

The Properties of PdRu /C with respect to the Electro-oxidation of Methanol and Ethanol

Yingjia Yang¹, Shaofeng Yu¹, Lizhen Gao¹, Xiaomin Wang², Shaohui Yan^{1,2,*}

¹ College of Environmental Science and Engineering, Taiyuan University of Technology, Taiyuan, 030024, China

² Laboratory of Green Energy Materials and Storage Systems, Taiyuan University of Technology, Taiyuan, 030024, China

*E-mail: yanshaohui@tyut.edu.cn

Received: 9 October 2018 / Accepted: 4 December 2018 / Published: 5 January 2019

An activated carbon supported PdRu bimetallic nanocatalyst (PdRu/C) was prepared by microwave heating reduction method. TEM results showed that, when Ru was added, the catalyst can get better dispersion and smaller particle radius, the PdRu/C catalysts possess smaller mean grain size. XRD data indicate that the Pd-Ru is supported on the activated carbon as an alloy. The catalytic property was determined by analyzing the oxidation and reduction peaks of methanol and ethanol at different molar ratios of PdRu. The PdRu/C catalyst exhibits a good CO-tolerance. In addition, all the catalysts revealed better electrocatalytic performance towards ethanol oxidation than methanol oxidation under alkaline conditions. The current intensity of the PdRu(1:1)/C catalysts for the ethanol electrooxidation reached about 991 mA mg⁻¹ Pd; while the methanol was only 375 mA mg⁻¹ Pd. Besides, the catalytic property of the PdRu(1:1)/C for the electrooxidation of alcohol was 1.1 times than the Pd/C catalyst synthesized in the same way. The PdRu(1:1)/C has slightly higher current intensity than the Pd/C, and exhibits excellent durability after a long time test to ethanol oxidation. It also has a very fast charge transfer rate as shown in EIS test.

Keywords: PdRu Nano-catalysts, Microwave assisted polyol method, electrocatalytic properties, Methanol Electro-oxidation, Ethanol Electro-oxidation

1. INTRODUCTION

Direct alcohol fuel cell has good application value in electric cars and portable equipment due to its advantages in many aspects such as high energy efficiency, environmental benignity, easy transportation and storage of the fuel and other features [1,2].

However, it is still far from a wide range of practical applications. An important factor is the high

price of Pt-based catalysts [3]. Platinum has always been the optimum material for the electrochemical oxidation of alcohols. However, such catalysts can easily be adsorbed by certain reaction intermediates, CO_{ads} , produced during the methanol electro-oxidation reaction, decreasing its catalytic performance [4,5]. Therefore, it is very valuable to find a more valid, cheaper and non-platinum based anode catalyst material for DAFCs.

Pd plays a significant role in the alternative materials [6-8] for its higher availability in alcohol oxidation under alkaline conditions. For example, according to reports in the literature, under alkaline solution, the Pd/C catalyst has a preferable electro-oxidation activity than Pt/C in ethanol solution, which is attributable to the cleavage of the C-C bond promotes the oxidation of ethanol and further oxidizes the products CO to CO_2 . In addition, the stability and toxicity resistance of Pd/C catalyst are better than those of Pt/C catalyst at low temperature [9]. At the same time, Pd has a similar atomic radius and lattice structure as Pt [10]. Pd adsorbs OH^- more easily in alkaline solutions, which enhances the oxidation kinetics of alcohols [11,12]. Furthermore, the presence of Ru in the PdRu bimetallic catalyst can not only weaken the interaction between Pd and CO [13], but also can decompose H_2O to produce oxygen species, such as $-\text{OH}_{\text{ads}}$, at a lower potential, which can oxidize intermediate products, such as CO which can be oxidized to CO_2 [14]. Therefore, the catalyst contained Ru has high electrocatalytic activity and methanol-tolerant ability [15].

In addition, the influence of the preparation method on the activity of the electrocatalyst cannot be ignored. Impregnation method and colloid method are two conventional methods preparing nanoparticles, yet with many disadvantages. For example, impregnation method is difficult to control the particle size and colloid method is cumbersome to operate and not suitable for large-scale preparation of electrocatalysts in the future [16-19]. Electrodeposition method is difficult to achieve uniform deposition on large area electrodes [20,21]. Also, the surfactants used in the microemulsion method are expensive and cumbersome to clean and not suitable for large-scale production [22,23]. In contrast, physical assistance methods such as microwave assisted ethylene glycol reduction and ultrasonic assisted methods are the latest methods for the preparation of nanocatalysts. They have caused widespread concern for the fast preparation speed, small nanoparticle size, and good dispersion properties [24,25].

Here, the PdRu/C and Pd/C nanocatalysts are synthesized using a microwave heating reduction method aiming at developing a novel anode catalyst for DAFCs. In the investigation of the PdRu/C bimetallic catalysts, the effect of the molar ratio between Pd and Ru, the mean size and distribution of the nanoparticles on the catalytic activity were fully discussed.

2. EXPERIMENTAL

2.1 Fabrication of nanocatalysts

24 mg Vulcan XC-72 were firstly impregnated with 1 ml of 0.0564 mol/L PdCl_2 and 1.17 ml of 0.0482 mol/L RuCl_3 in 20 ml ethylene glycol, and ultrasonically disperse for 30 min (Maintain a molar ratio of Pd to Ru of about 1:1). Then, 3.8 mL 0.1 mol/L KOH was instilled in the above solution under ultrasonic treatment using about 2 min. After that, the small beaker added another 20ml of ethylene

glycol was placed in a household microwave oven and heated about 1 minute. After cooling, the mixture was carefully filtered and rinsed using distilled water adequately. Then dried at 80 °C for 6 hours, it was grinded using an agate mortar, and kept in a plastic centrifuge tube. Thus, a PdRu (1:1)/C catalyst was obtained. The Pd/C, PdRu(2:1)/C, PdRu(1:2)/C and PdRu(1:3)/C composite catalysts were prepared in the same manner for comparison.

