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Short Communication

Direct ammonia fuel cell performance using PtIr/C as anode electrocatalysts

*Mônica H.M.T. Assumpção, Sirlane G. da Silva, Rodrigo F.B. de Souza, Guilherme S. Buzzo, Estevam V. Spinacé, Almir O. Neto, Júlio César M. Silva**

Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP, Av. Prof. Lineu Prestes, 2242 Cidade Universitária, CEP 05508-900 São Paulo, SP, Brazil

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ABSTRACT

Direct ammonia fuel cell (DAFC) performance was investigated using as anode PtIr/C electrocatalysts (Pt:Ir atomic ratios of 50:50, 70:30, 80:20 and 90:10) prepared by the borohydride reduction process and NH_4OH 1.0, 3.0 and 5.0 mol L^{-1} in KOH 1.0 mol L^{-1} as fuel. X-ray analyses of PtIr/C electrocatalysts suggested the formation of PtIr alloy and the transmission electron micrographs showed the average particle diameters between 4.5 and 6.0 nm. Using PtIr/C 50:50 electrocatalyst and NH_4OH 5.0 mol L^{-1} in KOH 1.0 mol L^{-1} at 40 °C a maximum power density was 48% and 70% higher than that obtained using Pt/C and Ir/C electrocatalysts, respectively. The increase of electroactivity using PtIr/C electrocatalysts might be related to a decrease of poisoning on catalyst surface by N_{ads} species and to an improved kinetic for ammonia oxidation reaction.

1. Introduction

Ammonia has been considered as a potential fuel for alkaline fuel cells since ammonia has low production cost, is easily to handle and to transport as liquid or as concentrated aqueous solution and is easy in liquefaction at ambient temperature [1,2]. Moreover, the theoretical charge for ammonia oxidation to N_2 is 4.75 Ah g^{-1} that compares very well with the theoretical charge of methanol in its oxidation to CO_2 5.02 Ah g^{-1} [2]. Furthermore, liquid ammonia has 70% more hydrogen content and 50% higher specific energy density than liquid hydrogen per unit volume [3]. However, the main drawback of ammonia is its toxicity, but it is self alarming and any leakage can be detected by nose in concentrations as low as 5 ppm, and due to its lower density than the air if escapes into the atmosphere ammonia dissipates rapidly [4].

The studies about ammonia electro-oxidation have been increasing in the last years, and good articles have been published [3,5–7]. To improve the ammonia oxidation reaction at low temperature, efficient catalysts are required and for this proposed, Pt-group metals show promising catalytic activity [3]. Considering this process, Pt is the most active catalyst [8], but it is expensive and easily poisoning by N_{ads} species [5]. Lomocso and Baranova [5] studied by electrochemical techniques (cyclic voltammetry and chronoamperommetry) the

* *Corresponding author*. Tel.: +55 11 3133 9284; fax: +55 11 3133 9285.
E-mail addresses: quimijulio@gmail.com, quimijulio@yahoo.com.br (J.C.M. Silva).
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electro-oxidation of ammonia using different concentrations in KOH 1 mol L^{-1} over Pt/C, PtIr/C, PtPd/C and $PtSnO_2$/C and reported that PtIr/C as promising material due to the good catalytic activity and enhanced stability for ammonia electro-oxidation. Another important point of using Ir electrode is that it has lower overpotential of ammonia oxidation (0.35 V *vs.* RHE) than Pt (0.43 V *vs.* RHE) in 0.1 mol L^{-1} NH_3 and 1 mol L^{-1} KOH [3]. Zhong et al. [7] published recently a review concerning the electrocatalysts for ammonia electro-oxidation and according to the authors Ir is able to dehydrogenate ammonia at lower potential than Pt. Furthermore, Ir is about 35% cheaper than Pt [9].

Recently Suzuki et al. [1] reported a studied of a DAFC using Pt/C, Ru/C and PtRu/C as anode electrocatalysts, and it was shown that the open circuit voltage (OCV) is dependent on the catalysts compositions, it has been achieved 0.54 V for PtRu/C, 0.37 V for Pt/C and 0.08 V for Ru/C, values below theoretical of 1.17 V. Lan and Tao [10] also reported the results of a DAFC, and from this study it was demonstrated that the better results was obtained using NH_4OH aqueous solution compared to NH_3 gas. However, considering the DAFCs works cited above, no systematic investigation was made in order to study different electrocatalysts compositions and ammonia concentrations. Taking in account the DAFCs development, the optimization of these parameters is extremely relevant.

