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High-quality hydrogen generated from formic acid triggered by in situ prepared Pd/C catalyst for fuel cells

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High-quality hydrogen can be generated from formic acid triggered by facilely in situ prepared Pd/C catalyst at ambient condition. The obtained gas can be directly fed into proton exchange membrane fuel cells indicating a very promising application.

Hydrogen economy has received considerable attention due to the human society development, but the storage and transportation problems severely hinder the wide-spread application.[1] Recently, formic acid has been considered as a convenient hydrogen carrier for portable hydrogen storage application.[2] Formic acid is a non-toxic liquid at room temperature which is adaptable to the existing liquid-based distribution infrastructure, thus makes it more competitive compared with other hydrogen storage approaches.[3] Further, the hydrogen generated from formic acid can be directly employed in combination with the proton exchange membrane fuel cells.[1d, 4]However, it should be pointed out that the trace amount of CO in the gas adsorbed on the catalyst active sites could result in the fuel cells performance decay due to the catalyst poisoning.[5] Thus, both activity and selectivity should be considered in the catalyst preparation.[6]

Recent studies of noble metal nanoparticles supported on various materials showed promising catalyst systems for formic acid decomposition.[2d, 5b,7] Unfortunately, the trace amount of CO in the mixed gas is not suitable for fuel cells application, and high temperature is in need to retain acceptable catalytic activity.[2h, i, 8]Moreover, such kind of catalysts need to be prepared in advance, which increases the additional work for practical fuel cells application.[7b, 8]As a result, there were very limited reports about the hydrogen application in fuel cells by formic acid decomposition.

It is desired but still challenging to develop facile and selective evolution of CO-free H_2 especially at lower temperatures. Pd/C as a simple catalyst intrigued the researchers' attention[8]. However, the complicated preparation method or the low activity of Pd/C catalyst hindered the practical application. Herein, we demonstrated an approach to obtain high-quality hydrogen triggered by the in situ generated Pd/C catalyst at ambient condition without any complicated post-treatment. No CO was detected in the gas products that can be directly fed into fuel cells and the power density as high as 80 mW cm^{-2} was achieved, which competes well over several alternative power supply approaches. Moreover, as a bi-functional application, the resulted Pd/C catalyst also showed comparable catalytic performances for formic acid electrooxidation to a commercial Pd/C catalyst.

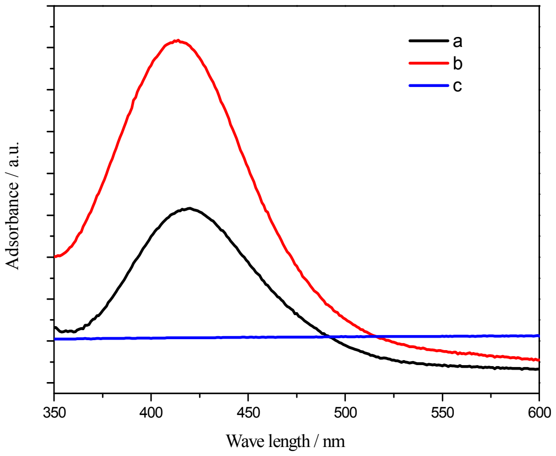

Fig.1 UV-vis spectra for aqueous solution of H_2PdCl_4 aqueous solution (a), H_2PdCl_4 solution mixed with HCOOH after 3 hours (b), H_2PdCl_4 solution mixed with NaOH and HCOOH after 2 minutes (c) at ambient condition.

$PdCl_4^{2-}$ can be reduced by formic acid, a kind of weak reducing agent, but it will take a relatively long time. However, when the pH was adjusted by adding NaOH, Pd particles were formed in a very short time. Digital photos showed that there was no colourchanges when the H_2PdCl_4solutionwas mixed with formic acid after 3 hours(Figure S1); however, the colour change occurred shortly when the mixture of sodium hydroxide and formic acid added to the H_2PdCl_4 solution. The colour was changed from yellow to light grey soon within 30 seconds, and finally changed to dark grey after 2 minutes. Figure 1 shows the UV-Vis spectra changes for H_2PdCl_4 solution in different mixed solution. An obvious peak at ca. 415 nm was observed for the pure H_2PdCl_4solution,and almost no changes occurred when HCOOH was added after3 hours. However, there was no peak after the mixture of formic acid and sodium hydroxide added to the H_2PdCl_4 solution after 2 minutes. Thus, the presence of the NaOH accelerated the reduction rate of Pd precursors.