2.2 Electrochemical measurements

The working electrode is manufactured by the method reported in literatures [26,27]. In brief, 1 ml Nafion solution (0.2 wt%) containing 2.0 mg catalysts were fused together by ultrasonic treatment for 30 minutes. Afterwards, 5 μ l suspension was transferred using a micro sampler and dropped on the surface of a glassy carbon electrode ($d = 5$ mm). Thereafter the sample was dried at room temperature for about 20 min, this working electrode is critical to the electrochemical activity of the test catalyst. The reference electrode is a saturated Ag|AgCl electrode (Ag|AgCl), and the counter electrode is a graphite electrode (4 cm^2). The testing electrolytes are 0.5 mol/L H_2SO_4 and 0.1 mol/L KOH mixed liquor respectively as the acidic electrolyte solution and alkaline electrolyte solution. The electrochemical data are recorded by the computer connected to the CHI760E electrochemical workstation (Shanghai, China). All the electrochemical experiments are performed at 25 °C. The scan rate for the test of cyclic voltammetry (CV) is 50 mV s^{-1} . Dissolved oxygen was expelled by N_2 before each electrochemical test. Chronoamperometric tests were performed at 0.1 V at room temperature for 3600 s. Electrochemical impedance spectra (EIS) was carried out at an AC frequency of 1000 k Hz $\sim$ 0.005Hz.

2.3 Characterization of electro-catalysts

The morphology of the PdRu/C catalysts were detected by transmission electron microscope (TEM, JEM-1200EX). X-ray diffraction (XRD) patterns was carried out on a BRUCKER D8 wide-angle goniometer employing a Cu target, $\text{K}\alpha$ radiation with a scanning range (2θ) from 10 to 90° at 6 °/min, Scan step length is 0.02. X-ray photoelectron spectroscopy (XPS) was investigated by Thermo Scientific Escalab 250Xi. The metal content of the nanocatalyst was obtained by applying Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

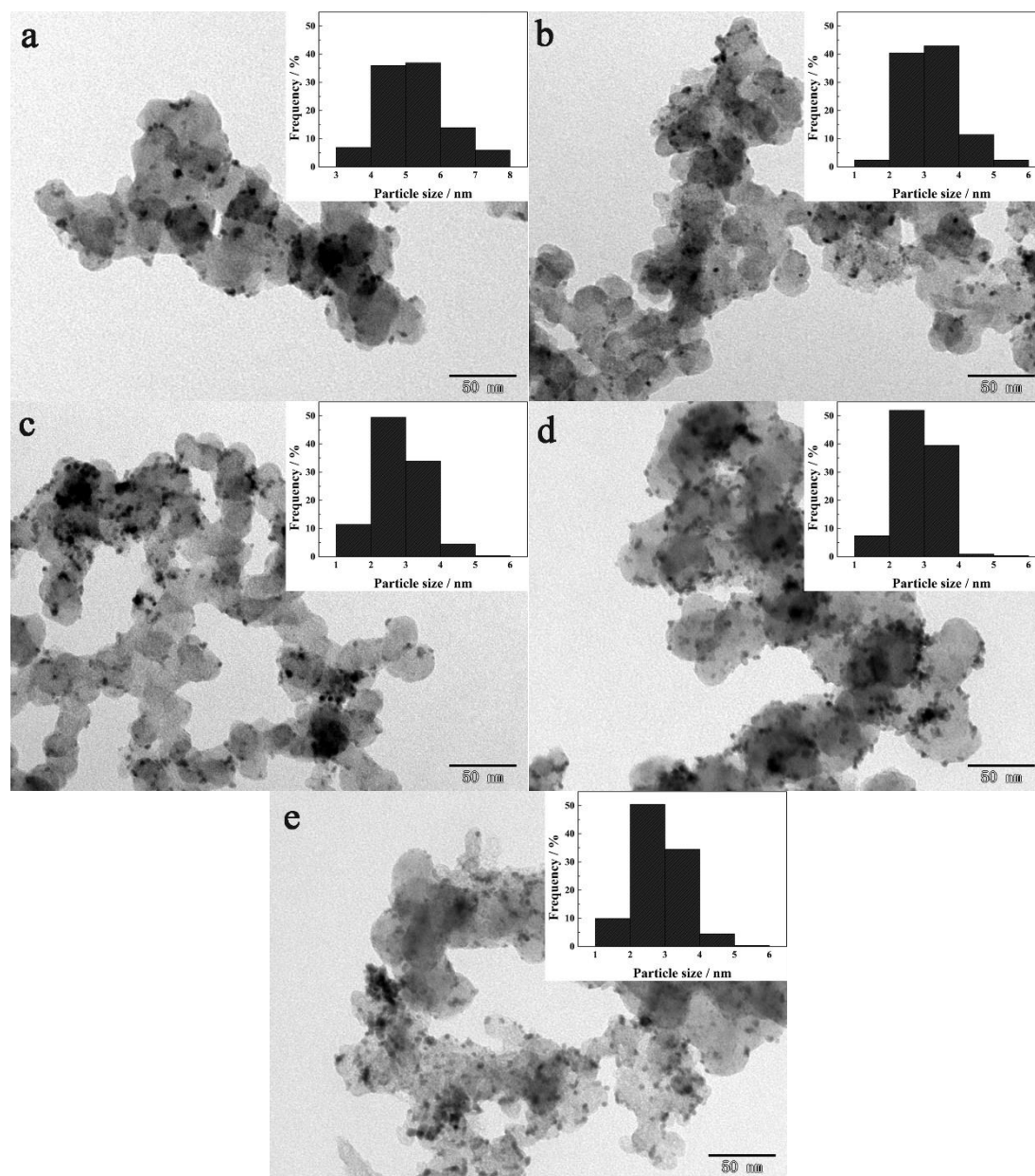
3. RESULTS AND DISCUSSION

3.1 Characterization of electro-catalysts

Analyzing ICP-OES determines the actual metal loading of catalysts, and Table 1 lists the corresponding conclusion. The measured total metal load is lower than the theoretical total metal load. It can be seen intuitively that the reduction effect of Ru is relatively poor, but with the addition of Ru, the reduction amount of ruthenium is also increasing [28].