Aiming the development of DAFCs the present study describes not only the investigation of different compositions of PtIr/C as anode electrocatalysts but also different NH_4OH concentrations in KOH 1 mol L^{-1} as a fuel. For comparison, commercial Pt/C from BASF and Ir/C were also evaluated.

2. Experimental

PtIr/C electrocatalyts (20 wt% of metals loading) with Pt:Ir atomic ratios of 50:50, 70:30, 80:20 and 90:10 and Ir/C (20 wt% metal loading) were prepared by the borohydride reduction process [11,12] using $H_2PtCl_6 \cdot 6H_2O$ 37.5% (Sigma–Aldrich) and $IrCl_3$ 99.8% (Sigma–Aldrich), as metal source. In this process Vulcan XC72 was firstly dispersed in an isopropyl alcohol/water solution (50/50, v/v). The mixture was homogenized under stirring and then the metals sources were added and put on an ultrasonic bath for 5 min. After that, a solution of $NaBH_4$ in 0.1 mol L^{-1} KOH was added in one portion under stirring at room temperature and the resulting solution was maintained under stirring for 15 min more. After this, the final mixture was filtered and the solids washed with water and then dried at 70 °C for 2 h.

The electrocatalysts were characterized by X-ray diffraction (XRD) using a Rigaku diffractometer model Miniflex II using Cu Kα radiation source (0.15406 nm). The X-ray diffraction patterns were recorded in the range of $2\theta = 20°–85°$ with a step size of 0.05° and a scan time of 2 s per step. The atomic ratios of Pt and Ir in the synthesized materials were measured by energy dispersive spectroscopy (EDS) by using a JEOL – JSM6010 LA equipment.

Transmission electron microscopy (TEM) images were also carried out using a JEOL transmission electron microscope model JEM-2100 operated at 200 kV in order to obtain the morphology, distribution and nanoparticles size which were determined by counting about 100 particles at different regions of the different electrocatalysts [13].

The DAFCs experiments took placed in a single cell with an area of 5 cm^2. The temperature was set to 40 °C for the fuel cell and 85 °C for the oxygen humidifier. All electrodes contained 1 mg of Pt per cm^2 in the anode or in the cathode excepted for Ir/C which contained 1 mg of Ir per cm^2. In all experiments commercial Pt/C from BASF was used in the cathode. The electrocatalyst was painted over carbon cloth in the form of a homogeneous dispersion prepared using Nafion® solution (5 wt%, Aldrich). After the preparation, the electrodes were hot pressed on both sides of a Nafion® 117 membrane at 125 °C for 3 min under a pressure of 247 kgf cm^{-2}. Prior to use, the membranes were exposed to KOH 6 mol L^{-1} for 24 h, this procedure was based on Hou et al. article [14]. The fuels, 1.0, 3.0 and 5.0 mol L^{-1} NH_4OH in 1.0 mol L^{-1} KOH, were delivered at 2.0 mL min^{-1}, and the oxygen flow was regulated at 150 mL min^{-1}. Polarization curves were obtained by using a potentiostat/galvanostat PGSTAT 302NAutolab.

3. Results and discussion

Fig. 1 shows the XRD patterns for PtIr/C and Ir/C catalysts. In this Figure, it can be observed that all catalysts have a peak around $2\theta = 25°$, which is attributed to the hexagonal structure (002) of Vulcan Carbon XC-72 [5]. The face-centered cubic systems of Pt and Ir can be seen by the peaks at approximately $2\theta = 39°$, 46°, 67° and 81° [15]. In all XRD patterns were not observed the peaks characteristic of IrO_2 at $2\theta = 34.5°$ and 54° [16] suggesting the alloying of PtIr for binary catalysts. Another evidence of PtIr alloy formation is that the positions of (220) crystalline plane is shifted to high 2θ values (67.7°) [5] compared to Pt ($2\theta = 67°$) [15]. The mean crystallite sizes were estimated by Scherrer's equation using the (220) peak [5,16]. The values were 5.1 nm for PtIr/C 90:10, 5.0 nm for PtIr/C 80:20, 5.4 nm for PtIr/C 70:30 and 4.8 nm for PtIr/C 50:50. The experimental compositions of all PtIr/C materials using the EDS analysis were 89:11 (nominal 90:10), 79:21 (nominal 80:20), 68:32 (nominal 70:30), 53:47 (nominal 50:50). As can be seen the percentage of each metal is close to nominal values in all cases.

