Research Article

Promoting Effect of Third Metal (M = Ni, Mo and Rh) on Pd–Ir Binary Alloy Catalysts in Membraneless Sodium Perborate Fuel Cells

K. Vijayaramalingam[1], S. Kiruthika[2], B. Muthukumaran[1],*

[1]Department of Chemistry, Presidency College, Chennai – 600 005, India.
[2]Department of Chemical Engineering, SRM University, Chennai – 603 203, India.

*Corresponding author's e-mail: dr.muthukumaran@yahoo.com

Abstract

The fabrication, characterization and performance of Pd–Ir–M (M = Ni, Mo and Rh) electrocatalysts supported on carbon leading to enhancement of the electrocatalytic oxidation of sodium perborate is presented. The combination of monometallic Pd/C, bimetallic Pd–Ir/C and tri-metallic Pd–Ir–Ni/C, Pd–Ir–Mo/C and Pd–Ir–Rh/C electrocatalysts were prepared by the ultrasonic-assisted chemical reduction method. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-Ray spectroscopy (EDX) and X-Ray diffraction (XRD) were used for the catalyst characterization. The prepared catalysts had similar particle morphology and their particle sizes were 3-5 nm. The EDX results of the binary Pd–Ir/C and the ternary Pd–Ir–Ni/C, Pd–Ir–Mo/C and Pd–Ir–Rh/C catalysts were extremely close to the nominal values, indicating that the metals were loaded onto the carbon support without any obvious loss. The electrocatalytic activities of the catalysts were investigated in half-cell experiments using cyclic voltammetry (CV), CO stripping voltammetry and chronoamperometry (CA). The electrochemical results obtained at room temperature showed that the tri-metallic Pd–Ir–M (M = Ni, Mo and Rh) electrocatalysts displayed better catalytic activity toward sodium perborate oxidation compared to the other catalysts. In this study, the carbon-supported binary Pd–Ir/C and ternary Pd–Ir–M/C (M = Ni, Mo and Rh) anode catalysts were successfully tested in a single membraneless fuel cell using 0.15 M sodium perborate as the fuel and 0.1 M sodium perborate as the oxidant with 0.5 M H_2SO_4 as the electrolyte respectively. Based on the experimental results, we conclude that the Pd–Ir–Ni/C demonstrates superior sodium perborate electro-oxidation than Pd–Ir–Mo/C, Pd–Ir–Rh/C, Pd–Ir/C and Pd/C.

Keywords: Electrocatalysts; Fabrication; Characterization; Ultrasonication; Membraneless fuel cell.

Introduction

Membraneless Sodium Perborate Fuel Cell (MLSPBFC) is attractive as power sources as they exhibit high efficiency and operate at low temperatures. However, their commercialization is hindered by the high cost of platinum and the slow kinetics of the fuel oxidation reaction. Remarkable efforts have been made to identify alternative electrocatalysts that improve the performance of MLSPBFC significantly while reducing the cost as well. However, it was revealed that electro-oxidation of sodium perborate, in the presence of Pd catalysts was severely poisoned by an adsorbed CO intermediate [1]. The use of palladium as the anode catalyst for the sodium perborate oxidation reaction in membraneless fuel cells offers two significant advantages as compared

with the use of pure Pt [2]. First, Pd shows both a higher catalytic activity and better stability for sodium perborate oxidation than Pt does. Secondly Pd is more abundant than Pt and has a much lower price and thus the cost of fuel cell technology can be greatly reduced. However, there still exists a poisoning effect for the sodium perborate oxidation on the monometallic Pd catalyst, indicating that both the catalytic activity and the stability of Pd for the sodium perborate oxidation need to be enhanced further.

