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High performance of ethanol co-laminar flow fuel cells based on acrylic, paper and Pd-NiO as anodic catalyst



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ABSTRACT

Ethanol co-laminar flow fuel cells operating at room temperature have rarely been reported, primarily due to problems associated with the kinetics of ethanol oxidation. In this work, we present a study of the effect of ethanol concentration, pH of anodic and cathodic streams, and nature of the oxidant on the performances of an acrylic cell and a paper-based, membraneless co-laminar flow fuel cell (LFFC), with total cell volumes of 14.29 cm³ and 0.62 cm³, respectively. Additionally, this work reports the synthesis of a Pd-NiO anodic nanocatalyst by a simple, fast, and environmentally friendly method in order to match the clean, easy-to-use, and simple fabrication methods of these ethanol co-laminar flow fuel cells. The synthesized Pd-NiO exhibited a crystallite size of 8.1 nm and an average particle size of 8.7 nm for Pd-NiO/C. The highest performances were obtained by combining an alkaline anodic stream with an acidic cathodic stream, increasing the cell voltage, and decreasing cathodic limitations caused by the simultaneous occurrence of oxygen reduction as well as hydrogen reduction reactions. With these improvements, power densities of 108 and 85.5 mW cm⁻² were obtained for the acrylic and the paperbased co-laminar flow fuel cell, respectively, which are the highest values reported to date for ethanol LFFCs at room temperature.

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1. INTRODUCTION

Short-chain alcohols are used as liquid fuels in energy conversion due to their high theoretical energy densities (ethanol: 8010, glycerol: 5000, and ethylene glycol: 5300 Wh·kg⁻¹), low toxicity, and ease of storage and handling [1]. The electro-oxidation of these alcohols and therefore, the release of electrons to produce electrical energy is usually favorable when Pd-based nanomaterials are used as electrocatalysts [2]. Metal-metal and/or metal-metal oxide combinations could result in enhancement of the electronic structure of materials, thereby improving their activity and stability, as has been reported for Pd-NiO/C synthesized by an intermittent microwave heating method [3]; Pt-NiO/C synthesized by a chemical reduction method [4]; and certain

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E-mail addresses: minbalca@yahoo.com.mx (M. Guerra-Balcázar), noe.arjona@yahoo.com.mx, wvelazquez@cideteq.mx (N. Arjona). others metal oxides, such as CeO_2 , Co_3O_4 and Mn_3O_4 [5]. Additionally, Pd-NiO mixtures have been obtained through several sophisticated (sometimes expensive) techniques, such as intermittent microwave heating [3], reactive evaporation [6], rf sputtering, [7] and reaction under autogenic pressure at elevated temperatures [8].

New methods are needed to address challenges related to production costs for industrial scaling (i.e., synthesis at room temperature and ambient pressure and reduction of the number of involved reagents) and because of the environmental impact of reaction by-products. In this sense, ionic liquids (ILs) are a good alternative. ILs are considered neoteric solvents that melt at temperatures below 100 °C (this property differentiates them from molten salts) and are sometimes called "room temperature ionic liquids" (RTILs) when they are liquids at ambient conditions [9]. ILs exhibit several extraordinary properties, including low vapor pressure, low relative viscosity, high ionic conductivity, high reactivity, and high stability to water and air [10]. According to their nature and procedure of synthesis, ILs can be classified as: I)

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ionic liquids and II) protic ionic liquids (PILs). ILs are frequently composed of inorganic anions and inorganic cations. Proton transfer is a characteristic of PIL syntheses because of the addition of Brønsted acids to Brønsted bases [11]. The "green aspect" of new-generation ionic liquids in chemical syntheses is related to i) their low vapor pressure, ii) water/air stability, iii) hydrophobicity/ hydrophilicity, iv) low flammability, v) low toxicity, and vi) biodegradability. These characteristics could allow the separation of products and by-products, thereby enabling recycling and reuse of ionic liquids [12–14]. Furthermore, most of the principles of green chemistry can be satisfied using ionic liquids as greener substitutes to common organic solvents which are volatile and hazardous.

It is desired that ionic liquids act as ideal solvents for applications in catalysis and electrocatalysis. In order to be useful for catalysis, ionic liquids must be able to dissolve large quantities of starting materials, products, catalysts, and/or co-solvents. Additionally, ILs should show specific interactions with their surroundings, enhancing or reducing the reactivity of solute species as required [15]. In electrocatalysis, ILs should be able to act not only as solvents for electrosynthesis of electrocatalysts (because of their typically large electrochemical window) but also as "all-in-one" media for the green synthesis of electrocatalysts. In other words, to be considered an ideal medium, ILs should simultaneously play the role of reaction medium, molecular precursor, and capping and reducing agent [10]. To date, RTILs have been used only as solvents [8,16,17] or as composite constituents [18]. Furthermore, few studies have reported the successful use of ionic liquids as "all-in-one" solvents. Such studies are mainly related to the synthesis of CuCl [19]. Au. [20] and ZnO [21] nanostructures, and report the synthesis of particles with sizes from few tens of nanometers to up of hundreds of nanometers.

The use of ionic liquids in green synthesis of metal nanoparticles suggests that they could be similarly used to develop environmentally friendly methods in order to be coupled to fuel cell technology. The latter are considered as one of the cleanest methods to obtain electricity [22]. Membraneless co-laminar flow fuel cells (LFFCs) as well as fuel cells are defined as electrochemical devices for converting chemical energy to electrical energy. In LFFCs, the fuel and oxidant, both flow in a co-laminar manner, forming a natural interface due to diffusional transport between them [23]. Such cells present the advantage of ease of using liquid fuels, liquid oxidants, and their mixtures. Almost all reports of these fuel cells are focused on the use of methanol or formic acid as fuels because both of these are small molecules that can be easily broken to form CO₂ [24]. Ethanol and other larger-chain molecules such as glycerol and ethylene glycol have been rarely reported in this class of devices. One of the most important strategies to increase their cell performance is related with the usage of streams with mixed-pH, combining an alkaline anodic stream with an acidic cathodic stream. This strategy has been implemented in proton-exchange membrane fuel cells (PEM-FCs) [25]. Recently Lu et al., have demonstrated its usage in switchable pH unitized regenerative fuel cells (URFC), where the URFC with mixed-pH showed an improvement in the cell performance [26]. Moreover, this strategy has also employed in aluminum-air cells, Chen et al., have recently presented a membraneless aluminum-air cell which follows the flow-over concept in a "Y"-like cell architecture, finding a superior performance [27]. To date, the use of mixed-pH streams has not been tested in co-laminar flow fuel cells which operate with a complex flow-through concept in which fuel and oxidant react before encountering at the natural interface.