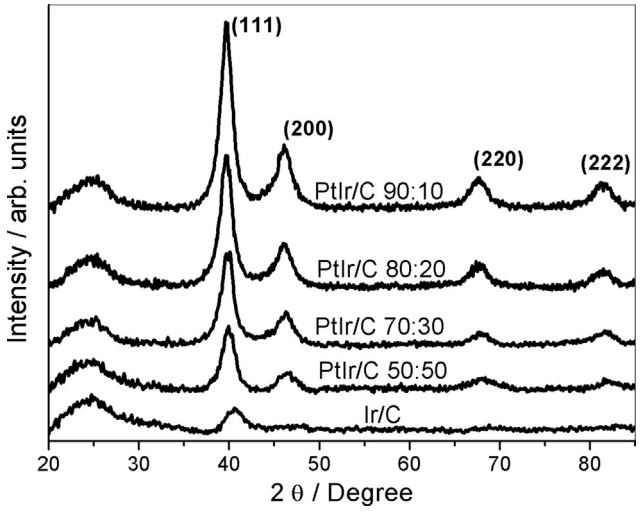

Fig. 1 – X-ray diffraction patterns for the Ir/C and PtIr/C electrocatalysts.

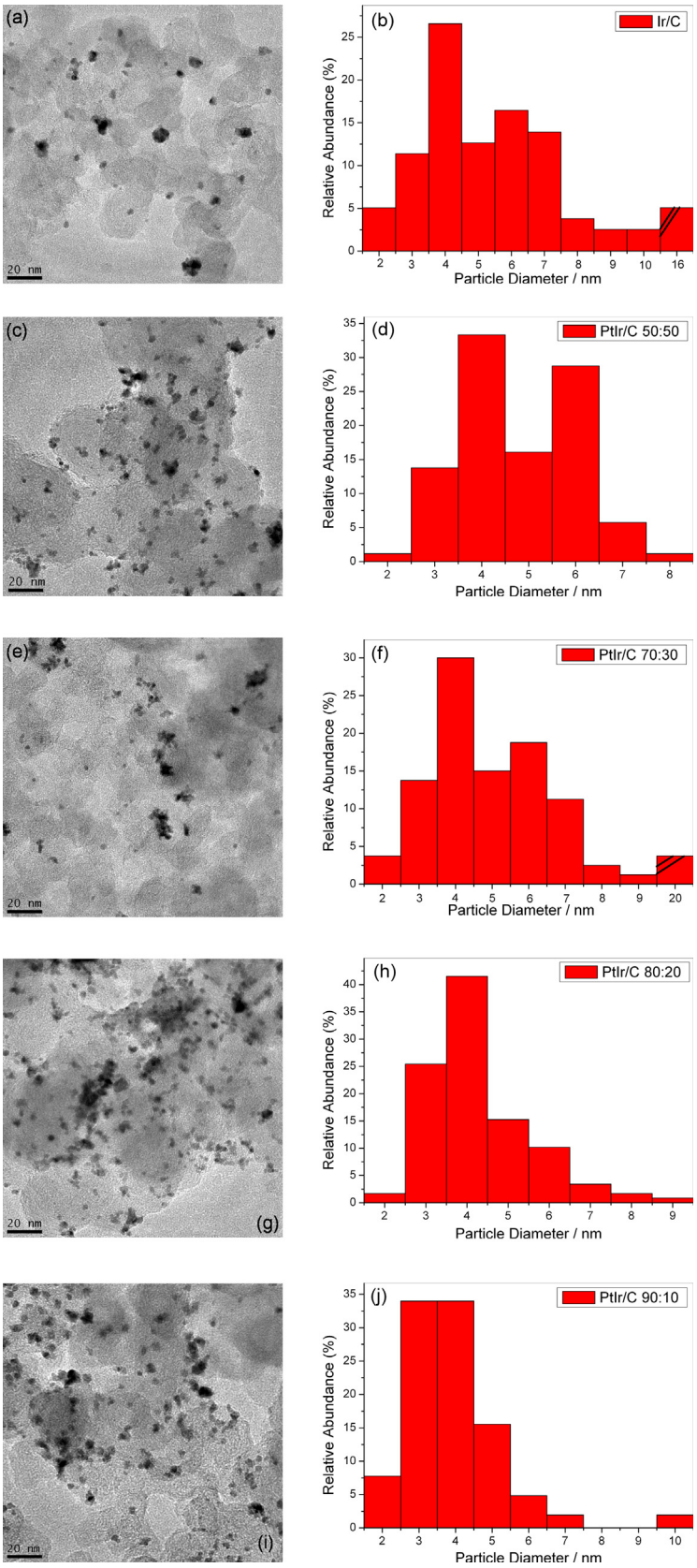

Fig. 2 – The TEM micrographs a, c, e, g and i corresponds to Ir/C, PtIr/C 50:50, PtIr/C 70:30, PtIr/C 80:20 and PtIr/C 90:10 respectively. The histograms are on the right side of the respective micrographs.