In this regard, the effect of adding another component to Pd on the sodium perborate oxidation reaction has been intensively studied. Recent reports have shown an improved activity for various Pd–based catalysts, such as Pd–Co, Pd–Ni, Pd–Fe, Pd–Au, Pd–Sn, Pd–Ru, Pd–Cu and Pd–Mo compositions [3-6]. Nevertheless, it

is an ongoing task to improve the performance of anode catalysts to a level suitable for commercialization. A great attention has been paid to Ni addition, which is much cheaper and can greatly promote the sodium perborate oxidation on Pd. Recently; ternary electro-catalysts have been proved to be more active than their original mono- and bimetallic counterparts, as the addition of a third component may modify the bifunctional, electronic or structural characteristics of the mono- and bimetallic catalyst surface [7-9]. With this regard, carbon supported ternary Pd–Ir–Ni catalyst was synthesized in the present work for the sodium perborate oxidation reaction and the effect of the addition of Ir, along with Ni to Pd on the sodium perborate oxidation in membraneless fuel cells was examined.

Materials and methods

Materials

The metal precursors used for the preparation of electrocatalysts were adequate amounts of the $Pd(NO_3)_2 \cdot 2H_2O$, Aldrich Chem. Co., $IrCl_3$, Sigma Aldrich, $NiCl_2.6H_2O$, Sigma Aldrich, and $NaBO_3$ (from Riedel) reducing agent. Vulcan XC-72R carbon black (from Cabot Corp.,) was used as a support for the catalysts. Graphite plates (from E-TEK) were used as substrates for the catalyst to prepare the electrodes. Nafion® (DE 521, DuPont USA) dispersion was used to make the catalyst slurry. Sodium perborate (from Riedel) and H_2SO_4 (from Merck) were used as the fuel and as the electrolyte for electrochemical analysis respectively. All the chemicals were of

analytical grade. Pt/C (40-wt%, from E-TEK) was used as the cathode catalyst.

Catalyst preparation

Carbon supported ternary Pd–Ir–Ni nanoparticles were synthesized by ultrasonic assisted chemical reduction method (Wang et al. 2014). First, the required amounts of Vulcan XC-72R carbon black (from Cabot Corp.,) were ultrasonically dispersed in a mixture of ultrapure water (Millipore MilliQ, 18 MΩ cm) and then adequate amounts of the precursors were added to the solution. After mixing the solutions, the metal salts were reduced by $NaBH_4$ [10-13]. The prepared materials were washed with distilled water and dried in a vacuum oven at 70 °C. For comparison, the monometallic Pd/C and bimetallic Pd–Ir/C catalysts were synthesized under the same conditions. The electrocatalytic mixtures and atomic ratios were Pd/C (100), Pd–Ir/C (60:40), Pd–Ir–Ni/C (60:30:10), Pd–Ir–Mo/C (60:30:10) and Pd–Ir–Rh/C (60:30:10). The nominal loading of metals in the electrocatalysts was 40% (w/w) and rest 60% (w/w) was carbon.

Result and discussions

Physical characterization

X-ray Diffraction analysis

The structural information of the Pd–Ir–Ni/C (60:30:10) catalyst was obtained by XRD and is shown in Fig. 1. The first peak located at the 2θ value of about 25° refers to the Vulcan XC-72R carbon black.
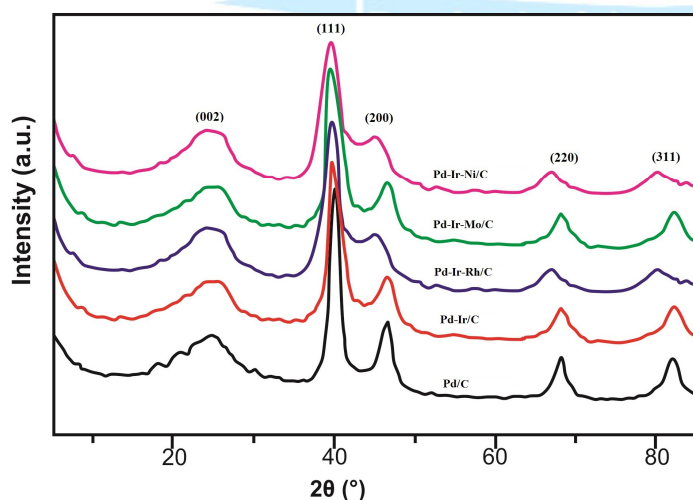
The diffraction peaks at the 2θ values of 40.5°, 47.07°, 67.9°, and 81.90° are assigned to the (111), (200), (220) and (311) facets of the face-centered cubic (fcc) crystalline structure, respectively and these four peaks are located at higher 2θ values with respect to that of pure Pd/C, while at lower 2θ values with respect to that of bimetallic Pd–Ir (60:40) and trimetallic Pd–Ir–Ni/C (60:30:10) catalysts and this can be attributed to the incorporation of a lower d space crystal structure of Ir than that of Pd suggesting the formation of Pd–Ir/C alloy [14-15]. No significant shift is observed for Pd–Ni/C catalysts, which suggests that Pd and Ni do not alloy well with this preparation method. The absence of peaks for either Ir or Ni or its oxides may be due to their poor crystallinity or