Table 1. Metal element loading of the prepared catalyst

Entry	Catalyst	Pd (wt%)	Ru (wt%)	Actual total metal content (wt%)	Theoretical total metal content (wt%)
1	Pd/C	39.7	NA	39.7	40
2	PdRu(2:1)/C	22.7	1.47	24.17	42.4
3	PdRu(1:1)/C	20.5	2.45	22.95	32.7
4	PdRu(1:2)/C	20.8	4.45	25.25	42.1
5	PdRu(1:3)/C	19.3	4.36	23.66	49.0

**Figure 1.** TEM pictures of the Pd/C (a), PdRu(2:1)/C (b), PdRu(1:1)/C (c), PdRu(1:2)/C (d) and PdRu(1:3)/C (e) catalysts

The representative TEM images and nanoparticle morphologies of the Pd/C, PdRu(2:1)/C,

PdRu(1:1)/C, PdRu(1:2)/C and PdRu(1:3)/C catalysts are displayed in Fig. 1. The dark particles in the figure are activated carbon, and the small black dots are Pd or PdRu nanoparticles. This illustrates the successful combination of activated carbon and metal nanoparticles in these catalysts prepared by the microwave method. It can be clearly seen that the PdRu(1:3)/C particles are the smallest and are very uniformly distributed on the support, while the Pd/C catalyst has a large agglomerated particles. In bimetallic catalysts, particle size tends to decrease as the molar ratio of Ru increases. At the same time, studies have found that the introduction of Ru will promote the dispersion of Pd [29].

The histogram of the particle size distribution of all nanocatalysts was obtained by randomly selecting 200 nanoparticles in the TEM image. From the illustration, the average particle diameter of the Pd/C catalyst is 5.26 nm. The PdRu(2:1)/C, PdRu(1:1)/C, PdRu(1:2)/C and PdRu(1:3)/C catalysts were 3.23 nm, 2.85 nm, 2.85 nm and 2.84 nm in diameter, respectively. High resolution graphics show that the distribution of the PdRu/C catalyst is more dispersed, wherein the mean diameter of the PdRu(1:3)/C catalyst is about half of the Pd/C. The rate of reduction of precious metals has a profound influence on the size and dispersion of nanoparticles during the preparation process.

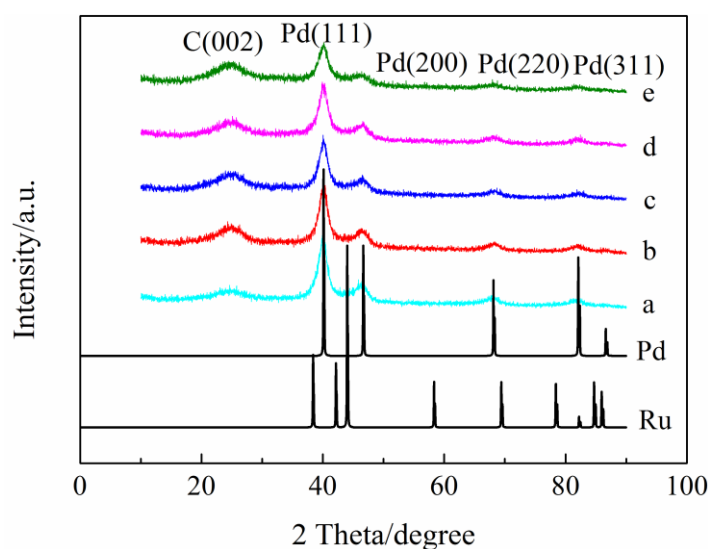


Figure 2. XRD spectra of Pd/C (a), PdRu(2:1)/C (b), PdRu(1:1)/C (c), PdRu(1:2)/C (d) and PdRu(1:3)/C (e)

Under the same conditions, XRD has become an effective method for studying the composition and crystal structure of materials. In Figure 2, all the catalysts display a large angle diffraction peak corresponding the C (002) crystal plane at $2\theta = 23.2^\circ$, which is attributed to the carbon carrier in the catalyst. Referring to the XRD standard spectra of the contained metal, the spectrum line around 40.1° , 46.6° , 68.1° and 82.0° correspond to the diffraction peaks of the Pd (111), Pd (200), Pd (220) and Pd (311), respectively [30]. However, the characteristic peaks of Ru crystal grains were undetected. In addition, the intensity of the Pd peak also decreased, possibly because of an increase in ruthenium element in the sediment.

The energy state distribution and element valence composition of the PdRu(1:1)/C surface of the catalyst identified using the XPS are shown in Fig. 3.

