Effect of pH in a Pd-based ethanol membraneless air breathing nanofluidic fuel cell with flow-through electrodes

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Abstract. In this work, a nanofluidic fuel cell (NFC) in which streams flow through electrodes was used to investigate the role of pH in the cell performance using ethanol as fuel and two Pd nanoparticles as electrocatalysts: one commercially available (Pd/C from ETEK) and other synthesized using ionic liquids (Pd/C IL). The cell performances for both electrocatalysts in acid/acid (anodic/cathodic) streams were of 18.05 and 9.55 mW cm^{-2} for Pd/C ETEK and Pd/C IL. In alkaline/alkaline streams, decrease to 15.94 mW cm^{-2} for Pd/C ETEK and increase to 15.37 mW cm^{-2} for Pd/C IL. In alkaline/acidic streams both electrocatalysts showed similar cell voltages (up to 1 V); meanwhile power densities were of 87.6 and 99.4 mW cm^{-2} for Pd/C ETEK and Pd/C IL. The raise in cell performance can be related to a decrease in activation losses, the combined used of alkaline and acidic streams and these high values compared with flow-over fuel cells can be related to the enhancement of the cathodic mass transport by using three dimensional porous electrodes and two sources of oxygen: from air and from a saturated solution.

1. Introduction

Membraneless microfluidic fuel cells (MMFCs), are a type of fuel cells which operate with both, liquid fuel and oxidant under a co-laminar regime, flowing tangentially, and forming a natural interface between them. This interface carry out a similar function than typical exchange ion membranes. [1] The advantages of these MMFCs over traditional fuel cells are therefore, a decrease of ohmic losses because the absence of a physical barrier, the possibility to mix electrolytic solutions of different pH, [2] and the advantages of usage of all kind of liquid fuels (i.e. methanol, ethanol, glycerol, vanadium, glucose, etc.) and oxidants (hydrogen peroxide, potassium permanganate). [3] Thermodynamically, the ethanol electro-oxidation reaction occurs at 0.09 V *vs*. NHE in an acidic pH and at -0.74 V in alkaline pH [4]. Moreover, the oxygen reduction reaction in acidic and alkaline take place at 1.23 and 0.4 V *vs*. NHE,

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respectively. Their use in a fuel cell as fuel and oxidant can thermodynamically result, in cell voltages from 1.17 V to 2 V.

Some features to improve in MMFCs are as well as in fuel cells, the synthesis of highly active electrocatalysts, development of supports with high surface area, and the decrease of mass transport limitations [5]. For the synthesis of electrocatalysts, the use of ionic liquids as "all-in-one" reaction medium: solvent, reducing and stabilizer agent, can allow to obtain nanoparticles by a clean pathway [6] and they could follow most of the twelve principles of green chemistry [7]. Which combined with the clean technology of membraneless micro/nanofluidic fuel cells, can be an attractive green solution to supply energy requirements of small devices. In this work, Pd/C nanoparticles from a commercially available source (ETEK) as well as synthesized using an "all-in-one" ionic liquid, were used as anodic electrocatalysts in a membraneless nanofluidic fuel cell (MNFC). This novel MNFC operates using three dimensional flow-through electrodes, and combines two sources of oxygen: from air and from an saturated aqueous electrolyte. The aim of this work, was to evaluate -for the first time- the effect of changing the nature of the electrolyte (in terms of pH) in the cell performance (voltage, current density and power density) using two different anodic electrocatalysts.

2. Experimental

2.1. Synthesis of Pd/C

Pd/C nanoparticles were easily synthesized using 2-hydroxy ethylammonium formate ionic liquid as a green chemistry "all-in-one" solvent. Briefly, 50 mg of Na_2PdCl_4 (Sigma-Aldrich, 98%) were dissolved in the ionic liquid and sonicated by 10 minutes. It is important to denote, that a dark color was observed 3 minutes after the addition of the metallic salt precursor. After that, 150 mg of Vulcan carbon (XC-72, Cabot®) were added and the sonication was retained another 30 minutes. The mixture was preserved under refrigeration (at -20°C) for 24 h to ensure a complete reaction. Finally, the solution was centrifuged at 4000 rpm for 30 minutes and the resulting powder was washed several times with deionized water.