Fig. 2. X-ray diffraction patterns of Pd–Ir–Ni/C, Pd–Ir–Mo/C, Pd–Ir–Rh/C, Pd–Ir/C and Pd/C electrocatalysts

low concentration. According to the Scherrer equation, the average crystallite size of the metal particles on the Pd–Ir–Ni/C (60:30:10) catalyst is 4.9 nm. All the lattice parameters obtained from the XRD data are listed in Table 1. It should be noted that the change in the lattice parameters of

all the alloy catalysts is not tremendous and this means the catalysts are not perfectly alloyed. However the small differences in lattice constant may suggest a prominent role of the electrocatalysts for their enhancement in catalytic activity.

Table 1. The EDX composition, XRD and TEM particle size obtained for different atomic ratios of electrocatalysts

Electrocatalyst	Nominal atomic ratio			EDX atomic Ratio			Lattice parameter (nm)	Crystallite size (nm)	Particle size from TEM (nm)
	Pd	Ir	M*	Pd	Ir	M			
Pd/C	100	-	-	99	-	-	0.3894	5.6	5.4
Pd–Ir/C	60	40	-	58	42	-	0.3889	5.4	5.3
Pd–Ir–Rh/C	60	30	10	62	29	09	0.3886	5.3	5.2
Pd–Ir–Mo/C	60	30	10	61	31	08	0.3885	5.1	5.0
Pd–Ir–Ni/C	60	30	10	62	29	09	0.3883	5.0	4.9

(*M = Rh, Mo and Ni)

The average crystallite sizes were calculated from the (2 2 0) plane using a Scherrer equation for Pd/C (100), Pd–Ir/C (60:40), Pd–Ir–Ni/C (60:30:10), Pd–Ir–Mo/C (60:30:10) and Pd–Ir–Rh/C (60:30:10) alloy catalysts. The mean crystallite sizes of the prepared electrocatalysts were shown in Table 1.

Transmission Electron Microscopy analysis

Fig. 2 shows the TEM image and histogram of the metal particle size distribution of the Pd–Ir–Ni/C (60:30:10) catalyst. It can be observed that the metal particles on the Pd–Ir–Ni/C catalyst exhibit a spherical shape and are well dispersed on the carbon powder support without severe aggregation. The metal particle size distribution of the Pd–Ir–Ni/C catalyst was evaluated from an ensemble of 200 particles. Based on this evaluation, the Pd–Ir–Ni/C catalyst shows a metal particle size distribution ranging from 1.5 to 7 nm and the average metal particle size is 4.9 nm, which is almost the same as the value predicted from the XRD data.

