Catalysis
Science &
Technology

COMMUNICATION

View Article Online
View Journal

Cite this: DOI: 10.1039/c5cy00245a

Received 14th February 2015,
Accepted 5th March 2015

DOI: 10.1039/c5cy00245a

www.rsc.org/catalysis

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

Qing Lv,[a] Ligang Feng,*[b] Chaoquan Hu,[b] Changpeng Liu[a] and Wei Xing*[a]

High-quality hydrogen can be generated from formic acid triggered by facilely *in situ* prepared Pd/C catalyst in ambient conditions. 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 development by human society, but 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 cell performance decay due to 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 cell application, and high temperature is needed to retain acceptable catalytic activity.[2a,10a] Moreover, such kinds of catalysts need to be prepared in advance, which increases the additional work for practical fuel cell application.[7b,8] As a result, there were very limited reports about 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 in ambient conditions 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 performance for formic acid electro-oxidation to a commercial Pd/C catalyst.

$PdCl_4^{2-}$ 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 colour change when the H_2PdCl_4 solution was mixed with formic acid after 3 hours (Fig. S1†); however, the colour change occurred shortly when the mixture of sodium hydroxide and formic acid was added to the H_2PdCl_4 solution. The colour changed from yellow to light grey soon within 30 seconds, and finally changed to dark grey after 2 minutes. Fig. 1 shows the UV-vis spectral changes for H_2PdCl_4 solution in different mixed solutions. An obvious peak at *ca.* 415 nm was observed for the pure H_2PdCl_4 solution, and almost no changes occurred when HCOOH was added after 3 hours. However, there was no peak after the mixture of formic acid and sodium hydroxide was added to the H_2PdCl_4 solution after 2 minutes. Thus, the presence of NaOH accelerated the reduction rate of Pd precursors.

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 (Fig. S2 and see ESI† for experimental details).

---

[a] *State Key Laboratory of Electroanalytical Chemistry, Laboratory of Advanced Power Sources, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China. E-mail: xingwei@ciac.ac.cn*
[b] *Department of Applied Physics, Chalmers University of Technology, SE-41296, Göteborg, Sweden. E-mail: ligang.feng@chalmers.se, fenglg11@gmail.com*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5cy00245a

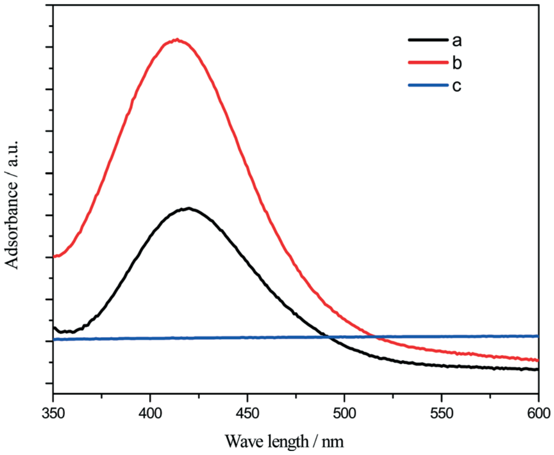

Fig. 1 UV-vis spectra of an aqueous solution of H_2PdCl_4 (a), H_2PdCl_4 solution mixed with HCOOH after 3 hours (b), and H_2PdCl_4 solution mixed with NaOH and HCOOH after 2 minutes (c) in ambient conditions.

For a clear understanding, the composition of the different mixtures is shown in Table S1.† With the increase in the $HCOO^-$, the amount of gas was increased till 60% of $HCOO^-$ in the solution. Fig. 2 displays the plot of formate molar percent dependence of the gas evolution rate in the linear range from Fig. S2.† It is evident that with more $HCOO^-$ in the solution, the gas evolution rate was increased largely. Further increasing the $HCOO^-$ concentration, the formic acid decomposed completely around 50 minutes. It was in agreement with the above-mentioned result that the Pd reduction rate increased with more $HCOO^-$ 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 is attached in the ESI.† 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 the initial 1 hour, which is also higher than some reports in similar conditions.[10a,b] The effect of the temperature on the catalytic performance of formic acid decomposition was also evaluated (Fig. S3†). With the increase in the temperature, the performance was improved, and the activation energy from Fig. S4† was calculated to be 38.9 kJ mol^{-1}, which is lower than some similar reports.[1a,2a,10] For example, it is 53 kJ mol^{-1} for Au/Al_2O_3,[11] 72 kJ mol^{-1} for Pt/Al_2O_3 (ref. 11) and 49.3 kJ mol^{-1} for Au/ZrO_2 catalyst.[2b]