2.2. Membraneless nanofluidic fuel cell operation.

Pd/C ETEK and Pd/C IL were deposited on carbon nanofoam by spray coating as well as Pt/C (ETEK, 30 wt. %) used as the cathodic electrocatalyst, maintaining a total mass content of 0.3 mg of electrocatalyst. The membraneless nanofluidic fuel cell (Fig. 1) was patterned and fabricated using a computer numerical control, and was composed of i) two plates of poly-methyl methacrylate (PMMA, Fig. 1b). ii) A silicone-based film (Silastic®) which acted not only as gasket but also as pattern to place the porous electrodes (Fig. 1a). And iii) the carbon nanofoam (Marketech® International Inc.) slides as three dimensional electrodes. The geometrical area of electrodes was of 0.015 cm^2.

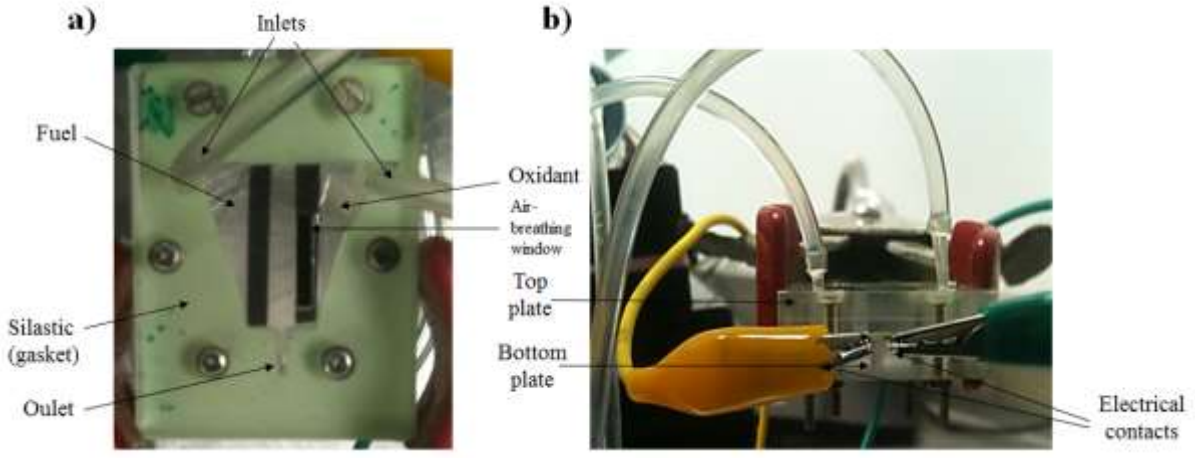


Figure 1. Components of the membraneless nanofluidic fuel cell

The cell design herein presented take advantage of the high surface area of carbon nanofoam (450 $m^2\ g^{-1}$) in order to enhance the electrocatalytic activity. Ethanol (Denatured, 96%, J.T. Baker) was used as fuel at three concentrations: 0.5, 1 and 1.5 M and an oxygen-saturated solution (4.3 U.A.P. Praxair) combined with oxygen from air was used as oxidant (open window of 0.22 cm^2). Both streams were prepared using 0.3 M KOH (87%, J.T. Baker) as the electrolyte for an alkaline fuel cell and 0.5 M H_2SO_4 (98.5%, J.T. Baker) for the acidic fuel cell. Also, an alkaline anodic stream and an acidic cathodic stream were combined. The streams were pressure-driven using a Harvard apparatus syringe pump (PHD Ultra Syringe Pump).

3. Results and discussion

X-ray diffraction patterns are shown in Figure 2a. The (111), (200), (220), (311) and (222) crystallographic planes were identified in both, Pd/C ETEK and Pd/C IL, and are characteristics of a face-centred cubic structure. Crystallite sizes were determined using the Scherrer´s equation and lattice parameters applying the Bragg's law (Table 1). Average crystallite sizes were of 8.5 and 4.5 nm for Pd/C IL and ETEK, respectively.