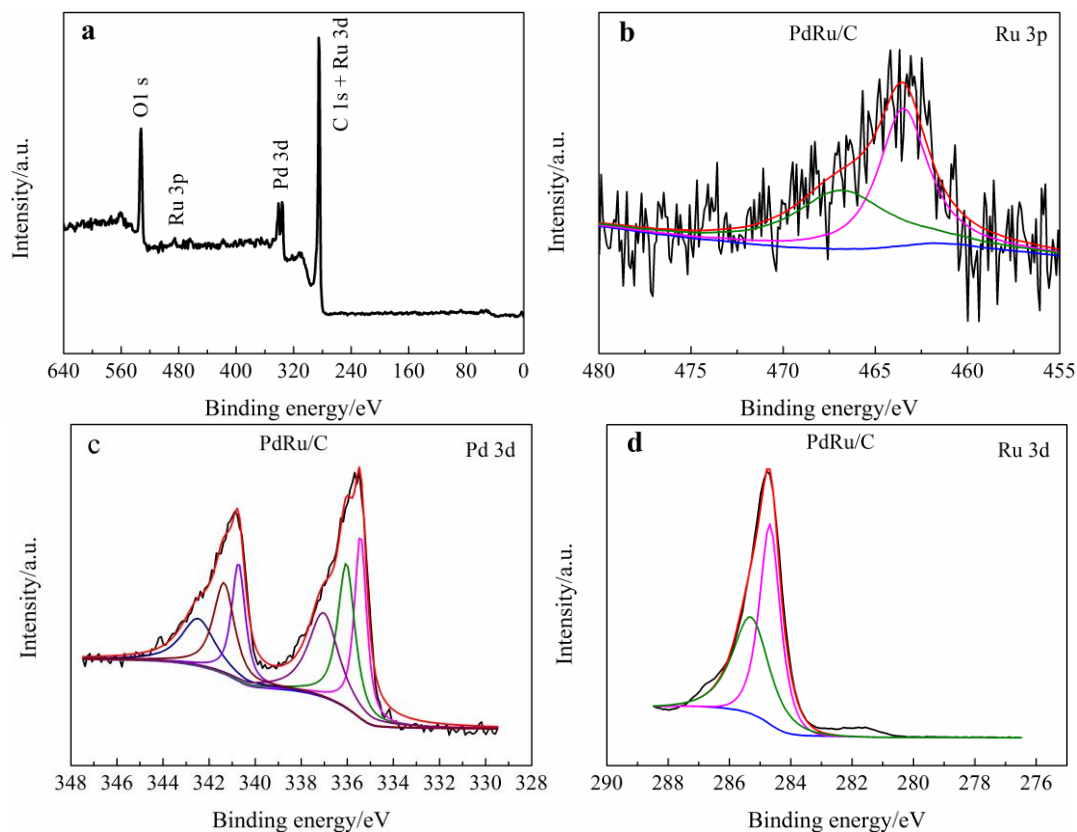


Figure 3. (a) Wide-scan survey of PdRu(1:1)/C. (b-d) Accurate scan results of Ru 3p, Pd 3d and Ru 3d in PdRu(1:1)/C.

The XPS test is used to illustrate the presence and valence of metals in composite materials. The PdRu(1:1)/C is used for analysis and elaboration. Four more obvious peaks appeared in the 250-600 eV range of this score. After comparison with the database, the peak positions of C 1s, Ru 3p, Pd 3d and O 1s were 285.0, 463.3, 335.1 and 532.8 eV, respectively. [31]. In Fig. 3(b-d), the precise scan spectrum was fitted to the analysis by software XPSPEAK41. In Fig. 3(c), the peaks at the 340.7 and 335.4 eV bond strengths are Pd 3d_{3/2} and Pd 3d_{5/2}, respectively. To explore the oxidation state of Pd, the total curves were divided into three groups of peaks with corresponding bond energy values of 340.5 and 335.4 eV, 341.3 and 336.0 eV, and 342.5 and 336.9 eV, respectively. These three groups of peaks represent different Pd elements. In the oxidation state, the first group is metal Pd, the second group is PdO_x/Pd or PdO, and the third group is usually PdO [32,33]. Obviously, metal Pd is the main form of the catalyst. There are other forms of the catalyst exists such as a small quantity of Pd²⁺, confirmed by the high-resolution Pd 3d spectrum peak-differentiating and imitating [34]. As shown in Fig. 3(b), Ru 3p_{3/2} is divided into two peaks, which are located at 463.6 and 466.5 eV, respectively, indicating mainly RuCl₂ and K₂[RuCl₅(H₂O)] [35]. Since the Ru 3p peak in Fig. 3(b) is weak, it is not sufficient to explain the state of Ru. Therefore, the spectrum of Ru 3d was taken as a research object. As shown in Fig. 3(d), Ru 3d_{3/2} is separated into two parts at 284.5 and 285.4 eV, respectively, which mainly indicate Ru/RuO_x and RuCl₃.