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 Fig. 3, it takes about 100 min for Pd/C catalyst (10 mg Pd) to fully decompose 0.5 or 1 mL of formic acid.[12] With the further increase in formic acid volume to 1.5 ml, the produced gas volume was increased to a 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 of hydrogen (400 mL mixed gas) was released in one hour with only 10 mg of Pd and 1 mL of initial 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 of 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, Fig. S5 in ESI†). The quality of the reforming gas reaches the fuel cell standard with the CO concentration lower than

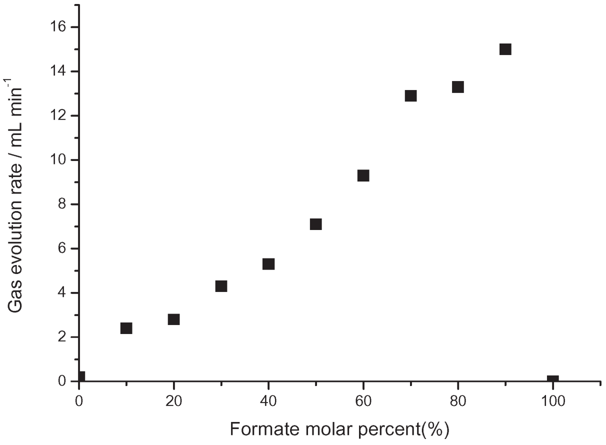

Fig. 2 Formate molar percent dependence of the gas evolution rate in the initial linear range.

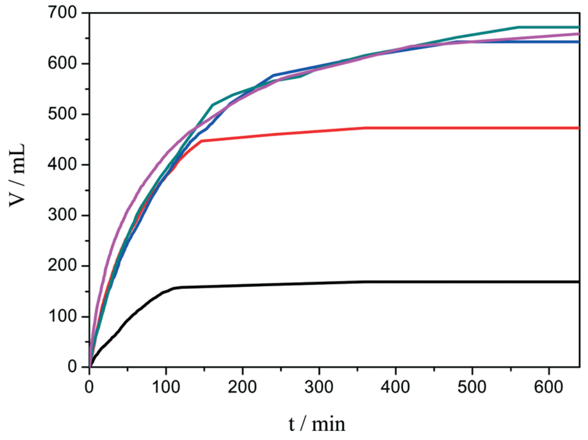

Fig. 3 The change in gas-evolution amount *vs.* time for different formic acid and formate mixtures catalyzed by *in situ* prepared Pd/C at 313 K. Initially added formic acid of 0.5 mL (—), 1.0 mL (—), 1.5 mL (—), 2.0 mL (—) and 2.5 mL (—). The molar percent of formate was 60%.

100 ppm. The molar ratio of H_2 to 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 more clear that the presence of formate accelerates the reduction of Pd ions, and the *in situ* generated Pd/C is active for the formic acid decomposition.

Here, taking an 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 is shown in Scheme S1.† Without removal of CO_2, a power density of *ca.* 60 mW cm^{-2} was achieved (Fig. 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 on 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 (Fig. 4), which competes well over several alternative power supply approaches, such as fuel cells fed with methanol (30 mW cm^{-2},[15] 45 mW cm^{-2},[16] 65 mW cm^{-2} (ref. 17)), ethanol (40 mW cm^{-2},[18] 52 mW cm^{-2},[19] 30 mW cm^{-2} (ref. 20)), sodium borohydride (30 mW cm^{-2},[21] 18 mW cm^{-2} (ref. 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 times during the formic acid decomposition were also recorded, which showed a stable performance (Fig. S6†). The result demonstrated the promising applications as a power supply approach.

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 is shown in Fig. 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 Fig. 2) are shown in Fig. 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 Fig. 2 might be influenced by the ratios of formic acid to 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 (for 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 studies are required to fully clarify the reaction nature of Pd-catalyzed H_2 generation from an 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 (Fig. S9†). All the catalysts showed comparable catalytic activity to the commercial Pd/C catalyst that increased the economic value for promising application.[23]

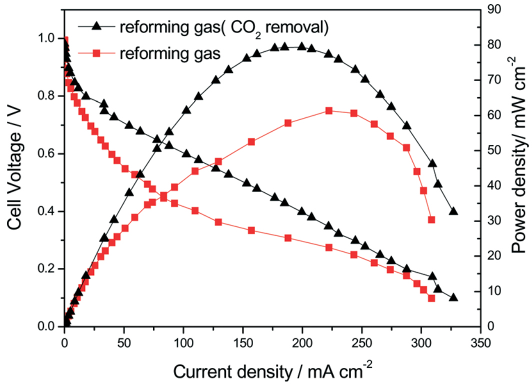

Fig. 4 Steady-state polarization curves for proton exchange membrane fuel cells with the produced gas and CO_2 removed gas. The experiment was performed at room temperature and atmospheric pressure. 1.5 ml of formic acid (60% formate); anode: Pt loading (1.0 mg cm^{-2}); cathode: Pt loading (1.0 mg cm^{-2}).