Energy Dispersive X-ray Spectroscopy analysis

The composition of carbon-supported Pd–Ir–Ni electrocatalysts was determined by EDX analysis and the corresponding results are shown in Fig. 3. It was found that EDX composition of the prepared catalyst is close to the nominal values which indicate the presence of Pd, Ir and Ni along with carbon.
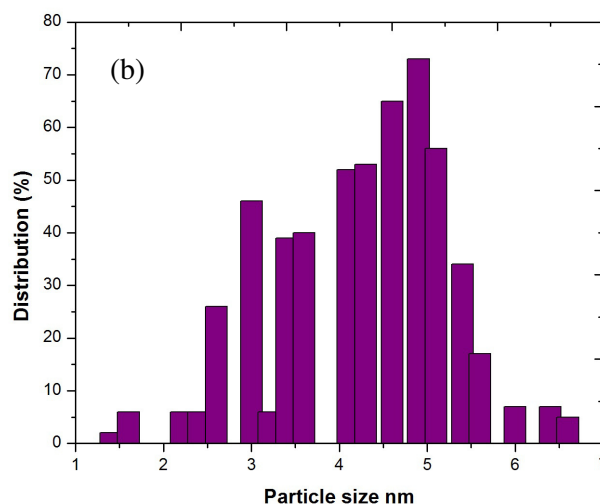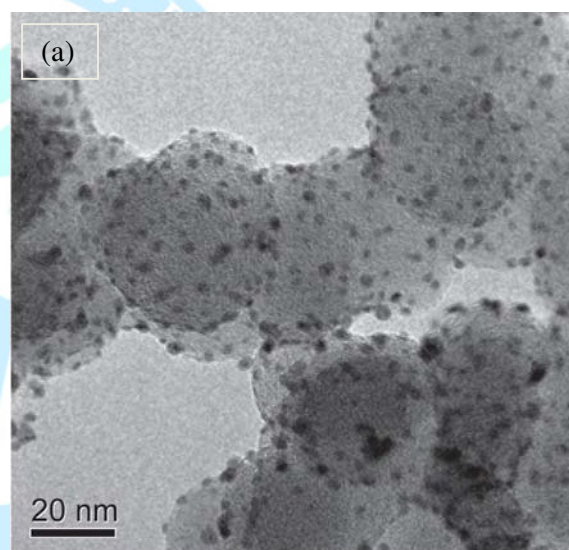

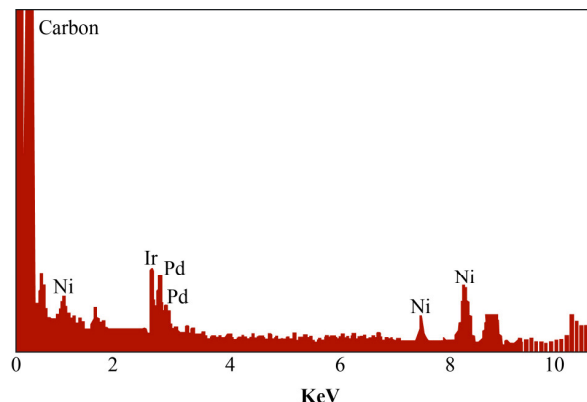Fig. 2. (a) TEM image and (b) histogram of Pd–Ir–Ni/C catalysts

Fig. 3. EDX spectra of Pd–Ir–Ni/C catalysts

is anodic sweep curve and the other one is cathodic sweep curve.
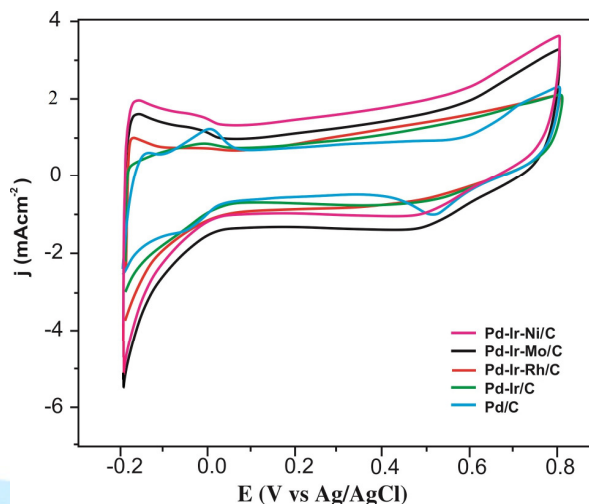

Fig. 4a. Cyclic voltammograms of Pd–Ir–Ni/C (60:30:10), Pd–Ir–Mo/C (60:30:10), Pd–Ir–Rh/C (60:30:10), Pd–Ir/C (60:40) and Pd/C (100) catalysts in 0.5M H_2SO_4

Electrochemical Characterization

Cyclic Voltammetry (CV)

Fig. 4a presents the cyclic voltammograms of 0.5M H_2SO_4 solution at the different catalyst electrodes. The charge–discharge current of the double layer at the Pd–Ir–Ni/C catalyst electrode is largest among all the catalyst electrodes because as mentioned above, the Pd–Ir–Ni/C catalyst possesses the smallest average size of the metal particles and thus the largest surface area among all the catalysts.

