]. Thus, a relative low CO accumulation on the Pd-CoP/C catalyst was observed. According the relevant reports, a possible approach based on the well recognized bi-functional mechanism and hydrogen spill-over effect for formic acid oxidation was shown in Supporting information on Page S27. Hopefully the speculation could be answered by theory work soon. Moreover, the effect of different members in the phosphide family on the catalyst stability, activity and catalytic mechanism should be also probed in the subsequent work; it involves the different members of phosphide in different compositions, surface states, structures, morphology and so on [23,46–50]. The further contribution will be helpful in discovering the origin of catalytic promotion effect.

3. Conclusion

Successful preparation of a highly active and cost-effective anode catalyst for direct formic acid fuel cell is demonstrated. The Pd-CoP/C catalyst can be prepared easily from the cheap and earth-abundant elements which is suitable for large-scale fabrication. High fuel cell power density of 150 mW cm^{-2} was achieved when using Pd-CoP/C catalyst containing only 5 wt% of Pd as anode catalyst, which is comparable to that of the commercial Pd/C catalyst containing 20 wt % Pd. Excellent catalytic activity and stability for formic acid oxidation are observed by electrochemical measurements, which is due to the action of CoP in the hybrid catalyst. It is found that CoP can largely depress the CO intermediates poisoning problem on Pd catalyst during formic acid electrooxidation, thus, higher catalytic activity and stability were observed. The present work opens an avenue to overcome the universal catalyst poisoning issue and make more practicable catalyst in fuel cells technology.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2016.10.023.

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