In summary, high-quality hydrogen can be generated from formic acid triggered by *in situ* prepared Pd/C catalyst in ambient conditions. The $HCOO^-$ concentration has a large impact on Pd formation, thus a great effect on the gas evolution rate. Due to the complicated system, further studies using calculation or spectroscopy are required to fully clarify the reaction mechanism. Moreover, as bi-functional catalyst, the used catalyst has comparable performance to the commercial Pd/C catalyst for formic acid electrooxidation. Such a facile approach makes it successful as a quick response technology to get high purity H_2 from formic acid. The 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.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (no. 21373199), the National High Technology Research and Development Program of China (863 program, no. 2012AA053401, 2013AA051002), the

National Basic Research Program of China (973 program, no. 2012CB932800, 2012CB215500 and 2011CB935702), the Strategic Priority Research Program of the Chinese Academy of Sciences (grant no. XDA09030104) and the Science & Technology Research Programs of Jilin Province (no. 20102204, 20100420).

Notes and references

1 (*a*) D. A. Bulushev, L. Jia, S. Beloshapkin and J. R. H. Ross, *Chem. Commun.*, 2012, **48**, 4184–4186; (*b*) M. Navlani-Garcia, M. Martis, D. Lozano-Castello, D. Cazorla-Amoros, K. Mori and H. Yamashita, *Catal. Sci. Technol.*, 2015, **5**, 364–371; (*c*) A. Boddien, D. Mellmann, F. Gärtner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig and M. Beller, *Science*, 2011, **333**, 1733–1736; (*d*) A. Boddien, B. Loges, H. Junge and M. Beller, *ChemSusChem*, 2008, **1**, 751–758; (*e*) P. Hu, Y. Diskin-Posner, Y. Ben-David and D. Milstein, *ACS Catal.*, 2014, **4**, 2649–2652.

2 (*a*) S.-W. Ting, S. Cheng, K.-Y. Tsang, N. van der Laak and K.-Y. Chan, *Chem. Commun.*, 2009, 7333–7335; (*b*) Y. Manaka, W.-H. Wang, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita and Y. Himeda, *Catal. Sci. Technol.*, 2014, **4**, 34–37; (*c*) A. Majewski, D. J. Morris, K. Kendall and M. Wills, *ChemSusChem*, 2010, **3**, 431–434; (*d*) M. Yurderi, A. Bulut, M. Zahmakiran and M. Kaya, *Appl. Catal., B*, 2014, **160–161**, 514–524; (*e*) M. Grasemann and G. Laurenczy, *Energy Environ. Sci.*, 2012, **5**, 8171–8181; (*f*) S. Enthaler, J. von Langermann and T. Schmidt, *Energy Environ. Sci.*, 2010, **3**, 1207–1217; (*g*) M. Yadav and Q. Xu, *Energy Environ. Sci.*, 2012, **5**, 9698–9725.

3 J. S. Yoo, F. Abild-Pedersen, J. K. Nørskov and F. Studt, *ACS Catal.*, 2014, **4**, 1226–1233.

4 X. Gu, Z.-H. Lu, H.-L. Jiang, T. Akita and Q. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 11822–11825.

5 (*a*) Y. Ping, J.-M. Yan, Z.-L. Wang, H.-L. Wang and Q. Jiang, *J. Mater. Chem. A*, 2013, **1**, 12188–12191; (*b*) W.-Y. Yu, G. M. Mullen, D. W. Flaherty and C. B. Mullins, *J. Am. Chem. Soc.*, 2014, **136**, 11070–11078.