Hence Pd–Ir–Ni/C catalyst possesses the excellent ability whereas Pd–Ir/C and Pd/C has the poor ability for the adsorption/desorption of hydrogen, the current densities of the peaks of the adsorption/desorption of hydrogen around 0V are decreased according to the order of the Pd–Ir–Ni/C > Pd–Ir–Mo/C > Pd–Ir–Rh/C > Pd–Ir/C > Pd/C catalysts. These results are similar to the results observed and calculated from XRD data.

The catalytic activity of cyclic voltammetry for sodium perborate electro-oxidation of Pd/C (100), Pd–Ir/C (60:40), Pd–Ir–Ni/C (60:30:10), Pd–Ir–Mo/C (60:30:10) and Pd–Ir–Rh/C (60:30:10) electrocatalysts in 0.5 M H_2SO_4 with 0.15 M sodium perborate solution in the potential range of -0.2 V to 0.8 V vs. Ag/AgCl were shown in Fig. 4b and they are all characterized by two well-defined peaks, the one
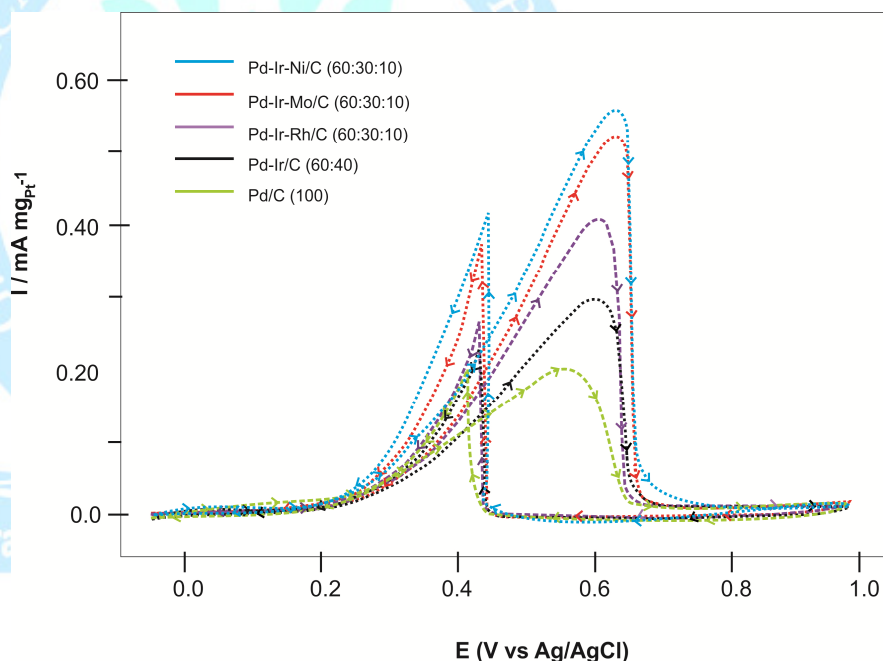

Fig. 4b. Cyclic voltammetry of Pd/C (100), Pd–Ir/C (60:40), Pd–Ir–Ni/C (60:30:10), Pd–Ir–Mo/C (60:30:10) and Pd–Ir–Rh/C (60:30:10) electrocatalysts

The Pd–Ir–Ni/C (60:30:10) exhibited the highest catalytic activity. For comparison, the catalytic activity of Pd/C (100), Pd–Ir/C (60:40), Pd–Ir–Mo/C (60:30:10) and Pd–Ir–Rh/C (60:30:10) catalysts were tested. The onset potential of sodium perborate oxidation for Pd–Ir–Ni/C (60:30:10) catalyst is less negative than those of Pd–Ir–Mo/C, Pd–Ir–Rh/C, Pd–Ir/C and

Pd/C catalysts, indicating good electrocatalytic activity as shown in Table 2.