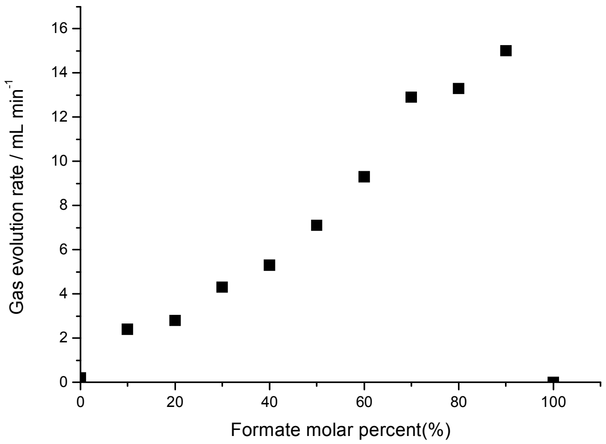

Fig.2 Formate molar percent dependence of the gas evolution rate in the initial linear range.

Owing to the important effect of the formate in the solution, the influence of HCOO$^-$ on the rate and quantity of gas evolution was compared with 1.5 ml of formic acid added[9], in which the formate ratio was adjusted by the amount of NaOH added(Figure S2 and see ESI for experimental details). For clearly understanding, the composition of the different mixtures was shown in Table S1. With the increase of the HCOO$^-$, the amount of gas was increased till 60% of HCOO$^-$ in the solution. Figure 2 displays the plot of formate molar percent dependence of the gas evolution rate in the linear range from the Figure S2.It is evident that with more HCOO$^-$ in the solution, the gas evolution rate was increased largely. Further increase the HCOO$^-$ concentration, the formic acid was decomposed completely around 50 minutes. It was in agreement with the above-mentioned result thatPd reduction rate was increasedwithmore HCOO$^-$ in the solution; thus more Pd was formed in less time, and would accelerate the formic acid decomposition rate (Table S2). Furthermore, a video of one of the experiments (using 0.955 g NaOH and 1.5 mL formic acid) starting after formic acid was added to the suspension for 15 minutes was attached in the supporting information. It can be seen that the gas-evolution rate was accelerated at first when the $PdCl_4^{2-}$was being reduced and then the rate became fast and relatively steady, which demonstrated further that the reduced Pd nanoparticles provide active sites for formic acid decomposition. Besides, the initial turnover frequency (TOF) for this system with 60% formate was calculated to be 79 h^{-1} after initial 1hour, which is also higher than some reports in the similar condition.[10a, b]The effect of the temperature on the catalytic performance of formic acid decomposition was also evaluated (Figure S3). With the increase of the temperature, the performance was improved, and the activation energy from figure S4was calculated to be 38.9kJ mol^{-1}, which is lower than some similar reports.[1a, 2a, 10] For example, it is 53kJ mol^{-1}for Au/Al_2O_3,[11] 72 kJ mol^{-1}for Pt/Al_2O_3[11]and 49.3kJ mol^{-1}for Au/ZrO_2 catalyst[2b].

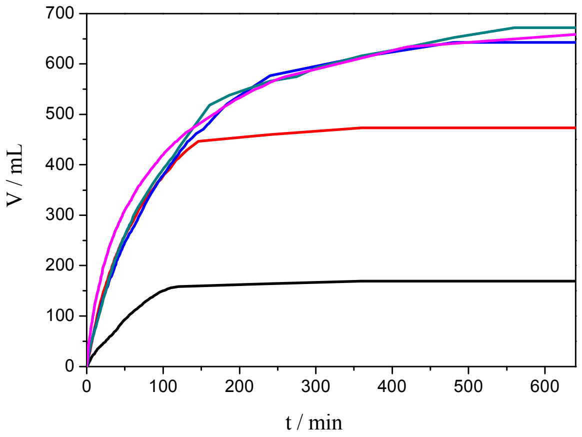

Fig. 3 The gas-evolution amount change vs. time for different formic acid and formate mixtures catalyzed by in situ prepared Pd/C at 313 K. Initial added formic acid of 0.5 mL (—), 1.0 mL (—), 1.5 mL (—), 2.0 mL (—) and 2.5 mL (—). The molar percent of formate was 60%.