6 K. Jiang, K. Xu, S. Zou and W.-B. Cai, *J. Am. Chem. Soc.*, 2014, **136**, 4861–4864.

7 (*a*) C. Hu, S.-W. Ting, J. Tsui and K.-Y. Chan, *Int. J. Hydrogen Energy*, 2012, **37**, 6372–6380; (*b*) S. Zhang, Ö. Metin, D. Su and S. Sun, *Angew. Chem., Int. Ed.*, 2013, **52**, 3681–3684; (*c*) H. Dai, N. Cao, L. Yang, J. Su, W. Luo and G. Cheng, *J. Mater. Chem. A*, 2014, **2**, 11060–11064; (*d*) Y.-L. Qin, J. Wang, F.-Z. Meng, L.-M. Wang and X.-B. Zhang, *Chem. Commun.*, 2013, **49**, 10028–10030; (*e*) Z.-L. Wang, H.-L. Wang, J.-M. Yan, Y. Ping, S.-I. O, S.-J. Li and Q. Jiang, *Chem. Commun.*, 2014, **50**, 2732–2734.

8 (*a*) K. Mori, M. Dojo and H. Yamashita, *ACS Catal.*, 2013, **3**, 1114–1119; (*b*) G. Lu, A. Crown and A. Wieckowski, *J. Phys. Chem. B*, 1999, **103**, 9700–9711; (*c*) Z.-L. Wang, J.-M. Yan, H.-L. Wang, Y. Ping and Q. Jiang, *Sci. Rep.*, 2012, 2.

9 Here, 1.5 mL of formic acid was added, and the formate ratios in the mixture were adjusted by the amount of NaOH added. Thus, the final amount of formic acid was changed. Details of the composition see Table S1.

10 (*a*) L. Jia, D. A. Bulushev, S. Beloshapkin and J. R. H. Ross, *Appl. Catal., B*, 2014, **160–161**, 35–43; (*b*) C. Hu, J. K. Pulleri, S.-W. Ting and K.-Y. Chan, *Int. J. Hydrogen Energy*, 2014, **39**, 381–390; (*c*) X. Zhou, Y. Huang, W. Xing, C. Liu, J. Liao and T. Lu, *Chem. Commun.*, 2008, 3540–3542.

11 M. Ojeda and E. Iglesia, *Angew. Chem.*, 2009, **121**, 4894–4897.

12 Here, 1.5 mL of formic acid was added, and the formate ratios in the mixture were adjusted by the amount of NaOH added. Thus, the final amount of formic acid was changed. Details of the composition see Table S1.

13 Here, 60% of 1 mL of formic acid has reacted with NaOH to form formate. Only 0.4 mL of formic acid was remained in the mixture, which can be decomposed to generate hydrogen.

14 (*a*) J.-Y. Wang, H.-X. Zhang, K. Jiang and W.-B. Cai, *J. Am. Chem. Soc.*, 2011, **133**, 14876–14879; (*b*) H.-X. Zhang, S.-H. Wang, K. Jiang, T. André and W.-B. Cai, *J. Power Sources*, 2012, **199**, 165–169.

15 H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang and D. P. Wilkinson, *J. Power Sources*, 2006, **155**, 95–110.

16 J. W. Guo, T. S. Zhao, J. Prabhuram, R. Chen and C. W. Wong, *Electrochim. Acta*, 2005, **51**, 754–763.

17 J. Chang, L. Feng, C. Liu, W. Xing and X. Hu, *Energy Environ. Sci.*, 2014, **7**, 1628–1632.

18 F. Vigier, C. Coutanceau, A. Perrard, E. M. Belgsir and C. Lamy, *J. Appl. Electrochem.*, 2004, **34**, 439–446.

19 W. Zhou, Z. Zhou, S. Song, W. Li, G. Sun, P. Tsiakaras and Q. Xin, *Appl. Catal., B*, 2003, **46**, 273–285.

20 W. J. Zhou, S. Q. Song, W. Z. Li, Z. H. Zhou, G. Q. Sun, Q. Xin, S. Douvartzides and P. Tsiakaras, *J. Power Sources*, 2005, **140**, 50–58.

21 B. H. Liu, Z. P. Li, K. Arai and S. Suda, *Electrochim. Acta*, 2005, **50**, 3719–3725.

22 A. Verma, A. K. Jha and S. Basu, *J. Power Sources*, 2005, **141**, 30–34.

23 (*a*) L. Feng, S. Yao, X. Zhao, L. Yan, C. Liu and W. Xing, *J. Power Sources*, 2012, **197**, 38–43; (*b*) L. Feng, X. Sun, C. Liu and W. Xing, *Chem. Commun.*, 2012, **48**, 419–421; (*c*) J. Chang, L. Feng, C. Liu, W. Xing and X. Hu, *Angew. Chem., Int. Ed.*, 2014, **53**, 122–126.