Table 2. CV results of Pd/C (100), Pd–Ir/C (60:40), Pd-Ir-Rh/C (60:30:10), Pd-Ir-Mo/C (60:30:10) and Pd–Ir–Ni/C (60:30:10) electrocatalysts

Catalyst	Scan rate 50 mVs^{-1}	
	Positive peak potential (V vs. Ag/ AgCl)	Peak current density (mA/cm^2)
Pd/C (100)	0.513	19.3
Pd–Ir/C (60:40)	0.585	29.9
Pd–Ir–Rh/C (60:30:10)	0.589	40.1
Pd–Ir-Mo/C (60:30:10)	0.598	52.3
Pd–Ir-Ni/C (60:30:10)	0.605	55.6

The onset potential of sodium perborate on Pd–Ir–Ni/C (60:30:10) is at 0.605 V which is a factor of 0.1 V negative than that of the Pd/C (100) catalysts. The Pd–Ir–Ni/C (60:30:10) shows highest peak current density at 0.605 V peak potential and hence possesses highest catalytic activity towards sodium perborate oxidation than Pd–Ir-Mo/C (60:30:10), Pd–Ir-Rh/C (60:30:10), Pd–Ir/C (60:40) and Pd/C (100) catalysts indicating that Pd–Ir–Ni/C (60:30:10) is a promising catalyst for sodium perborate electro-oxidation.

Chronoamperometry

Fig. 5 shows the long-term reactivity of sodium perborate oxidation on Pd–Ir–Ni/C (60:30:10), Pd-Ir–Mo/C (60:30:10), Pd-Ir–Rh/C (60:30:10), Pd–Ir/C (60:40) and Pd/C (100) catalysts have been investigated by chronoamperometry (CA) in a 0.15 M sodium perborate + 0.5M H_2SO_4 solution with an applied potential of 0.1 V vs. Ag/AgCl. The durability test was taken for about 3000s. The results clearly show a strong correlation between Pd–Ir–Ni/C contacts and long-term sodium perborate oxidation reaction. During the experiment, there was a sharp decrease in the current density and after 120 s, it becomes relatively stable. This behavior can be explained assuming that initially the active sites are free from adsorbed sodium perborate molecules, but a new adsorption of sodium perborate molecules

is a function of the liberation of the active sites by sodium perborate oxidation.
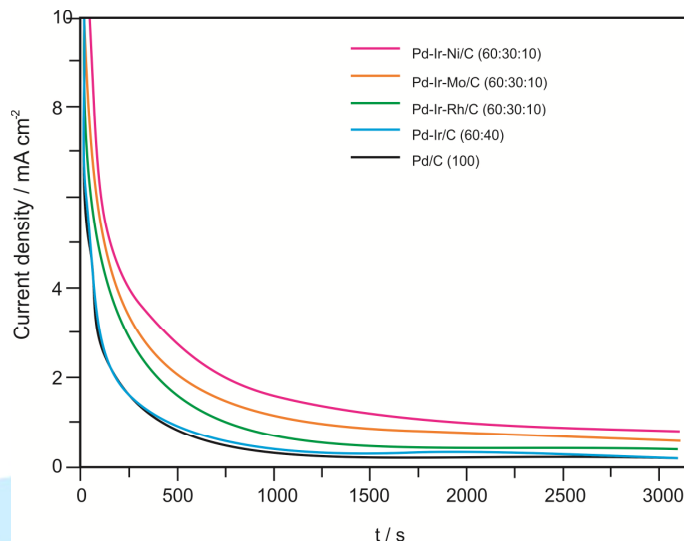

Fig. 5. CA of Pd/C (100), Pd–Ir/C (60:40), Pd–Ir–Ni/C (60:30:10), Pd–Ir–Mo/C (60:30:10) and Pd–Ir–Rh/C (60:30:10) electrocatalysts

The ternary Pd–Ir–Ni/C (60:30:10) electrocatalysts gave higher current than the other electrocatalysts. This is attributed to the change of electronic structure induced by ternary Pd–Ir–Ni/C (60:30:10) electrocatalysts.