3.2 Electrochemical analysis of PdRu/C and Pd/C nanocatalysts

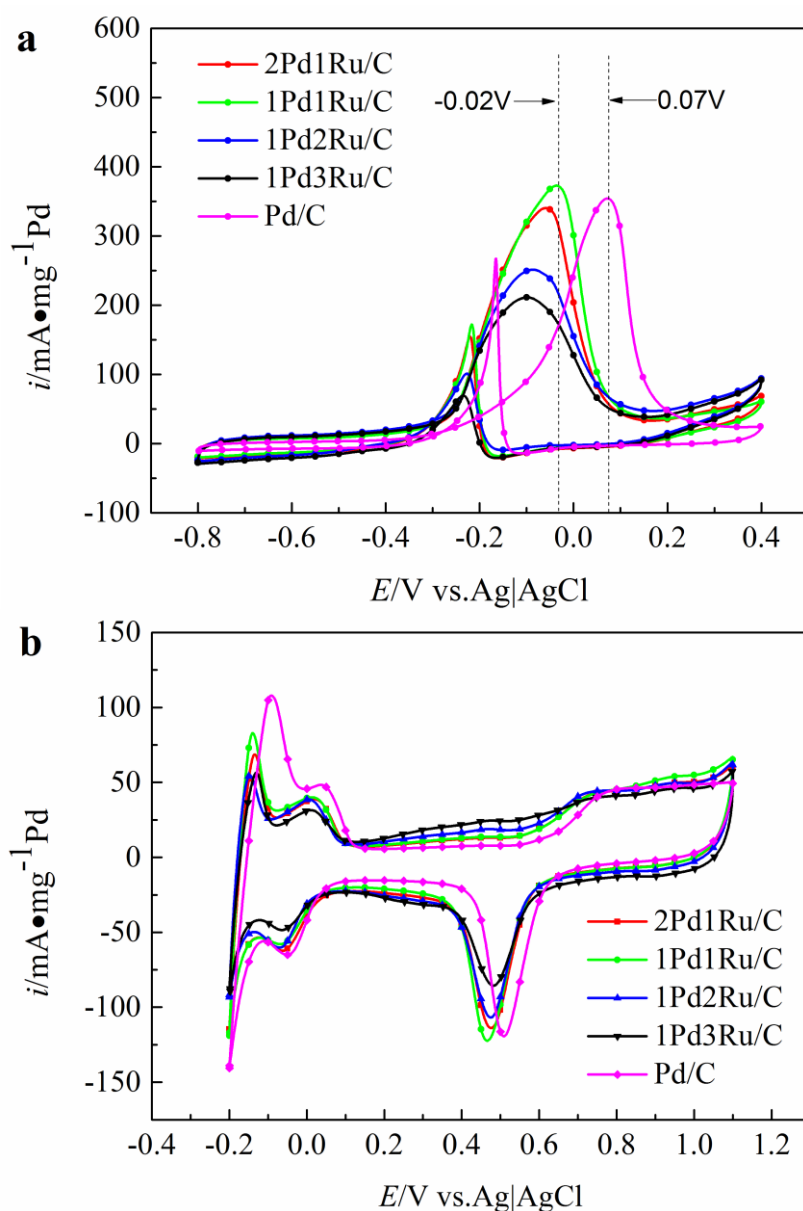


Figure 4. (a) CVs of Pd/C, PdRu(2:1)/C, PdRu(1:1)/C, PdRu(1:2)/C and PdRu(1:3)/C catalysts in 0.1 mol/L KOH + 1 mol/L CH₃OH at 50 mV/s. (b) These catalysts in 0.5 mol/L H₂SO₄ at 50 mV/s. (The 30th cycle)

As shown in Fig. 4(a), these catalysts were measured to evaluate the catalytic activity. All catalysts exhibit typical characteristics of methanol oxidation. That is to say, there are significant oxidation peaks in the scanning experiments. The positive scan is direct oxidation peak on the catalyst surface. The formation of reverse scan peaks is mainly for the oxidation of the intermediate product during the incomplete oxidation of methanol [36]. It can be found that the bimetallic catalyst PdRu(1:1)/C exhibited the optimum catalytic properties in oxidizing methanol. The forward peak current density of the PdRu(1:1)/C (375.06 mA mg⁻¹) is greater than Pd/C (353.35 mA mg⁻¹) at the 30th cycle. The CV curves indicate that the elemental palladium catalyst has a higher current density than the

PdRu(1:2)/C and PdRu(1:3)/C electrocatalysts.

The multiples of positive anode peak current density (I_f) and reverse anode peak current density (I_b) reflect the oxidation rate of the material and its tolerance to accumulated intermediate carbon product poisoning [37]. The higher the multiple, the stronger the tolerance to toxic substances on the catalyst surface. After calculation, PdRu(1:1)/C is 2.2, which is higher than Pd/C ($I_f/I_b = 1.3$). This phenomenon shows that the presence of an appropriate amount of Ru can weaken the occupation of active sites by carbon-containing intermediates such as CO, so that accelerating the oxidation of intermediates such as CO to CO₂ or other substances. It is beneficial to release more active sites and improve electro-catalytic stability.

Among these catalysts, the peak potential of PdRu(1:1)/C moves from 0.07 to -0.02V contrasted with Pd/C, and the peak current also increases. This phenomenon is due to the lattice strain effect leading to changes in the band structure, thereby increasing the mobility of carriers [38,39]. Consequently, more active sites promote the adsorption oxidation of CH₃OH, and the negative move of the peak potential refers to the electron mobility, which makes the catalyst have higher catalytic activity.

For the purpose of confirming the performance of the catalyst, the ECSAs can be obtained from the CV curve in the sulfuric acid system [40]. Fig. 1(b) displays CV curves of Pd/C, PdRu(2:1)/C, PdRu(1:1)/C, PdRu(1:2)/C and PdRu(1:3)/C catalysts at 50 mV/s scan in 0.5 mol/L H₂SO₄ liquor. The ECSAs increases with the decreasing addition of PdCl₂, and then decreaseing with the addition of RuCl₃. The PdRu(1:1)/C has the smallest particles size and highest specific area comparing with Pd/C [41].

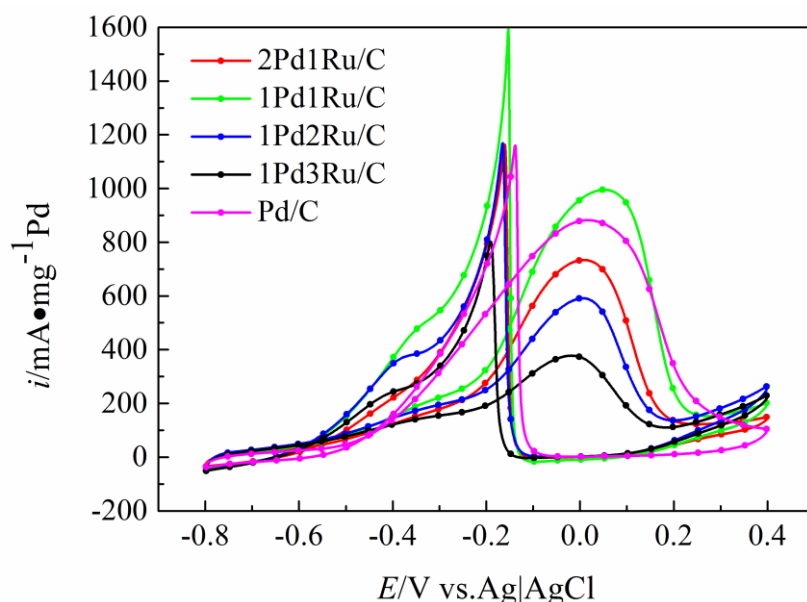


Figure 5. CVs of Pd/C, PdRu(2:1)/C, PdRu(1:1)/C, PdRu(1:2)/C and PdRu(1:3)/C catalysts in 0.1 mol/L KOH + 1 mol/L ethanol at 50 mV/s. (The 30th circle)

Fig. 5 displays the CVs on the PdRu/C and Pd/C catalysts in 0.1 mol/L KOH + 1 mol/L ethanol. When the Pd-Ru proportion is 1:1, the peak current of ethanol oxidation is the largest, about 991.57 mA mg⁻¹ at 0.036 V, and the peak current of Pd/C prepared under the same conditions is 884.10 mA mg⁻¹ at 0.02V, that is to say, PdRu(1:1)/C has the strongest electrocatalytic performance for ethanol oxidation. After all of the catalysts were reduced in the time of the forward scan, there was a peak at about -0.10 V

to -0.40 V during the negative scan, which may be a reaction to the intermediate product. Beyond that, PdRu/C has an initial potential of -0.60 V earlier than Pd/C (-0.50 V) reflecting the advantages of PdRu/C catalyst in the oxidation kinetics of ethanol.