In this work, we succeeded in obtaining Pd/C, NiO/C, and Pd-NiO/C materials with small particle sizes using 2-hydroxy ethylammonium formate protic ionic liquid as all-in-one solvent. This protic ionic liquid was synthesized by a Brønsted reaction between formic acid and ethanolamine. The resulting nanomaterials were physicochemical and electrochemically characterized and used as electrocatalysts toward the ethanol electro-oxidation reaction. An acrylic and a paper LFFC were constructed to evaluate performances of Pd/C and Pd-NiO/C using ethanol as fuel varying operational conditions, such as pH of streams, and nature of the oxidant.

2. EXPERIMENTAL SECTION

2.1. Synthesis of protic ionic liquid

2-hydroxy ethylammonium formate protic ionic liquid was synthesized by a simple acid-base Brønsted reaction involving formic acid (Sigma-Aldrich, \geq 98%) as the organic anionic source and ethanolamine (Sigma-Aldrich, \geq 99%) as the organic cationic source. All reagents reported in this study were used as received without further purification. Ethanolamine (0.5 mole fraction) was placed in a jacked glass cell, to which formic acid (0.5 mole fraction) was added at a flow rate of 12 mL/h using a syringe pump (Harvard Apparatus, PHD Ultra Syringe Pump Infuse/Withdraw). The cell was magnetically stirred conserving an inert atmosphere using gaseous nitrogen (Infra, 99.999%), and 4°C as the working temperature. A colorless, viscous liquid was obtained, the existence of the PIL was corroborated by ¹H nuclear magnetic resonance (Bruker, NMR 400 MHz) finding the following signals (Scheme 1): δ: 8.522 ppm (s, 1H, H-COO⁻); 7.944 ppm (s, 4H, -NH₃⁺OH); 3.769 ppm (t, 2H, -CH₂N); 3.085 (t, 2H, -O-CH₂).

2.2. Synthesis of electrocatalysts

The synthesis of Pd, NiO, and Pd-NiO was carried out at room temperature using Na₂PdCl₄ (Sigma-Aldrich, 99.8%) and NiSO₄ (J. T. Baker, 99.99%) as precursors. In a typical synthesis, 50 mg of Na₂PdCl₄ or 150 mg of NiSO₄ were placed in a vial containing 10 mL of PIL and dispersed by sonication. The Palladium precursor acquired a black coloration after 3 minutes of sonication, indicating the formation of Pd nanoparticles. The Nickel precursor also showed changes in coloration after 30 minutes of being in contact with the PIL; however, it was left for 2 hours to ensure a better reaction. The formation of bubbles was observed in all syntheses, suggesting that the metallic reduction of precursors involves the decomposition of the PIL when it acts as reducing agent. Further analysis of the gaseous species is required to clarify the mechanism of nanoparticle formation. On the other hand, 70 mg (for Pd nanoparticles) and 150 mg (for NiO and for Pd-NiO) of Vulcan carbon (Cabot® XC-72) were added after the reaction times and maintained in sonication for other 30 minutes. After this, the vials were kept under refrigeration (-18 °C) for 24 h to ensure complete reduction of metallic precursors. These materials were centrifuged at 4000 rpm and washed several times with deionized water. Finally, the resulting powders were dried overnight at 80 °C.

2.3. Physicochemical characterization

Pd/C, NiO/C, and Pd-NiO/C powders where characterized by means of X-ray diffraction using a Bruker D8 Advance apparatus operated at 30 kV and 30 mA. The X-ray fluorescence analyses were performed using a Bruker S2 PICOFOX spectrometer. Thermogravimetric analyses (TGA) were performed using a TA instrument apparatus with a temperature ramp of 10 °C min⁻¹ in air. Micrographs and energy dispersive X-ray spectroscopy analyses were obtained using a field-emission high resolution transmission electron microscope (HR-TEM) JEOL-JEM2200 Fs + Cs with spherical aberration control for condensed lens. Ionic conductivity of electrolytes was measured using a HACH multimeter HQ40d.



2.4. Electrochemical characterization

Electrochemical characterization was accomplished by obtaining electrochemical profiles of materials through cyclic voltammetry using a three-electrode electrochemical cell and a BioLogic VSP Potentiostat/Galvanostat. Glassy carbon plates (SPI[®], geometrical area: 1.2 cm²) were used as working electrodes. A saturated calomel electrode (0.241 V vs. NHE, BASi[®]) and a graphite rod were used as the reference and the counter electrode, respectively. 0.3 M KOH (J. T. Baker, 87%) solution was used as electrolyte and N₂ (Infra, 99.999%) as inert atmosphere. Cyclic voltammograms were recorded at 50 mV s^{-1} and the 10^{th} cycle was presented. The same electrochemical configuration was used for electrocatalytic evaluation of the ethanol electro-oxidation reaction (J. T. Baker, 99.99%). The scan rate for these experiments was 20 mV s⁻¹. The electrocatalysts were deposited onto glassy carbon electrodes by ink deposition using isopropyl alcohol as dispersant and Nafion as binding agent. For this purpose, 3 mg of catalysts were added to the alcohol (75 µL per milligram) and sonicated for 20 minutes. Nafion was then added to this mixture (7 μ L per milligram) which was stirred by sonication for another 20 minutes. Finally, 5 layers (20 µL ink per layer) of catalysts were deposited on glassy carbon electrodes.