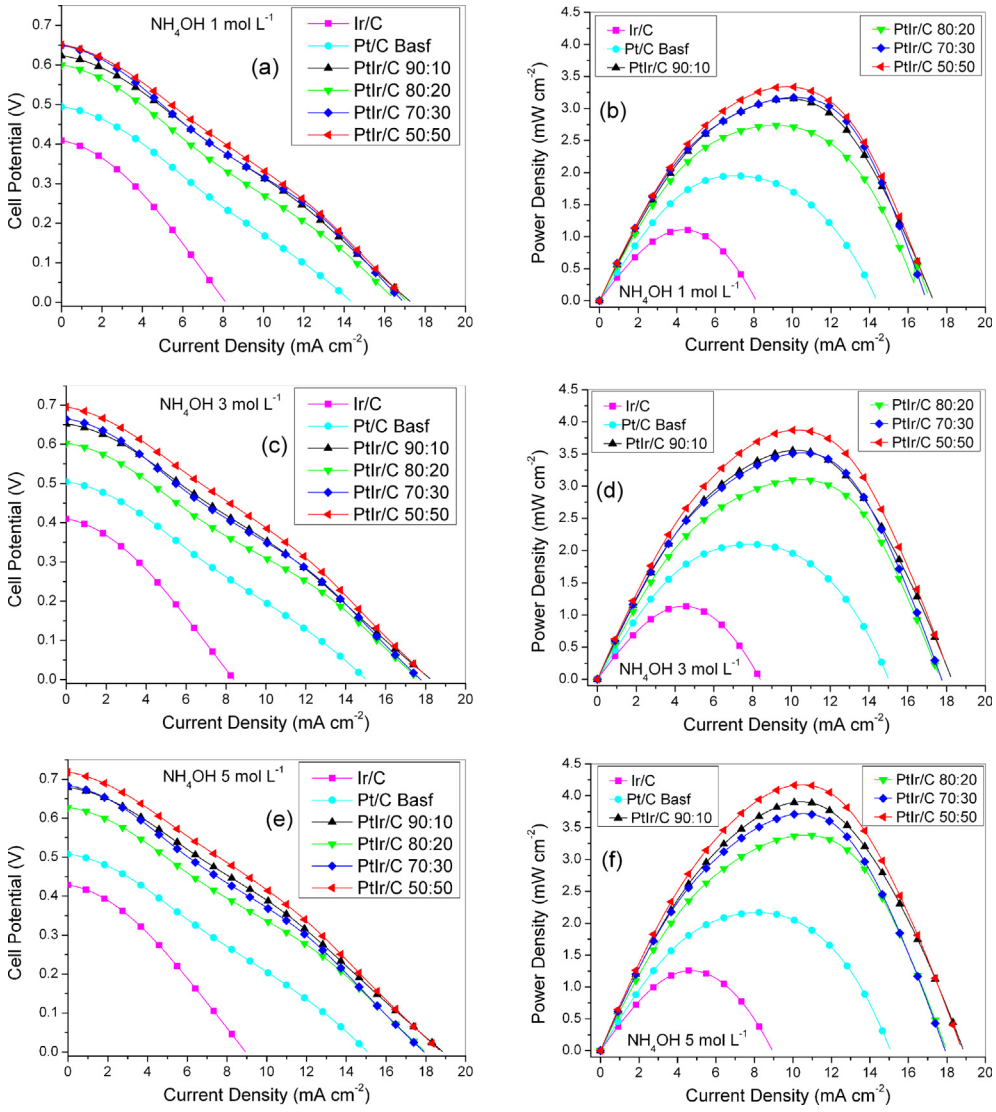

Fig. 3 – Polarization and power density curves of a 5 cm^2 DAFC at 40 °C. (a) and (b) using NH_4OH 1.0 mol L^{-1}. (c) and (d) using NH_4OH 3.0 mol L^{-1}.(e) and (f) using NH_4OH 5.0 (both in KOH 1 mol L^{-1}). Ir/C (1 mg Ir cm^{-2}), Pt/C BASF and PtIr/C (1 mg Pt cm^{-2}) compositions used as anode, for cathode in all experiments was used Pt/C BASF (1 mg Pt cm^{-2}).