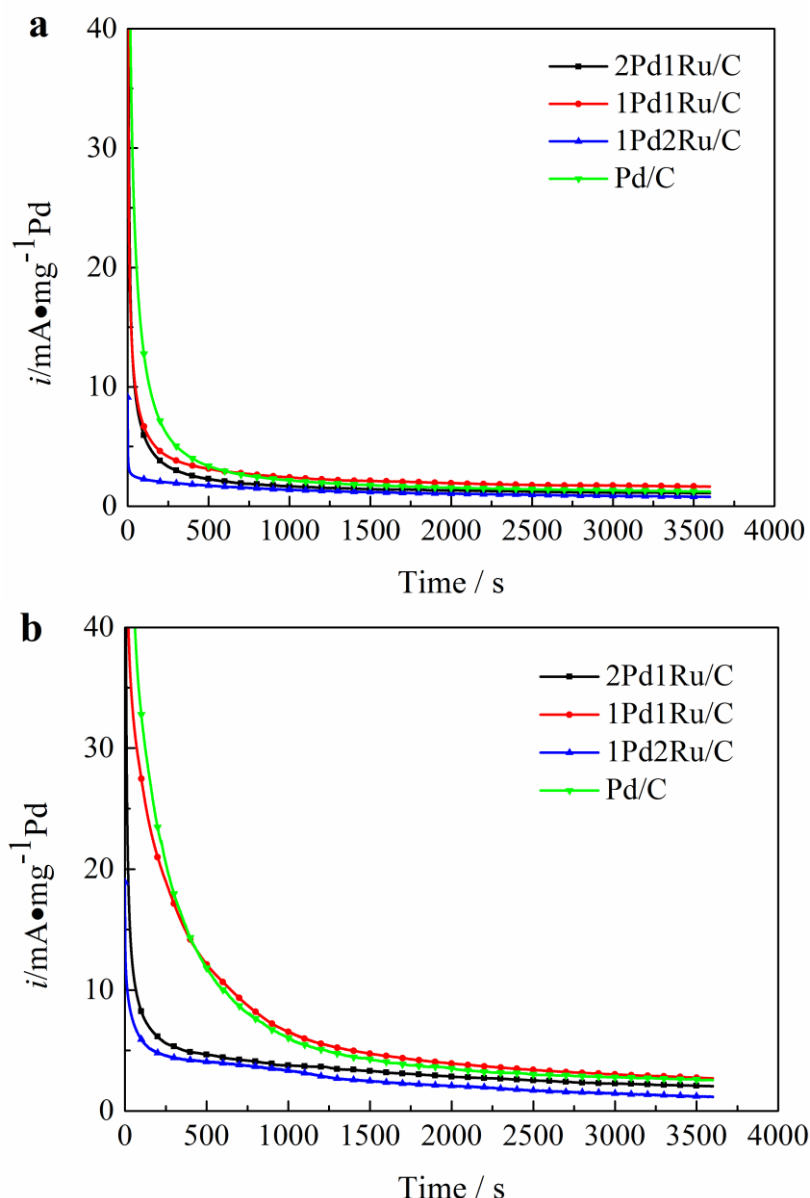


Figure 6. (a) Chronoamperometric curves at 0.1 V of Pd/C, PdRu(2:1)/C, PdRu(1:1)/C, PdRu(1:2)/C and PdRu(1:2)/C catalysts in a mix solution of 0.1 mol/L KOH + 1 mol/L CH₃OH at room temperature. (b) These catalysts in 0.1 mol/L KOH + 1 mol/L ethanol at 25 °C.

Chronoamperometry is an important approach to obtain the stability of the catalysts. The current density sharply decays at the initial stage and gradually stabilizes at the later stage. The initial higher current density value is mainly because of the existence of the double layer and sufficient active sites to catalyze the alcohol oxidation reaction. The rapid decline of the current density is partly because the methanol in the solution is continuously oxidized on catalyst surface, and the intermediate product continuously accumulates, thus occupying the active site and leading to a decrease in catalytic performance [42].