Single cell performance test

The microfluidic architecture of laminar flow-based membraneless fuel cells overcomes the fuel crossover and water management issues that plague membrane-based fuel cells (i.e., PEMFC, DMFC) and enables independent control of stream characteristics (i.e., flow-rate and composition). Here we focused on maximizing cell performance, in terms of power density, by tailoring various structural characteristics and catalytic activity of carbon supported ternary Pd–Ir–Ni catalysts. The electrocatalysts Pd–Ir–Ni/C (60:30:10), Pd–Ir–Mo/C (60:30:10), Pd–Ir–Rh/C (60:30:10), Pd–Ir/C (60:40) and Pd/C (100) evaluated as anode catalysts for sodium perborate electro-oxidation were shown in Fig. 6.

The ternary Pd–Ir–Ni/C (60:30:10) anode catalysts shows maximum catalytic activity towards sodium perborate electro-oxidation than the other electrocatalysts tested. It was observed that the cell performance of the ternary Pd–Ir–Ni/C (60:30:10) electrocatalyst was better than the other catalysts with a peak power density value of 34.93 mWcm^{-2}. The addition of Ni into

Pd–Ir/C results in the increases in the cell performances of single membraneless sodium perborate fuel cell test. The current densities for Pd–Ir–Ni/C (60:30:10), Pd–Ir-Mo/C (60:30:10), Pd–Ir-Rh/C (60:30:10), Pd–Ir/C (60:40), and Pd/C (100) were 75.56, 72.42, 63.5, 56.62 and 50.1 $mAcm^{-2}$ respectively. The enhanced catalytic performance of Pd–Ir–Ni/C (60:30:10) may be attributed to its special composition and surface electronic state in electro-oxidation of sodium perborate.
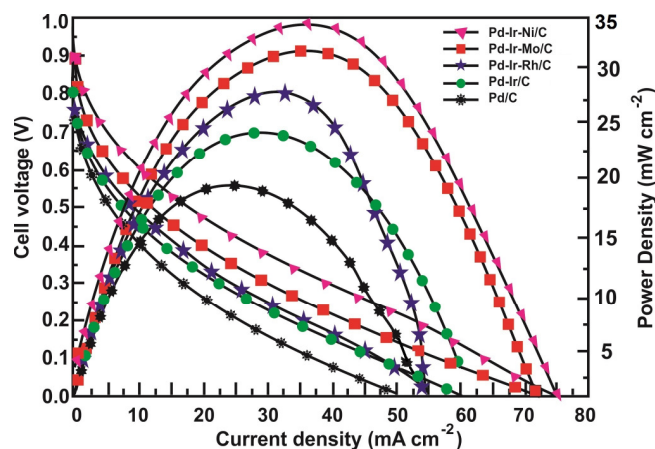

Fig. 6. Polarization and power density curves of different catalyst at 2 mg cm^{-2} catalyst loading on anode and cathode

Conclusions

In conclusion, the Pd–Ir–Ni/C (60:30:10) electrocatalyst with a small average size and low relative crystallinity of the Pd–Ir particles can be synthesized by ultrasonic assisted chemical reduction method at room temperature. When the atomic ratio of Pd, Ir and Ni is suitable the electrocatalytic activity of the Pd–Ir–Ni/C catalyst for the oxidation of sodium perborate is much better than that of the Pd/C catalyst. The onset potential of the anodic peak of sodium perborate at the Pd–Ir–Ni/C catalyst is negative than that of the Pd–Ir–Mo/C, Pd–Ir–Rh/C, Pd–Ir/C and Pd/C catalyst and the peak current density at the Pd–Ir–Ni/C catalyst is much higher than that at the Pd/C catalyst. This is attributed to that Ir can promote the oxidation of sodium perborate at Pd–Ni/C through the direct pathway. However, when the content of Ir in the Pd–Ir–Ni/C catalyst is too high the electrocatalytic activity of the Pd–Ir–Ni/C catalyst would be decreased. It is worth mentioning that these catalysts are less expensive compared to the commercial electrocatalysts.