The formic acid decomposition ability of Pd/C catalyst was further evaluated by changing the amount of formic acid and the formate ratio was maintained at 60% (Table S1). As shown in Figure 3, it takes about 100 min for Pd/C catalyst(10 mg Pd) to fully decompose 0.5 or 1 mL offormic acid[12]. With further increase of formic acid volume to 1.5 ml, the produced gas volume was increased to the maximum value of 640 mL, and the gas evolution became very slow (0.35 mL min^{-1}) after 2 hours. We should also notice that as a quick response technology, it is still attractive that about 200 mL hydrogen (400 mL mixed gas) was released in one hour with only 10 mg of Pd and 1mL ofinitial formic acid. Here it should be pointed out that the real amount of formic acid is 0.4 mL[13], thus theoretically the produced hydrogen is 250 ml; a conversion as high as 80% is obtained. As the poor recycling ability is a common problem for this kind catalyst, unfortunately in our case, the recycling performance was also bad; the deactivation might be caused by the absorption of hydrogen into the Pd bulk during the formation of Pd. Thus, increasing the catalysts' recycling performance is also needed in future work.

The obtained gas was detected by gas chromatography (GC), and no CO was detected (the CO concentration is < 50 ppm, Figure S5, and ESI). The quality of the reforming gas reaches the fuel cells standard with the CO concentration lower than 100 ppm. The molar ratio of H_2 and CO_2 in the reforming gas was about 1:1. Because hydrogen was the only gaseous product for formate hydrolysis,[6, 8c]and formic acid would give rise to H_2 and CO_2 with a molar ratio of 1:1; in this system, formic acid should be the overwhelming hydrogen source. Now, it is much clear that the presence of formate accelerates the reduction of Pd ion, and the in situ generated Pd/C is active for the formic acid decomposition.

Here, take initial 1.5 ml of formic acid (60% formate) as an example, the obtained gas was directly fed into home-made fuel cells. The schematic diagram for this system was shown in Scheme S1. Without removal of CO_2, a power density of ca.60 mW cm^{-2} was achieved (Figure 4). It is evident that the performance was affected by the mass transportation due to the presence of CO_2, and, moreover, CO_2 can be reduced to CO at Pt-H surfaces leading to a lower fuel cell performance[14]. After CO_2 removal, the power density as high as 80 mW cm^{-2} was obtained (Figure 4) , which competes well over several alternative power supply approaches, such as fuel cells fed with methanol(30 mW cm^{-2},[15]45mW cm^{-2},[16] 65 mW cm^{-2},[17]), ethanol (40 mW cm^{-2},[18] 52 mW cm^{-2},[19] 30 mW cm^{-2},[20]), sodium borohydride (30mW cm^{-2},[21]18mW cm^{-2},[22])etc. It should be noticed that this power density is inspirational and acceptable because it was only limited by the natural formic acid decomposition rate. The power density curves at different time during the formic acid decomposition were also recorded, which showed a stable performance (Figure S6). The result demonstrated the promising applications as a power supply approach.

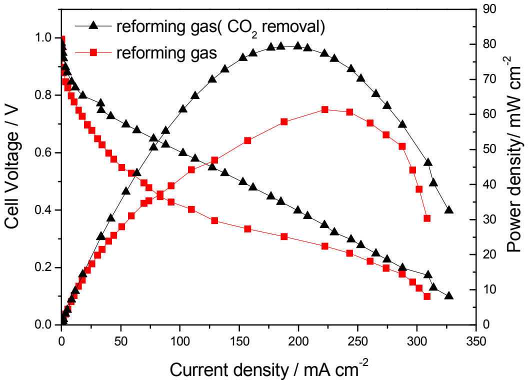

Fig.4 Steady-state polarization curves for proton exchange membrane fuel cells with the produced gas and CO_2 removed gas. The experiment was performed at room temperature and atmospheric pressure. 1.5 ml of formic acid (60% formate); Anode: Pt loading (1.0 mg cm^{-2}); cathode: Pt loading (1.0 mg cm^{-2}).