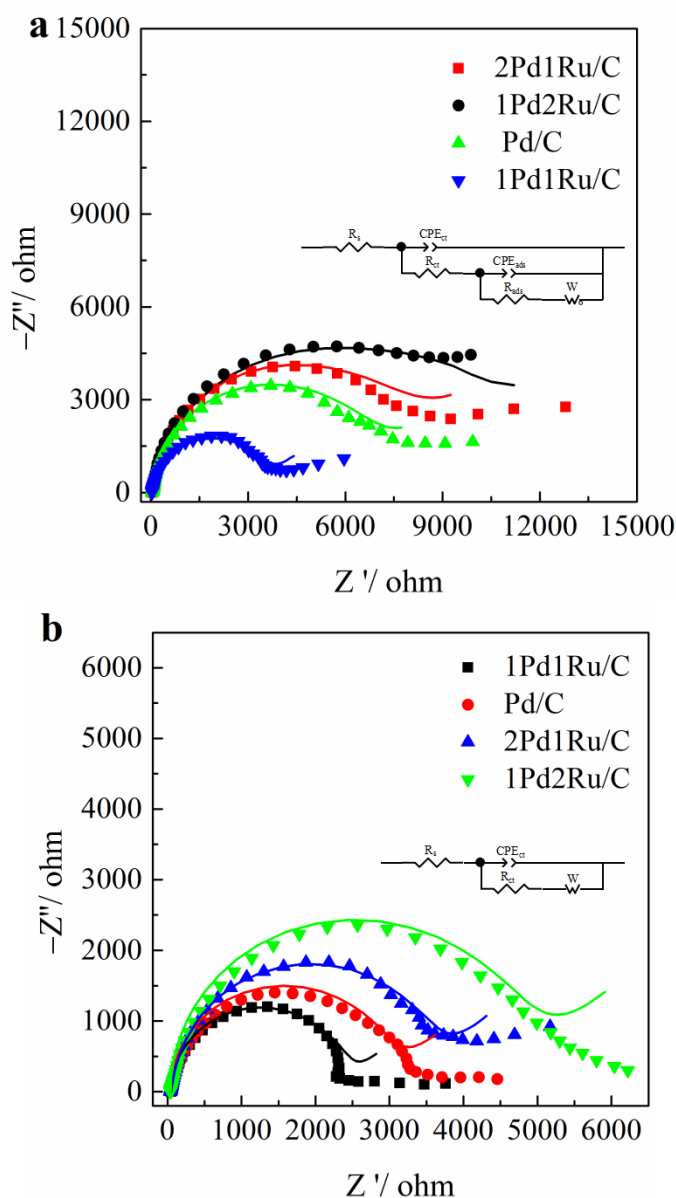


Figure 7. Electrochemical impedance spectra for alcohol oxidation on Pd/C, PdRu(2:1)/C, PdRu(1:1)/C and PdRu(1:2)/C catalysts in (a) 0.1 mol/L KOH + 1 mol/L CH₃OH, (b) 0.1 mol/L KOH + 1 mol/L ethanol solutions at a fixed potential of 0.1 V. The illustration is an equivalent circuit by fitting the impedance spectrum.

Fig. 6(a) depicts the chronoamperometry of Pd/C and PdRu/C for electrocatalytic oxidation of methanol in 0.1 mol/L KOH + 1 mol/L CH₃OH at 0.1 V. It can be seen from the figure that PdRu (1:1)/C has the highest current density after 3600s, showing the best electrocatalytic stability. Its current density value is stable at 1.9 mA/mg. In other three groups of curves, the initial value of the current density of the Pd/C is relatively high but the decay process is relatively slow. The highest among others shows the best catalytic methanol oxidation stability and resistance to poisoning.

Furthermore, with the addition of Ru in 0.1 mol/L KOH + 1 mol/L ethanol and a long period of testing, the current density of PdRu(1:1)/C is also the highest and exhibits excellent durability to ethanol oxidation under alkaline conditions in Fig. 6(b).

Table 2. The EIS Parameters of Pd/C, PdRu(2:1)/C, PdRu(1:1)/C and PdRu(1:2)/C electrodes

Electrode	0.1 M KOH + 1 M CH ₃ OH						0.1 M KOH + 1 M ethanol			
	R _s (ohm)	CPE _{ct} (μF)	R _{ct} (ohm)	CPE _{ads} (μF)	R _{ads} (ohm)	W	R _s (ohm)	CPE _{ct} (μF)	R _{ct} (ohm)	W
Pd/C	45.1	189.7	258.6	147.5	6321	2.6×10^{-3}	47.4	194.1	2842	5.2×10^{-3}
PdRu(2:1)/C	44.2	190.7	355.2	130.8	7185	1.7×10^{-4}	40.5	140.9	3134	2.5×10^{-3}
PdRu(1:1)/C	34.5	196.8	244.9	248.5	3034	3.2×10^{-3}	49.4	327.6	2315	9.6×10^{-3}
PdRu(1:2)/C	39.2	106.4	353.4	72.7	7834	1.3×10^{-4}	40.5	179.2	4672	3.6×10^{-3}

As shown in Figures 7(a) and 7(b), the electrocatalytic reaction of each electrode in different alcohol solutions was analyzed by electrochemical impedance spectroscopy (EIS). Nyquist Impedance map of each catalyst from 1000 kHz to 0.005 Hz was recorded. The relevant equivalent circuit is attached to the corresponding diagram, where R_s represents the solution resistance, CPE_{ct} and CPE_{ads} correspond to the constant phase element of the electrocatalytic oxidation of the alcohol, respectively, R_{ct} , R_{ads} and W reflect the impedance of charge transfer and the Warburg's diffusion element, respectively [43]. The relevant parameters are summarized in Table 2. In Figure 7(a), the radius of the arc reflects the charge transfer resistance (R_{ct}) between the surface of the electrode and the electrolyte when methanol is oxidized on the surface of the electrode. The smaller the radius of the impedance arc are, the smaller the obstacle to electron transfer and the higher the catalytic performance is [44]. Obviously, the corresponding R_{ct} of PdRu(1:1)/C is smaller than that of other catalysts. However, in the electro-catalytic oxidation impedance diagram of ethanol in Fig. 7(b), PdRu(1:1)/C corresponds to the smallest R_{ct} , showing the best performance.

4. CONCLUSIONS

The Pd/C and PdRu/C catalysts were prepared by microwave heating reduction method. The PdRu/C catalyst has excellent CO-tolerance, smaller particle radius and uniform dispersion. The PdRu nanoparticles exist on the activated carbon supported in an alloy form, which reveals better electrocatalytic performance towards ethanol oxidation than methanol oxidation in alkaline solutions, especially the PdRu(1:1)/C shows excellent activity for the ethanol oxidation. The mass activity reaches 991 mA mg⁻¹ Pd, which is slightly higher than that of the Pd/C. In the long-term methanol and ethanol oxidation test, the current density, durability and charge transfer rate of the PdRu(1:1)/C are slightly better than the Pd/C catalyst, as shown in both the chronoamperometry and EIS tests. The encouraging performance suggests that the PdRu/C catalysts can be promising catalysts for alcohol electrooxidation.

ACKNOWLEDGMENTS

We thank the natural science fund (2014011017-2) and key research and development plan (201603D321010) of Shanxi province for their financial supporting.