2.5. Construction of membraneless co-laminar flow fuel cells

Pd-NiO was evaluated in two membraneless co-laminar flow fuel cells (LFFCs), mainly differentiated by the materials used as top and bottom plates in these cells. The first design), hereafter called

PMMA LFFC, corresponded to a LFFC constructed using hard plates of poly-(methyl methacrylate) PMMA. The second LFFC was a miniaturization of the first design but using adhesive paper as the top and bottom plates. The PMMA LFFC has been reported previously and details of its construction can be found elsewhere [28]. Briefly, the PMMA plates were patterned using a CNC machine. Six holes for the screws were patterned in both plates in order to close the cell. In the top plate, two holes were made and used as inlets for fuel and oxidant solutions. Additionally, a small vent was constructed in the top plate, to be used as an oxygen source from air. A single outlet was patterned in the bottom plate. A silicone film (Silastic[®], 200 µm thickness) was prepared and used as gasket. In the case of the adhesive paper LFFC, the cell design, including inlets and the outlet, was patterned using a Silhouette[®] plotter. In this case, the adhesive paper (Adhesives Research®, 100 µm thickness) replaced screws and thus allowed the reduction of LFFC dimensions. The electrodes were fabricated using a commercial carbon nanofoam paper (Marketech International Inc.[®]) and were composed of slides of 20 mm length and 1 mm width. The final geometrical area in contact with the anodic and cathodic streams for both cells was 0.015 cm²; which value was used for normalization of the LFFCs.

2.6. Operation of membraneless co-laminar flow fuel cells

Pd-NiO/C and commercial Pt/C (ETEK, 30%) were used as anodic and cathodic catalysts, respectively. Both were prepared according to the methodology described in the electrochemical characterization section (2.4). Additionally, both were deposited on carbon nanofoam slides using the spray ink method. The final catalyst load was 1 mg per electrode (including weight of Vulcan carbon as support). The anodic stream was prepared using 1.5 M ethanol as fuel and 0.3 M KOH as electrolyte. The cathodic stream consisted of an oxygen-saturated (Praxair, 4.3 U.A.P.) solution of 0.3 M KOH as alkaline electrolyte or 0.5 M H₂SO₄ as acidic electrolyte. Additionally, 0.2 M hydrogen peroxide (J. T. Baker, 30%) was used as oxidant in an alkaline electrolyte. These cells are characterized by the combined use of oxygen from air as well as that from a saturated solution in order to enhance the oxidant concentration. On the other hand, both streams were pressure-driven using two Cole-Parmer syringe pumps (single-syringe infusion pump, 115 VAC). The flow rate was investigated through cell performance measurements, and a rate of $9 \text{ mL} \text{ h}^{-1}$ was determined to be optimal for both streams. Data were collected through a Biologic VSP Potentiostat/Galvanostat, and the scan rate of all experiments was 10 mV s⁻¹. The experiments were performed at room temperature, which was fixed at 25 °C. Polarization and power density curves were performed by triplicated, reporting only the average values. The standard deviation for both, polarization and power density experiments was <3% for the acrylic-based colaminar flow fuel cell, and lower than 7% for the paper-based NFC. Control experiments without metallic catalysts, without fuel, and using NiO as anodic catalyst are presented in the supplementary information.

3. RESULTS AND DISCUSSION

3.1. Physicochemical characterization

The X-ray diffraction patterns for Pd/C, NiO/C and Pd-NiO/C are shown in Fig. 1A. For Pd electrocatalyst, the (111), (200), (220), (311), and (222) crystallographic planes were observed at 40.0, 46.59, 68.02, 81.95, and 86.49° 2θ , respectively, revealing a typical face-centered cubic structure. For NiO, the (111), (200), and (220) peaks corresponding to a face-centered cubic structure were located at 36.85, 43.01 and 62.39°. In the case of Pd-NiO, the Pd (111), (200), (220), (311), (222), and the NiO (200) peaks were observed at 39.76, 46.3, 67.86, 81.88, 86.49, and 42.91°, respectively. The (111), (200), and (220) planes related to Pd were slightly shifted due to the presence of NiO in its structure. Crystallite sizes were calculated using the Scherrer equation. For Pd/C, an average size of 8.8 nm was determined through analysis of the (111), (200), (220), and (311) planes. In the case of Pd-NiO/C, an average size of 8.1 nm was calculated from the (111) and (220) planes. For NiO/C, a crystallite size of 2.45 nm from the (200) plane. The lattice parameters were calculated by the application of Bragg's Law to the (220) plane, resulting in values of 3.9065 Å and 3.9077 Å for Pd/C and Pd-NiO/C, respectively (Pd = 3.8898 Å, JCPDS card # 5-681). The metallic compositions were determined by X-ray fluorescence and electron dispersive X-ray spectroscopy analyses and are shown in Table 1. Peaks related to Pd and Ni materials were observed through XRF, while no traces of their precursors (i.e., Na, S, or Cl) were observed. This finding can be related to the use of 2-hydroxy ethylammonium PIL as an all-in-one solvent which, when combined with water as washed solvent, may well separate

Iadic I								
XRF and	EDX	analyses	for	Pd/C,	NiO/C	and	Pd-NiO	/C.

Tabla 1

Electrocatalyst XRF		EDX					
	Pd mass %	Ni mass %	Pd atomic%	Ni atomic%	C atomic%	O atomic%	
Pd/C	100	-	21.41	-	78.59	-	
NiO/C	-	100	-	26.44	31.43	42.13	
Pd-NiO/C	89	11	1.61	0.25	97.71	2.05	



Fig. 1. A) X-ray diffraction pattern for NiO/C, Pd/C and Pd-NiO/C electrocatalysts. Crystalline planes of Pd and NiO were labelled in grey and black, respectively. B) Thermogravimetric analysis for Pd/C (black line) and Pd-NiO/C (grey line).

products, by-products, and remnants of precursors from the resulting powders.

The EDX analyses on single particles (Table 1) were in concordance with the XRF results, corroborating the presence of palladium, carbon, nickel, and oxygen in the NiO electrocatalyst. TGA curves are shown in Fig. 1B. The first loss of weight, observed at approximately 100 °C, was related to the residual water used to wash the catalysts. A second drop was observed at approximately 150 °C and this was attributed to the decomposition of ionic liquid remnants [29]. A third drop was observed starting from 250 °C (Fig. 1B, grey line) and was attributed to the decomposition of Ni species [30]. The drop at 500 °C was attributed to rapid oxidation of

Vulcan carbon. The residual metal content was calculated through these TGA curves and used to normalize the electrocatalytic activity, which was found to be 26% for the Pd/C catalyst and 6.2% for the Pd-NiO/C catalyst.