Conflict of interest

Authors declare there are no conflicts of interest.

References

[1] Bagchi J, Bhattacharya SK. Properties of anodic RuNiOx (OH)y catalysts synthesized on carbon supports with various dispersion degree. Trans Metal Chemistry 32 (2007) 47-55.

[2] Priya M, Elumalai M, Kiruthika S, Muthukumaran B. Influences of supporting materials for Pt-Ru binary catalyst in ethanol fuel cell. International Journal of Modern Science and Technology 1 (2016) 5-11.

[3] He Q, Chen W, Chen S, Laufek F, Mukerjee S. Carbon-supported PdM (M= Au and Sn) nanocatalysts for the electrooxidation of ethanol in high pH media. J Power Sources 187 (2009) 298-304.

[4] Jingrong Yu, Ping Cheng, Zhiqi Ma, Baolian Yi. Fabrication of miniature silicon wafer fuel cells with improved performance. J Power Sources 124 (2003) 40-46.

[5] Ksar F, Ramos L, Keita B, Nadjo L, Beaunier P, Remita H. Bimetallic palladium-gold nanostructures: application in ethanol oxidation. Chem Mater 21 (2009) 3677-3683.

[6] Li X, Huang Q, Zou Z, Xia B, Yang H. Low temperature preparation of carbon-supported Pd Co alloy electrocatalysts for methanol-tolerant oxygen reduction reaction Electrochim Acta 52 (2008) 6662--6667.

[7] Liao S, Holmes KA, Tsaprailis H, Birss VI. High performance PtRuIr catalysts supported on carbon nanotubes for the anodic oxidation of methanol. J Am Chem Soc 128 (2006) 3504-3505.

[8] Qiu CC, Shang R, Xie YF, Bu YR, Li CY, Ma HY. Electrocatalytic activity of bimetallic Pd–Ni thin films towards the oxidation of methanol and ethanol. Mater Chem Phys 120 (2010) 323-330.

[9] Sanchez GR, Madeira HY, Feria OS. PdNi electrocatalyst for oxygen reduction in acid media. Int J Hydrogen Energy 33 (2008) 3596-3600.

[10] Sarkar A, Murugan AV, Manthiram A. Synthesis and characterization of

     262

nanostructured Pd– Mo electrocatalysts for oxygen reduction reaction in fuel cells, J Phys Chem C 112 (2008) 12037-12043.

[11] Shao MH, Sasaki K, Adzic RR. Pd-Fe nanoparticles as electrocatalysts for oxygen reduction. J Am Chem Soc 128 (2006) 3526-3527.

[12] Stamenkovic V, Moon BS, Mayerhofer KJ, Ross PN, Markovic N, Rossmeisl J, Greeley J, Norskov JK. Changing the activity of electrocatalysts for oxygen reduction by tuning the surface electronic structure. Angew Chem Int Ed 45 (2006) 2897-2901.

[13] Wang YH, Chen TH. A high dispersed $Pt_{0.35}$ $Pd_{0.35}$ $Co_{0.30}$/C as superior catalyst for methanol and formic acid electro-oxidation. Chin Chem Letters 25 (2014) 907-911.

[14] Xu JB, Zhao TS, Shen SY, Li YS. Stabilization of the palladium electrocatalyst with alloyed gold for ethanol oxidation. Int J Hydrogen Energy 35 (2010) 6490-6500.

[15] Zhu LD, Zhao TS, Xu JB, Liang ZX. Preparation and characterization of carbon-supported sub-monolayer palladium decorated gold nanoparticles for the electro-oxidation of ethanol in alkaline media. J Power Sources 187 (2009) 80-84.

*****