Representative TEM micrographs and histograms of particle mean diameter distribution for the binary catalysts of PtIr/C and Ir/C are shown in Fig. 2a–h. In both cases the particles were well dispersed on the carbon support, although some small particle agglomerations can be seen on PtIr/C 70:30 (Fig. 2e) and on PtIr/C 80:20 (Fig. 2g). The particles are with average diameter of 6.0 nm for Ir/C, 5.3 nm for PtIr/C (50:50), 5.7 nm for PtIr/C (70:30), 4.8 nm for PtIr/C (80:20) and 4.5 nm for PtIr/C (90:10). Only Ir/C and PtIr/C 70:30 showed a small percentage of particles higher than 10 nm, with a maximum mean diameter of 20 nm and 16 nm, respectively.

Table 1 – The main results of the DAFC experiments.

Catalyst	NH_4OH 1 mol L^{-1}		NH_4OH 3 mol L^{-1}		NH_4OH 5 mol L^{-1}	
	OCV/V	P_{max}/mW cm^{-2}	OCV/V	P_{max}/mW cm^{-2}	OCV/V	P_{max}/mW cm^{-2}
Ir/C	0.408	1.11	0.408	1.32	0.429	1.25
Pt/C	0.493	1.95	0.504	2.09	0.506	2.17
PtIr/C 90:10	0.623	3.15	0.651	3.55	0.677	3.90
PtIr/C 80:20	0.600	2.75	0.603	3.11	0.628	3.37
PtIr/C 70:30	0.650	3.16	0.664	3.52	0.683	3.71
PtIr/C 50:50	0.650	3.34	0.695	3.87	0.716	4.17

Fig. 3 shows the polarization and power density curves for 1.0, 3.0 and 5.0 NH_4OH mol L^{-1} in KOH 1 mol L^{-1} using Pt/C BASF, Ir/C and PtIr/C catalysts as anode in a DAFC operated at 40 °C, and Pt/C BASF as cathode in all experiments. The performance of each catalyst was improved as NH_4OH concentration increases, except for Ir/C (see Table 1). It is possible to be observed that using PtIr/C 50:50 the results are slightly higher when compared with the other PtIr/C compositions, and when compared to Pt/C the maximum current was between 42% and 48% higher for all the NH_4OH concentrations used. When the same comparison was made with Ir/C these values are between 66% and 70%.

It is also can be seen from Fig. 3 that the highest OCV (0.716 V) was obtained using PtIr/C 50:50 and NH_4OH 5 mol L^{-1}, which is significantly higher when compared to those obtained for Ir/C (0.429 V) and Pt/C (0.506 V) in the same NH_4OH concentration (see Table 1). This difference in OCV reflects the catalytic activity of each catalyst for NH_4OH oxidation [1].

The better results obtained using PtIr/C binary composition compared to Pt/C and Ir/C might be associated with the effect generated between Pt and Ir in close contact (alloy), since the upon contact of two metals of different work functions charge will be transported from one metal to another until the Fermi level of electrons at the interface is equilibrated (electronic effect) [5]. This phenomenon might cause a decrease of poisoning on catalyst surface by N_{ads} species facilitating the ammonia oxidation [5]. Furthermore, ammonia overpotential on Ir is lower than on Pt, and the bimetallic PtIr improves the kinetics of ammonia oxidation when compared to pure Pt [3].

The OCV values obtained in our experiments for PtIr/C compositions and Pt/C are higher than those obtained for Suzuki et al. [1] (0.54 V for PtRu/C and 0.37 V for Pt/C), however, the condition experiments are quite different, the experiments of Suzuki et al. [1] were carried out at 50 °C using NH_3 gas and different metal loading from that used in our experiments. In fact, a comparison with similar work is difficult, because of the different physicochemical properties presented by the catalysts used in such studies and different experimental conditions.

4. Conclusions

PtIr/C showed an improved performance as anode electrocatalyst for DAFC when compared to Pt/C and Ir/C electrocatalysts. The maximum power density and OCV were obtained using a Pt:Ir atomic ratio of 50:50 and 5.0 mol L^{-1} NH_4OH in KOH 1.0 mol L^{-1} as fuel. The increase of activity of PtIr/C electrocatalysts may be associated to the electronic effect between Pt and Ir that might cause a decrease of poisoning on catalyst surface by N_{ads} species and to an improved kinetic for ammonia oxidation reaction.

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