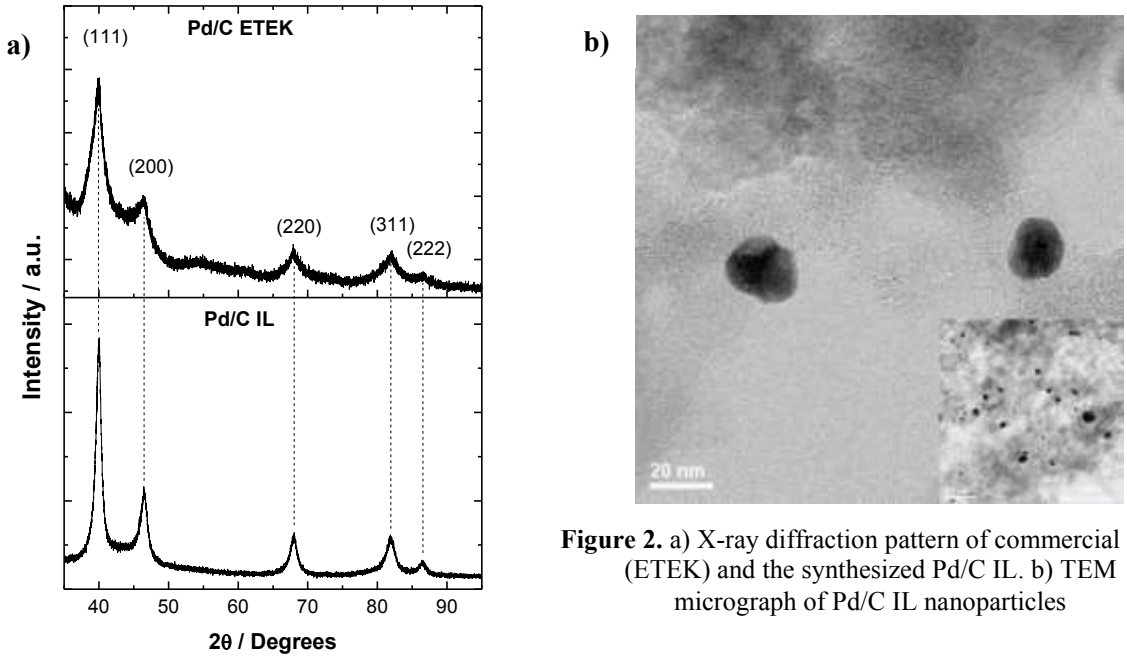


Figure 2. a) X-ray diffraction pattern of commercial Pd/C (ETEK) and the synthesized Pd/C IL. b) TEM micrograph of Pd/C IL nanoparticles

TEM micrographs of the synthesized Pd/C nanoparticles through the "all-in-one" 2-hydroxy ethylammonium formate ionic liquid are shown in Fig. 2b. Particles with sizes of 22 nm were found. Agglomeration of particles also occurred as a consequence of a weak stabilization by the ionic liquid. This could be related to the multiple tasks that the ionic liquid plays, reducing its capability to reduce and stabilize at the same time. TEM image of Pd/C ETEK can be found elsewhere [8].

Table 1. Summary of crystallite sizes, particles sizes, and mass content determined by XRD, TEM and TGA, respectively.

Material	Crystallite size		Lattice parameter (Å)	Particle size (nm)	Mass content / (%wt.)
	Plane	Size (nm)			
Pd/C (IL)	(111)	9.678	3.9024	22	74% XC-72
	(200)	8.524			
	(220)	7.636			26% Pd
	(311)	8.022			
Pd/C (ETEK)	(111)	4.098	3.8918	6	70% XC-72
	(200)	5.635			
	(220)	4.326			30% Pd
	(311)	3.902			

An analysis of effect of ethanol concentration was made in the three fuel cell configurations (alkaline, acidic, and alkaline anodic stream/acidic cathodic stream). For space purposes, in Figure 3 only results for Pd/C IL and Pd/C ETEK in the alkaline NFC are shown. The higher cell performances (1.5 M ethanol) in each fuel cell configuration are summarized in Figure 5.