References

1. E. Antolini and E. R. Gonzalez, *J. Power Sources*, 195 (2010) 3431.
2. Y. S. Li, T. S. Zhao and Z. X. Liang, *J. Power Sources*, 187 (2009) 387.
3. H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang and D. P. Wilkinson, *J. Power Sources*, 155 (2006) 95.
4. F. Wang, J. Qiao, J. Wang, H. Wu, X. Yue, Z. Wang, W. Sun and K. Sun, *Electrochim. Acta*, 271 (2018) 1.
5. H. C. Cha, C. Y. Chen and J. Y. Shiu, *J. Power Sources*, 192 (2009) 451.
6. H. T. Zheng, Y. Li, S. Chen and P. K. Shen, *J. Power Sources*, 163 (2006) 371.
7. E. Antolini, *J. Power Sources*, 170 (2007) 1.
8. Ermete, nbsp and Antolini, *Energ. Environ. Sci.*, 2 (2009) 915.
9. L. Ma, D. Chu and R. Chen, *Int. J. Hydrogen Energy*, 37 (2012) 11185.
10. Y. Tang, H. Zhang, H. Zhong, T. Xu and H. Jin, *J. Power Sources*, 196 (2011) 3523.
11. H. Gao, S. Liao, J. Zeng, Y. Xie and D. Dai, *Electrochim. Acta*, 56 (2011) 2024.
12. A. Sarkar, A. V. Murugan and A. Manthiram, *Langmuir*, 26 (2015) 2894.
13. Y. Chen, Z. Lin and L. U. Juntao, *Chinese J. Catal.*, 28 (2007) 870.
14. F. Braun, A. M. Tarditi and L. M. Cornaglia, *J. Membrane Sci.*, 382 (2011) 252.
15. A. Chen and P. Holthindle, *Chem. Rev.*, 110 (2010) 3767.
16. H. Bönemann, W. Brijoux, R. Brinkmann, T. Joußen, B. Korall and E. Dinjus, *Angew. Chem. Int. Edit.*, 30 (2010) 1312.
17. M. Watanabe, M. Uchida and S. Motoo, *J. Electroanal. Chem.*, 229 (1987) 395.
18. Z. B. Wang, G. P. Yin, J. Zhang, Y. C. Sun and P. F. Shi, *Electrochim. Acta*, 51 (2006) 5691.
19. B. Yang, Q. Lu, Y. Wang, L. Zhuang, A. Juntao Lu, P. Liu, J. W. And and R. Wang, *Chem. Mater.*, 15 (2003) 3552.
20. H. Kim, N. P. Subramanian and B. N. Popov, *J. Power Sources*, 138 (2004) 14.
21. E. J. Taylor, *J. Electrochem. Soc.*, 139 (1992) L45.
22. X. Z. and K. Y. Chan, *Chem. Mater.*, 15 (2003) 451.
23. J. Solla-Gullón, F. J. Vidal-Iglesias, V. Montiel and A. Aldaz, *Electrochim. Acta*, 49 (2004) 5079.
24. W. X. Chen, J. Y. Lee and Z. Liu, *Mater. Lett.*, 58 (2004) 3166.
25. H. Tong, H. L. Li and X. G. Zhang, *Carbon*, 45 (2007) 2424.
26. H. Li, S. Zhang, S. Yan, Y. Lin and Y. Ren, *Int. J. Electrochem. Sc.*, 8 (2013) 2996.
27. Q. Dong, Y. Zhao, X. Han, Y. Wang, M. Liu and Y. Li, *Int. J. Hydrogen Energy*, 39 (2014) 14669.
28. C.-H. Tsai, M. Xu, P. Kunal and B. G. Trewyn, *Catal. Today*, 306 (2018) 81.
29. A. V. Romanenko, E. A. Tyschishin, E. M. Moroz, V. A. Likholobov, V. I. Zaikovskii, S. H. Jung and Y. S. Park, *Appl. Catal. A-Gen.*, 227 (2002) 117.
30. H. Huang and X. Wang, *J. Mater. Chem.*, 22 (2012) 22533.
31. V. I. Nefedov, Y. V. Salyn, I. I. Moiseev, A. P. Sadovskii, A. S. Berenbljum, A. G. Knizhnik and S. L. Mund, *Inorg. Chim. Acta*, 35 (1979) L343.
32. X. Yang, M. Zhen, G. Li, X. Liu, X. Wang, C. Shu, L. Jiang and C. Wang, *J. Mater. Chem. A*, 1 (2013) 8105.
33. V. D. Noto, E. Negro, S. Lavina, S. Gross and G. Pace, *Electrochim. Acta*, 53 (2007) 1604.
34. J. N. Zheng, S. S. Li, X. Ma, F. Y. Chen, A. J. Wang, J. R. Chen and J. J. Feng, *J. Power Sources*, 262 (2014) 270.
35. X. Li and I. M. Hsing, *Electrochim. Acta*, 52 (2007) 1358.
36. R. K. Shervedani and A. Amini, *Electrochim. Acta*, 121 (2014) 376.
37. Y. Zhao, L. Zhan, J. Tian, S. Nie and Z. Ning, *Int. J. Hydrogen Energy*, 35 (2010) 10522.
38. D. Chen, C. Li, H. Liu, F. Ye and J. Yang, *Sci. Rep.*, 5 (2015) 11949.
39. C. H. Kuo, L. K. Lamontagne, C. N. Brodsky, L. Y. Chou, J. Zhuang, B. T. Sneed, M. K. Sheehan and C. K. Tsung, *Chemsuschem*, 6 (2013) 1993.

40. H. Zhao, J. Yang, L. Wang, C. Tian, B. Jiang and H. Fu, *Chem. Commun.*, 47 (2011) 2014.
41. W. Zhou, C. Zhai, Y. Du, J. Xu and Y. Ping, *Int. J. Hydrogen Energy*, 34 (2009) 9316.
42. J. Zhao, L. Zhang, H. Xue, Z. Wang and H. Hu, *Rsc Adv.*, 2 (2012) 9651.
43. S. Yan, S. Zhang, Y. Lin and G. Liu, *J. Phys. Chem. C*, 115 (2011) 6986.
44. S. Zhang, Y. Shao, G. Yin and Y. Lin, *J. Power Sources*, 195 (2010) 1103.

© 2019 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).