Morphology of materials is shown in Fig. 2; while particle size distribution calculated from TEM micrographs is shown in Fig. 3. In general, particles with undefined semispherical shape were observed. This behavior may be related to the complex ionic network which was affecting the electrostatic stabilization during

nanoparticle formation. Duant et al., [31] have mentioned that cations can serve as ionic stabilizers (or anions, depending on precursor salt charge) but their counter-ion will also adsorb on the resulting particle surface due to the effect of electrostatic attractions. The above discussion and the nanoparticle shape (Fig. 2 Pd-I and 2 Pd-II) suggest that charges of complex ion lattices present in the surrounding environment of seed crystals, have high influence on the electrostatic interactions of ions (attraction/ repulsion) which act as stabilizers. It is also most likely that



Fig. 2. TEM micrographs at different magnifications for NiO/C, Pd/C and Pd-NiO/C electrocatalysts.



Fig. 3. Particle distribution histograms for a) NiO/C, b) Pd/C and c) Pd-NiO/C.

Particle size / nm

electrostatic interactions with ions acting as reducing agents result in disordered crystal growth and non-homogeneous particle sizes [31,32]. Electrocatalysts showed average particle sizes of 5.3, 33.3, and 8.7 nanometers for NiO, Pd, and Pd-NiO, respectively. In the case of nickel-based materials (NiO/C and Pd-

NiO/C), subnanometric particles were observed together with particles of few nanometers in size (Fig. 2-NiO I and II). For the Pd-NiO electrocatalysts (Fig. 2, Pd-NiO I and II), the EDS analysis shows that subnanometric particles are single NiO particles and the bigger particles are Pd-NiO nanoparticles. The subnanometric size of NiO particles was not unexpected. These are frequently obtained in typical aqueous chemical reductions where it has been observed that NiO promotes the decrease of particle size of Pd and Pt basedmaterials: [33,34] This phenomenon could explain the decrease of size from 33.3 nm for monometallic Pd nanoparticles to 8.7 nm for Pd-NiO. Considerable work remains to be performed for detailing the mechanism of nanoparticle formation in the ionic liquid method. Nuclear magnetic resonance (NMR) experiments have been planned in order to identify the role of each component of the ionic liquid in the nanoparticle formation mechanism. The summary of XRD, TEM, and TGA data are presented in Table 2.

A poor particle size distribution was observed (Fig. 3), which can be related to several factors, such as i) the relatively high viscosity of the ionic liquid (223 cP) which limited mass transport; ii) ineffective sonication leading to poor dispersal of metallic precursors over the entire solution, due to their confinement to vials; and iii) the effect of the surrounding ions (i.e., electrostatic and steric interactions) was not sufficient to control the particle growth resulting in nanoparticles with multiple sizes. Alternative methodologies are now being explored to improve this aspect, such as the use of an ultrasonic probe and the use of small amount of water to reduce the viscosity of the 2-hydroxy ethylammonium formate ionic liquid.

3.2. Electrochemical characterization

The electrochemical profiles of NiO/C, Pd/C, and Pd-NiO/C are shown in Fig. 4. NiO/C showed the characteristic peaks related to the Ni²⁺/Ni³⁺ redox couple observed at 0.67 V vs. NHE in the forward scan and at 0.43 V vs. NHE in the backward scan. [35] For Pd/C, the formation of Pd oxides was observed in the region from -0.2 to 0.3 V vs. NHE, while, their reduction was observed at -0.2 V vs. NHE. In the case of Pd-NiO/C the redox couple of Ni species was slightly shifted as was the peak related to the reduction peak of NiO was located at -0.16 V vs. NHE. Electrochemical characterization in alkaline medium (Fig. 4) was performed, not only to corroborate the electrochemical presence of metals but also to calculate the electrochemically active surface area (Eq. ((1)).

$$ECSA = \frac{Q_E}{Q_T} \tag{1}$$

Where Q_E is the experimental charge determined by integrating the reduction peak of palladium oxides. Q_T is the theoretical charge needed to reduce a full monolayer of Pd or Ni oxides; in alkaline medium, these values correspond to 405 and 430 µC cm⁻², respectively [36,37]. Pd/C, NiO/C and Pd-NiO/C (Fig. 4) exhibited electrochemical areas of 46.0988, 18.1582, and 18.60 cm², respectively. These ECSA values together with the Pd mass obtained from TGA curves (0.38 mg for Pd/C and 0.08 mg for Pd-NiO/C), were used

Table 2

Summary of crystal and nanoparticle sizes, lattice parameters and metallic loadings of Pd, NiO and Pd-NiO electrocatalysts.

Material	XRD		TEM	TGA
	Crystal size/nm	Lattice parameter/Å	Particle size/nm	Metal content/%
Pd	8.8	3.9065	33.3	26
Pd-NiO	8.1	3.9077	8.7	6.2
NiO	2.5	-	5.3	-



Fig. 4. Cyclic voltammograms of Pd/C, NiO/C and Pd-NiO/C obtained using 0.3 M KOH as electrolyte. Scan rate: 50 mV s^{-1} .

to normalize voltammograms for the evaluation of electrocatalytic activity. NiO is known to exhibit antiferromagnetic behavior, [38] which, in this case, impeded data acquisition by TGA. Therefore, NiO was arbitrarily normalized, using the mass content of Pd-NiO. Furthermore, NiO is only presented in Fig. 5C for its demonstrated lack of activity toward the electro-oxidation reactions.