Finally, the Pd/C was collected to analyse the properties by physical measurements. Inductively coupled plasma optical emission spectrometry (ICP-OES) indicated that the mass fraction of Pd in Pd/C catalyst is ca. 20 wt.% which agreed very well with the Pd amount added(table S3) initially. The crystal structure of Pd/C was characterized by X-ray diffraction (XRD) technology, and shown in figures S7. The peak at ca.25° is evidently attributed to the (002) plane reflection of Vulcan XC-72 carbon. The diffraction peaks at ca. 40, 47, 68, 82 and 87° correspond to the face-centered-cubic phase of Pd. TEM images of the reduced Pd/C catalyst with different formate ratios(0% to 100%; from Figure 2) are shown in figures S8. We didn't observe obvious differences about the morphology of Pd particles except that $PdCl_4^{2-}$ was not reduced completely by pure formic acid. For all cases, the particle size distribution is within the optimal particle size of Pd for formic acid decomposition in aqueous solution[10b], and also it shows that such a small particle size could be obtained facilely without adding any protective agent. Thus, the gas evolution rate differences observed in Figure 2 might be influenced by the ratios of formic acid and formate. As pointed out, the presence of formate in the solution considerably improved the Pd reduction rate, thus largely increased the production rate of H_2 over the in situ generated Pd/C catalyst. This appears to be consistent with the previously proposed reaction mechanism based on $HCOO^-$ as the rapidest H donator at ambient temperatures (details see ESI). If this is the only case, a pure formate solution with the use of the Pd/C catalyst should provide a faster H_2 production rate at least than a mixture solution containing formic acid and formate. However, this is against the experimental results observed with a pure formate solution over the catalyst. It is likely that some aspects, such as Pd particle size, space repulsion, and bonding competition, may also have important effects on the hydrogen evolution from the mixture solution over the Pd surface. Further study is required to fully clarify the reaction nature of Pd-catalyzed H_2 generation from aqueous solution containing formic acid and formate. Finally, as a bi-functional application, the electrocatalytic activity of several Pd/C catalysts toward formic acid oxidation was compared with a commercial Pd/C catalyst (Figure S9). All the catalyst showed comparable catalytic activity to the commercial Pd/C catalyst that increased the economic value for promising application[23].

In summary, high-quality hydrogen can be generated from formic acid triggered by in situ prepared Pd/C catalyst at ambient condition. The $HCOO^-$ concentration has large impact on Pd formation, thus great effect on the gas evolution rate. Due to the complicated system, further study of calculation or spectroscopy is required to fully clarify the reaction mechanism. Moreover, as bi-functional catalyst, the used catalyst has comparableperformance to the commercial Pd/C catalyst for formic acid electrooxidation. Such a facile approach makes it successfully as a quick response technology to get high purity H_2 from formic acid. Power density as high as 80 mW cm^{-2} was achieved in combination with fuel cells indicating a very promising application as a power supply approach.

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Notes and references

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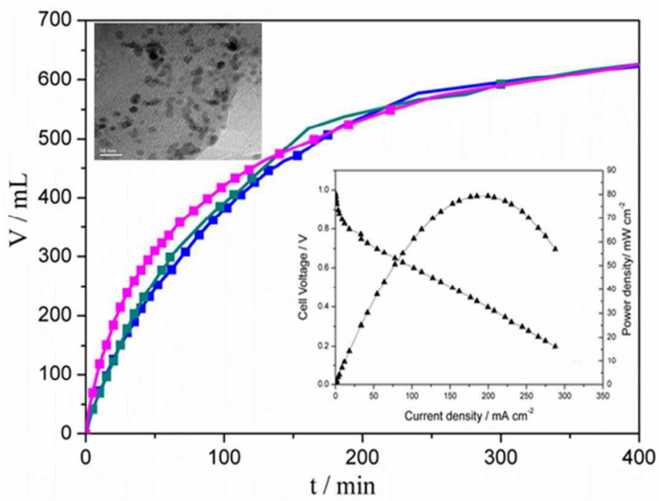
TOC figure



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