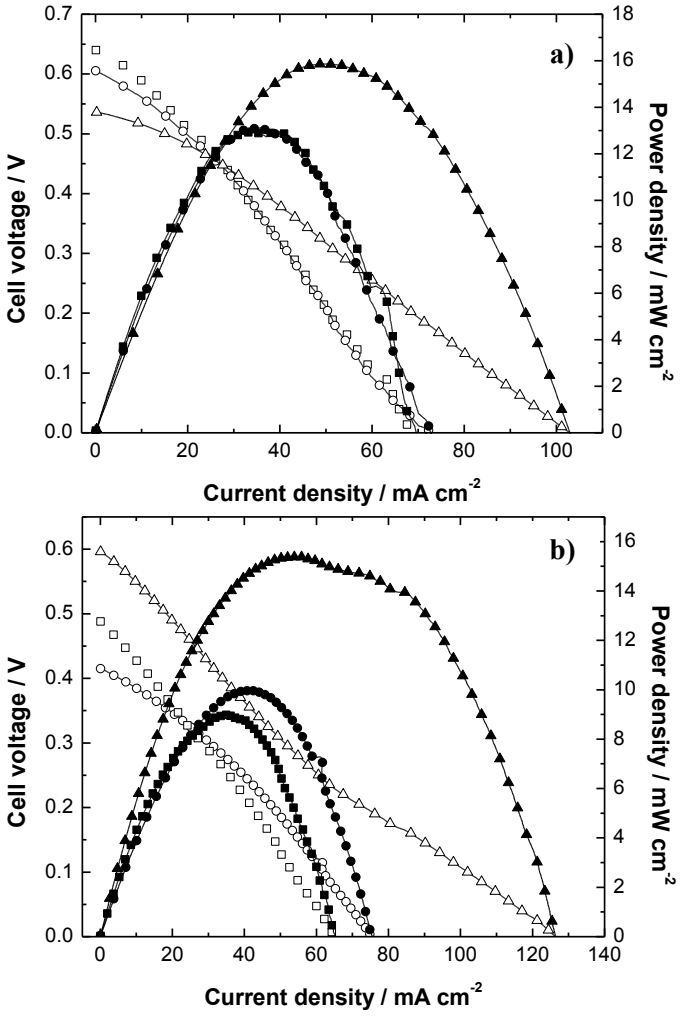


Figure 3. Polarization and performance curves for a) Pd/C ETEK and b) Pd IL as function of concentration 0.5 (squares), 1 (circles) and 1.5 M (triangles) in an alkaline ethanol NFC

Pd/C ETEK showed better performance at 0.5 M ethanol (Fig. 3a). However, Pd/C IL improved its performance with the increase in the ethanol concentration (Fig. 3b). The higher performance was achieve using Pd/C IL with 1.5 M ethanol showing a cell voltage of 0.6 V, a current density of 126 mA cm^{-2} and a power density of 15.4 mW cm^{-2} (Fig. 3b, triangles). The cell performance of a complete alkaline nanofluidic fuel cell (NFC) is showed in Figure 4a. The results obtained for the acidic NFC are showed in Figure 4b and the combined NFC in Figure 4c. It was observed from figures 5a and 5b that these materials showed different behaviour in both, alkaline and acidic medium. Pd/C IL showed better performance in alkaline than in acidic and could be related to the enhancement of reaction kinetics at higher pH [1]. On the other hand, Pd/C ETEK showed similar performances in alkaline and acidic media. In the combined MNFC, the use of alkaline anodic stream and the acidic cathodic stream resulted in cell voltages of 1.11 and 1.03 V for Pd/C ETEK and Pd/C IL. Furthermore, this combination enhanced the power density, obtaining values of 87.66 and 99.42 mW cm^{-2}, respectively.