In the ethanol electro-oxidation reaction (Fig. 5), Pd/C as well as Pd-NiO/C showed an increase of current density as a function of ethanol concentration (Fig. 5A and 5B, respectively). Both materials showed the maximum current density at the highest ethanol concentration evaluated herein (3 M). Comparing both materials, Pd-NiO/C exhibited an almost 24-fold higher current density than Pd/C. This could be due to the effect of incorporation of Ni into the Pd structure, which, i) decreased the particle size of Pd-NiO/C, ii) adsorbed additional hydroxyl species renewing the Pd surface [3], and iii) promoted oxidation of CO by Ni, enhancing the tolerance to poisoning of Pd-NiO [40]. In terms of reaction potential, Pd/C showed a value close to -0.4 V and Pd-NiO/C was approximately at -0.37 V vs. NHE. Both materials showed similar oxidation potentials compared to Pd nanocubes enclosed in the (100) plane [43], which was previously reported by our group (the electrocatalytic activity for this reaction follows the order: 100 > 110 > 111) [44]. A further comparison with other Pd and Ptbased Ni materials is presented in Table 3. As observed, the Pd-NiO/ C catalyst has been previously reported by different authors. However, this is the first time in which the successful use of an ionic liquid for the green synthesis of Pd-NiO/C is reported. Moreover, the Pd-NiO/C nanoparticles presented herein showed higher current densities and similar onset potentials, compared to those found in literature (Table 3, considering values normalized by geometrical area).

3.3. Evaluation of acrylic-based membraneless co-laminar flow fuel cell

Components of the fabricated alkaline ethanol membraneless co-laminar flow fuel cell with PMMA plates are shown in Fig. 6A.



Fig. 5. Cyclic voltammograms of the electrocatalytic evaluation of a) Pd/C and b) Pd-NiO/C for the ethanol electro-oxidation reaction at function of concentration and c) comparison of activity at 3 M ethanol for Pd/C, NiO/C and Pd-NiO/C. Scan rate: 20 mV s^{-1} .

Table 3

Comparison of current densities and onset potentials of different Pd and Pt Ni-based materials toward the ethanol electro-oxidation reaction.

Material	Electrolyte	Fuel	Current density/mA cm ⁻²	Potential/V vs. NHE	Reference
Pd-NiO/C	1 M KOH	1 M Et.	14.76	-0.30*	[3]
Pt-NiO/C	1 M KOH	1 M Et.	11.5	-0.35^{*}	[3]
PdNi/MWCNT	1 M KOH	1 M Et.	~25	-0.36	[39]
NiPd/Ti	1 M KOH	1 M Et.	~2.35	-0.41^{*}	[40]
PdNi/C	0.5 M NaOH	1 M Et.	100 ^{NS}	-0.46^{*}	[41]
Pd-NiO/C	1 M KOH	1 M Et.	94 ^{NS}	-0.46	[42]
Pd-NiO/C	0.3 M KOH	3 M Et.	24.98	-0.37	This work



Fig. 6. A) Scheme of the acrylic membraneless co-laminar flow fuel cell and performances B) using Pd-NiO/C (circles) and Pd/C (squares) as anode catalysts using alkaline streams and the combined source of oxygen as oxidant, C) anodic alkaline stream and acidic cathodic stream with the two sources of oxygen, and D) alkaline streams but using 0.2 M H₂O₂ in 0.3 M KOH as oxidant.

Polarization and power density curves are illustrated in Fig. 6B for Pd-NiO/C and Pd/C. The latest data were used for comparison purposes because Pd/C has shown superior performance than commercial Pd/C (ETEK), as previously reported [45].

The ethanol electro-oxidation by a direct pathway in alkaline medium is illustrated in Eq. (2). Additionally, the oxygen reduction reaction (ORR) using an alkaline electrolyte is shown in Equation 3. The overall cell reaction for an alkaline ethanol fuel cell is illustrated in Eq. (4).

$$CH_3CH_2OH + 12OH^- \rightarrow 2CO_2 + 9H_2O + 12e^-$$
 (2)

 $3O_2 + 6H_2O + 12e^- \rightarrow 12OH^- \tag{3}$

 $E^0 = 0.40 V$

$$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$
 (4)

 $E_{cell} = 1.14 V$

From Fig. 6B, cell voltages of 0.55 V and 0.6 V for Pd-NiO/C and Pd/C were observed in the polarization region. Both values were

 $E^0 = -0.74 V$

lower than the theoretical cell voltage using oxygen as oxidant (Equation 4), exhibiting voltage efficiencies of 48 and 53%, respectively. Nonetheless, these voltages were consistent with typical values for direct ethanol proton exchange membrane fuel cells (PEMFCs), which operate at higher temperatures (60–100 °C) than membraneless co-laminar flow fuel cells (~25 °C). For example, PEMFCs containing Pd-based anodes have shown typical values from 0.63 to 0.78 V for Pd/MWCNT and PdSn/MWCNT at 60 °C. [46] and 0.7 and 0.88 V for Pd/C and PdNi/C, respectively, at 80 °C. [47] Pt-Ru supported in Vulcan and Pt-Ru/MWCNTs showed cell voltages of 0.6 V and 0.81 V, respectively, when both were operated at 100 °C [48]. On the other hand, in the ohmic region, voltages at maximum power density were 0.29 and 0.30 V for Pd/C and Pd-NiO/C, respectively. At these voltages, the current densities of both materials were 52.6 and 43.9 mA cm⁻², respectively. In general, these low voltages at maximum current density can be associated to ohmic losses and mass transport limitations, due to the fast drop in current density observed in the polarization curves presented in Fig. 6B. In the mass transport region, it was observed that Pd/C showed a maximum current density of 125 mA cm^{-2} . Meanwhile, Pd-NiO/C showed a maximum current density of 105 mA cm⁻². The resulting maximum power densities were 15.3 and 13.8 mW cm⁻² for Pd/C and Pd-NiO/C LFFCs, respectively. The fuel utilization at the condition of maximum current density using 1.5 M ethanol and at a flow rate of 150 μ L min⁻¹, was 0.26% for Pd/C and 0.217% for Pd-NiO/C. Additionally, the oxidant utilization for 10 mM oxygen was 19.34 and 16.28% for Pd and Pd-NiO, respectively. The net cell efficiency was calculated by multiplying the voltage efficiency and the fuel utilization, resulting in cell efficiencies of 13.78% for Pd/C and 10.416% for Pd-NiO/C. It is important to remark that the Pd/C-based LFFC had an almost 6-fold higher amount of Pd that the Pd-NiO/C based LFFC. For equivalent amounts of Pd, the membraneless co-laminar flow fuel cell which employed Pd-NiO/C as anode catalyst showed a current density of $1750 \text{ mAmg}^{-1} \text{ cm}^{-2}$, while the LFFC with Pd/C as anode catalyst showed a current density of 416.17 mA mg^{-1} cm⁻².