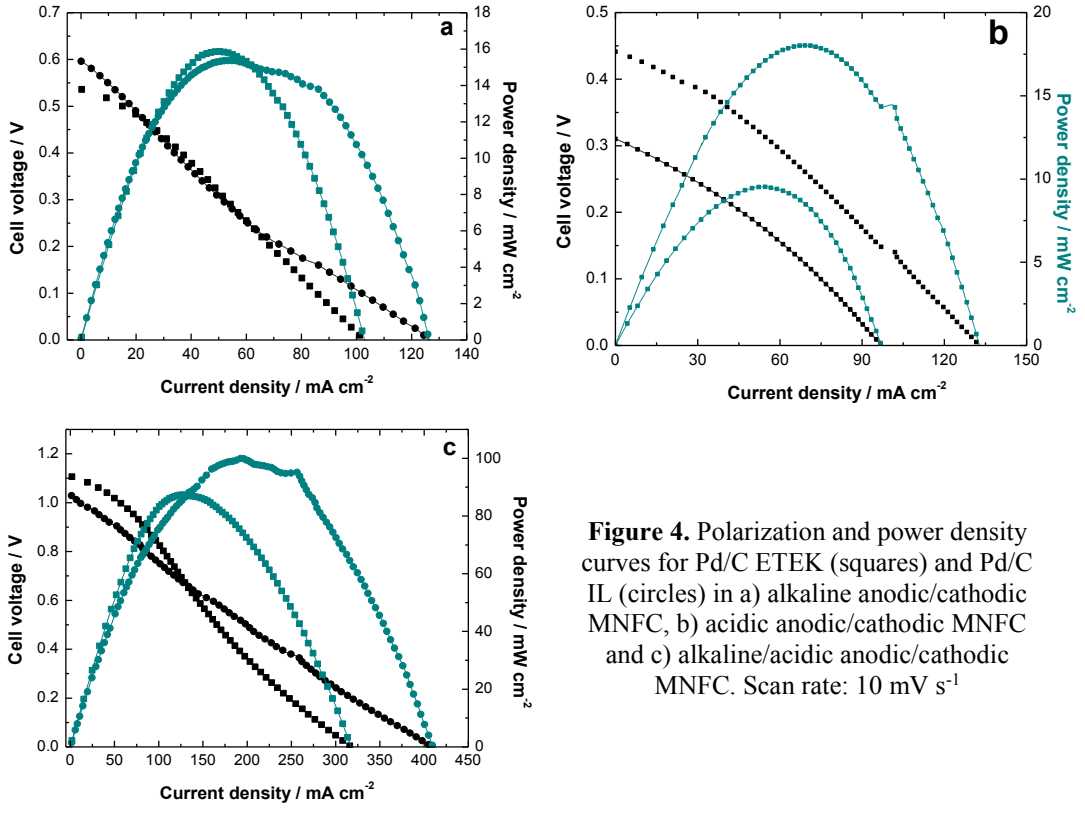


Figure 4. Polarization and power density curves for Pd/C ETEK (squares) and Pd/C IL (circles) in a) alkaline anodic/cathodic MNFC, b) acidic anodic/cathodic MNFC and c) alkaline/acidic anodic/cathodic MNFC. Scan rate: 10 mV s^{-1}

4. Conclusions

Commercial Pd/C and Pd/C synthesized using ionic liquids were successfully used as electrocatalysts in a nanofluidic fuel cell with flow through electrodes. Pd/C IL showed better activity in an alkaline environment showing higher performance in alkaline than in the acidic MNFC because of an enhancement of the ethanol reaction kinetic at high pH. The MNFC which employed commercial Pd/C showed no significant change with changes in pH. The mix of streams alkaline (anode)/acidic (cathode) resulted in power densities up to 4-fold higher than using equal electrolytes. This can be related to the mobility of protons produced in the anode toward the cathode and their further reduction forming multiple oxidant species (oxygen from the saturated aqueous solution, from air and protons). The use of ionic liquids as a reaction medium resulted in a Pd/C material which showed a higher cell performance than commercial Pd/C in the mixed streams despite that it has a particle size almost 3-fold bigger.

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