Two strategies were followed to increase the cell performance of the acrylic-based membraneless co-laminar flow fuel cell operating with Pd-NiO/C as anode catalyst. The first strategy was to employ streams with different pH because, following the Nernst equation, pH has a considerable effect on thermodynamic potential of both reactions, and hence on cell voltage, as demonstrated in Fig. 6C. The combination of an alkaline anodic stream and an acidic cathodic stream resulted in a cell voltage of 1.11 V, which was twice that for a completely alkaline LFFC (Fig. 6B, circles). The increase in cell voltage was expected because the ethanol electro-oxidation has a potential of -0.77 V in alkaline medium (Eq. (2)), and the oxygen reduction reaction rises from 0.4 V in alkaline medium (Eq. (3)) to 1.23 V in acidic medium (Eq. (5)), thus improving the theoretical cell voltage from 1.14 up to 1.97 V in mixed streams (Eq. (6)). The use of an acidic anodic stream/acidic cathodic stream was neglected because of the lower cell voltage than the alkaline/ acidic mixed streams and due to the lack of activity of Pd-NiO/C toward ethanol oxidation in acidic medium.

$$3O_2 + 12H^+ + 12e^- \to 6H_2O \tag{5}$$

 $E^0 = 1.23 V$

$$CH_3CH_2OH + 12OH^- + 12H^+ + 3O_2 \rightarrow 2CO_2 + 15H_2O$$
 (6)

E_{cell} = 1.97 V

The employment of mixed streams not only resulted in an increase of cell voltage but also in a decrease of ohmic losses, probably because of the rise in ionic conductivity by using 0.5 M H_2SO_4 (220 mS cm⁻¹) as electrolyte instead of 0.3 M KOH (71.7 mS cm⁻¹). The decrease of ohmic losses also resulted in a voltage at maximum power density of 0.72 V. Meanwhile, the resulting maximum power density was 108 mW cm⁻² (Fig. 6C). In the region of mass transfer, this LFFC showed a steady state from 0.4 V, with an enhancement of current density from 105 mA cm⁻² in an allalkaline LFFC to 242 mA cm^{-2} for the mixed-stream LFFC. The performances in alkaline and the mixed-stream LFFCs can be globally related to the high surface area of three dimensional electrodes, highly active anodes, and the combined used of two sources of oxygen (from air and from an aqueous solution). This last point is important because aqueously dissolved oxygen has shown limitations as an oxidant, due to its low solubility, diffusivity, and concentration (4 mM in solution) [49]. Furthermore, the use of air as a source of oxygen has been highly explored in membraneless micro and nanofluidic fuel cells because of the higher diffusivity of oxygen in air (10,000-fold higher) and slightly higher concentration (10 mM) than in aqueous solution [50-53]. However, even though both the alkaline and the mixed-stream LFFC had the same source of oxygen (Fig. 6B and 6C), the latter showed a current density twice higher than that of the former. The change of pH should not has an important effect in current density than it has in cell voltage. The only possible explanation is related to secondary reactions that could occur at both electrodes. E. R. Choban et al. observed the evolution of hydrogen (Eq. 7) in a Ptbased cathode working with an alkaline/acidic mixed stream in a methanol membraneless microfluidic fuel cell [54].

$$12H^+ + 12e^- \to 6H_2$$
 (7)

 $7 E^0 = 0 V$

In these terms, and from the results of cell voltage and current density (Fig. 6C), it can be inferred that hydrogen reduction could occur simultaneously with oxygen reduction in the cathode, increasing the current density (up to 2-fold) but decreasing cell voltage from 1.97 V to 1.11 V. The use of mixed-pH streams resulted in a voltage efficiency of 56.34% which was slightly higher than of all-alkaline acrylic LFFC (48%). Values of 0.499% and 37.48%, respectively, were obtained for fuel and oxidant utilization percentages. Additionally, the net cell efficiency for this configuration was 28.11%.

The second strategy to enhance cell performance was related to the use of hydrogen peroxide as alternative oxidant to oxygen (Fig. 6D). Hydrogen peroxide shows advantages such as higher solubility, can be used at higher concentrations in aqueous solution, and shows a more positive reduction potential than oxygen (0.48 V). In alkaline medium, hydrogen peroxide is reduced at 0.88 V (Eq. (8)) and, combined with an alkaline anodic stream, gives a cell voltage of 1.62 V (Eq. (9)).

$$6H_2O_2 + 12e^- \rightarrow 12OH^-$$
 (8)

 $E^0 = 0.88 V$

$$CH_3CH_2OH + 6H_2O_2 \to 2CO_2 + 9H_2O \tag{9}$$

 $E_{cell} = 1.62 V$

The cell voltage for the alkaline LFFC with H₂O₂ as oxidant and Pd-NiO/C as anode catalyst was 0.69 V (Fig. 6D). This value was nearly half the theoretical cell voltage, showing a voltage efficiency of 42.59%. This fall in potential could be related to the formation of O_2 (Eq. (3)) as an undesired by-product of H_2O_2 in the cathodic reaction. This behavior occurs at Pt surfaces, such as the commercial Pt/C (ETEK) used in this work. [55] Further work in modification of Pt-based cathodes for membraneless co-laminar flow fuel cells is ongoing. In the region of ohmic losses, a lower resistance was observed using H₂O₂ instead of O₂ (Fig. 6B), for the same cell configuration. This was complemented by better mass transport of reactants because of a higher availability of both fuel (1.5 M) and oxidant (0.2 M). For this reason, the current density increased to 150 mA cm⁻² and the power density to 33.6 mW cm⁻¹ 2.5-fold higher than those using the combined source of oxygen. In summary, cell voltage, current density and hence, power density of the LFFC which use hydrogen peroxide as oxidant showed higher values than the LFFC operated with the combined source of oxygen. This improvement in performance can be related to the lower activation barrier and hence, faster kinetics of oxidation using H_2O_2 compared with O_2 ; because the reaction of H_2O_2 involves breakage of single dioxygen bonds rather than breakage of double dioxygen bonds which is required for O₂. [56,57] The analysis of fuel and oxidant utilization for this alkaline LFFC operating with 0.2 M hydrogen peroxide as oxidant resulted in percentages of 0.3125 and 2.344, respectively. The net cell efficiency was also calculated for this cell configuration resulting in an efficiency of 13.31%.

8.1. Evaluation of the paper-based membraneless co-laminar flow fuel cell

Finally, the components of an adhesive paper-based co-laminar flow fuel cell are illustrated in Fig. 7A. This cell design has been recently reported by our group [58]. It was observed that the usage of paper decreased the number of components to only the gasket, paper slides, and electrodes. The gasket design used in the acrylic LFFC did not work in the paper LFFC, generating fuel/oxidant leakage. For this reason, a hexagon-like design was employed.

Results for an alkaline anode/cathode LFFC with Pd-NiO/C as anode catalyst are shown in Fig. 7B. The cell voltage was 0.6 V with a maximum current density of almost 130 mA cm⁻², with a resulting power density of 22.5 mW cm⁻². Contributions from polarization and ohmic losses decrease the voltage of maximum power density to 0.33 V. A voltage efficiency of 52.63% was obtained which was similar to that obtained in the acrylic LFFC. Additionally, the fuel utilization was slightly enhanced to a value of 0.2667%. The net cell efficiency was calculated with these values of voltage efficiency and fuel utilization, resulting in an efficiency of 14.03%, almost 3% higher than that of the acrylic LFFC. This increase in efficiency is related to the decrease of ohmic resistances because of the closer positioning of electrodes which results in a smaller volume for the paper LFFC (23-fold lower). A mix of streams involving an alkaline anodic stream and an acidic cathodic stream was made for the paper-based LFFC, as performed for the acrylic LFFC. The results for this mixture are presented in Fig. 7C. In this figure, it is observed that the use of an acidic electrolyte in the cathode increased the cell voltage to 1.05 V, resulting in a voltage efficiency of 53.30%. Compared with the all-alkaline paper-based LFFC (Fig. 7B), the cell voltage was improved to 0.45 V. Bigger ohmic losses are presented in the mixed-stream LFFC compared with the all-alkaline LFFC and are related to deformation of the natural interface and leakage of flows because of loss of adhesiveness in the paper-based LFFC. This loss only occurred when an alkaline and an acidic electrolyte were combined in the co-laminar flow fuel cell, regardless of its compartment structure



Fig. 7. A) Design of a membraneless co-laminar flow fuel cell constructed using adhesive paper, B) Cell performance using an ethanol LFFC with alkaline electrolytes and C) cell performance employing an alkaline anodic electrolyte and an acidic cathodic electrolyte. Ethanol concentration: 1.5 M. Scan rate: $10 \, \text{mV s}^{-1}$.

(alkaline-anode & acidic-cathode or acidic-anode & alkalinecathode). Despite these limitations, a current density of 365 mA cm⁻² was obtained, being the highest value obtained in this work and others (Table 4). The combination of streams (Fig. 7C) increased the power density by a factor of 3.8, when compared with the all-alkaline LFFC (Fig. 7B). Further, the combined used of streams with different pH and decrease of the cell volume resulted in a fuel and oxidant utilization of 0.757% and 113.559%, respectively. In the case of oxidant utilization, it is clearly observed the contribution of hydrogen reduction as secondary reaction, increased the efficiency to values upward of 100%. The resulting net cell efficiency was 40.348%, the highest found among all the cell configurations herein presented.

A comparison between the acrylic and the paper-based membraneless co-laminar flow fuel cells was made, and their results are illustrated in Fig. 8. Dimensions of the acrylic LFFC were

Comparison	of cell performanc	es of ethanol membraneless	co-laminar flow fuel	cells at room temperature	with air-breathing cathodes	an all-alkaline streams

Anode & cathode catalyst	Catalyst ink loading (mg)	Fuel & concentration/M	E/V	J/mA cm ⁻²	$W/mW \ cm^{-2}$	Ref.
Cu@Pd/C & Pt/C	2.2 & 2.9	0.1 M EtOH	0.67	153.7	25.75	[52]
Pt/Ru black & Pt black	$10 \& 2 \mathrm{mg}\mathrm{cm}^{-2}$	1 M EtOH	${\sim}0.7$	~ 90	12.21	[59]
PdNiO/C & Pt/C	1 mg	1.5 M EtOH	1.11	242	108	This work
PdNiO/C & Pt/C	1 mg	1.5 M EtOH	1.05	365	85.5	This Work



Fig. 8. Comparison between an acrylic and a paper-based LFFC a) in volume, B) in performance using alkaline-alkaline streams and C) using a mixed stream alkaline-acidic streams. Anode: Pd-NiO/C. Ethanol concentration: 1.5 M. Scan rate: 10 mV s⁻¹.

42 mm length, 32 mm width, and 10 mm thickness with a vent of 11×2 mm. Compared with this, dimensions of the paper LFFC were decreased to $30 \times 20 \times 1$ millimeters with a vent of 14×1 mm and a total volume of 0.62 cm³, 23-times smaller than the acrylic LFFC

(Fig. 8A). Cell performance of the all-alkaline paper-based membraneless co-laminar flow fuel cell was almost twice as high as that of the acrylic LFFC (Fig. 8B). Enhancement in open circuit potential was observed together with a decrease of ohmic losses, resulting in the increment of current and power density. Both can be related to the reduction of size, increase in the surface-to-volume ratio, and enhancement of the reaction kinetics and mass transport. For mixed streams (Fig. 8C), the acrylic LFFC showed lower ohmic resistance and hence, better power density (1.23-fold higher). However, the paper LFFC showed higher current density (1.5-fold higher) because of the enhanced surface-to-volume ratio, where the loss of power density was related to leakage of streams which increased the polarization and ohmic losses (Fig. 8C).

9. CONCLUSIONS

2-hydroxy ethylammonium formate as air and water-stable protic ionic liquid was used at room temperature in the green synthesis of NiO, Pd, and Pd-NiO materials. Changes in Pd coloration from orange to a darkened solution at low contact times (less than 3 minutes) indicated the formation of Pd nanoparticles. The X-ray diffractograms revealed that those materials had crystallite sizes of 2.45, 8.8, and 8.1 nm for NiO, Pd, and Pd-NiO. TEM images confirmed that nanoparticulate Ni and Pd-based materials can be successfully obtained through the use of this PIL. The introduction of Ni on Pd-NiO/C decreased its particle size compared with Pd/C, resulting in an improvement of the electrocatalytic properties for ethanol, as determined by the three-electrode electrochemical configuration. A 24-fold higher current density was obtained for Pd-NiO/C (6% of residual metal content) compared with Pd/C; where Pd-NiO/C had a 4-fold lower metal content than Pd/C. Both materials were successfully used in a membraneless co-laminar flow fuel cell based on both acrylic and paper as supporting plates. In the acrylic LFFC, Pd-NiO/C showed the maximum cell performance working with an alkaline anodic stream combined with an acidic cathodic stream, showing values of current density, cell voltage, and a power density of 242 mA cm⁻², 1.11 V, and 108 mw cm⁻², respectively. The paperbased LFFC as well as the acrylic LFFC showed maximum performance with combined streams, the paper-based LFFC showed 1.05 V in cell voltage, 365 mA cm⁻² in current density and 85.5 mW cm^{-2} in power density were obtained. In summary, membraneless co-laminar flow fuel cells with high net cell efficiencies (from 10% to up 40%) that employ Pd-NiO/C as anode catalyst can be easily constructed using PMMA or paper as simple and low-cost materials. Furthermore, this clean energy source was combined with green methods of synthesis of nanoparticles, such as the use of 2-hydroxy ethylammonium formate protic ionic liquid, leading to the development of a greener technology for energy conversion.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. electacta.2016.05.002.

References

- [1] L. Soloveichik, Liquid fuel cells, Beilstein J. Nanotechnol. 5 (2014) 1399.
- C. Bianchini, P.K. Shen, Palladium-Based Electrocatalysts for Alcohol Oxidation in Half Cells and in Direct Alcohol Fuel Cells, Chem. Rev. 109 (2009) 4183.
 F. Hu, C. Chen, Z. Wang, G. Wei, P.K. Shen, Mechanistic study of ethanol
- oxidation on Pd–NiO/C electrocatalyst, Electrochim Acta 52 (2006) 1087. [4] R.S. Amin, R.M. Abdel Hameed, K.M. El-Khatib, M. Elsayed Youssef, A.A.
- Elzatahry, Pt–NiO/C anode electrocatalysts for direct methanol fuel cells, Electrochim. Acta 59 (2012) 499.
- [5] K.-H. Ye, S.-A. Zhou, X.-C. Zhu, C.-W. Xu, P.K. Shen, Stability analysis of oxide (CeO₂, NiO, Co₃O₄ and Mn₃O₄) effect on Pd/C for methanol oxidation in alkaline medium, Electrochim. Acta 90 (2013) 108.
- [6] T. Manago, T. Ono, H. Miyajima, I. Yamaguchi, K. Kawaguchi, M. Sohma, Epitaxial growth of NiO/Pd superlattices by reactive evaporation method, Thin Solid Films 374 (2000) 21.
- [7] S.C. Chen, T.Y. Kuo, Y.C. Lin, S.W. Hsu, H.C. Lin, Effect of palladium content on microstructures, electrical and optical properties of NiO films by rf sputtering, Thin Solid Films 549 (2013) 50.
- [8] C. Mahendiran, T. Maiyalagan, K. Scott, A. Gedanken, Synthesis of a carboncoated NiO/MgO core/shell nanocomposite as a Pd electro-catalyst support for ethanol oxidation, Mater. Chem. Phys. 128 (2011) 341.
- [9] K.R. Seddon, A. Stark, M.-J. Torres, Influence of chloride, water, and organic solvents on the physical properties of ionic liquids, Pure Appl. Chem. 72 (2000) 2275.
- [10] Z. Li, Z. Jia, Y. Luan, T. Mu, Ionic liquids for synthesis of inorganic nanomaterials, Curr. Opin. Solid ST. M. 12 (2008) 1.
- [11] A. Ejigu, D.A. Walsh, The Role of Adsorbed lons during Electrocatalysis in Ionic Liquids, J. Phys. Chem. C 118 (2014) 7414.
- [12] A.A. Papadopoulou, A. Tzani, D. Alivertis, M.H. Katsoura, A.C. Polydera, A. Detsi, H. Stamatis, Hydroxyl ammonium ionic liquids as media for biocatalytic oxidations, Green Chem 18 (2016) 1147.
- [13] Y. Deng, I. Beadham, M. Ghavre, M.G. Costa Gomes, N. Gathergood, P. Husson, B. Légeret, B. Quilty, M. Sancelme, P. Besse-Hoggan, When can ionic liquids be considered readily biodegradable? Biodegradation pathways of pyridinium, pyrrolidinium and ammonium-based ionic liquids, Green Chem. 17 (2015) 1479.
- [14] M.J. Earle, K.R. Seddon, Ionic liquids. Green solvents for the future, Pure Appl. Chem. 72 (2000) 1391.
- [15] T. Welton, Ionic liquids in catalysis, Coordin. Chem. Rev. 248 (2004) 2459.
- [16] K. Ding, L. Liu, Y. Cao, X. Yan, H. Wei, Z. Guo, Formic acid oxidation reaction on a Pd_xNi_y bimetallic nanoparticle catalyst prepared by a thermal decomposition process using ionic liquids as the solvent, Int. J. Hydrogen Energy 39 (2014) 7326.
- [17] S. Dong, P. Zhang, H. Liu, N. Li, T. Huang, Direct electrochemistry and electrocatalysis of hemoglobin in composite film based on ionic liquid and NiO microspheres with different morphologies, Biosens. Bioelectron. 26 (2011) 4082.
- [18] Z. Ma, J. Yu, S. Dai, Preparation of inorganic materials using ionic liquids, Adv. Mater. 22 (2010) 261.
- [19] A. Taubert, CuCl Nanoplatelets from an Ionic Liquid-Crystal Precursor, Angew. Chem. 116 (2004) 5494.
- [20] K.-S. Kim, S. Choi, J.-H. Cha, S.-H. Yeon, H. Lee, Facile one-pot synthesis of gold nanoparticles using alcohol ionic liquids, J. Mater. Chem. 16 (2006) 1315.
- [21] Z. Li, Y. Luan, Q. Wang, G. Zhuang, Y. Qi, Y. Wang, C. Wang, ZnO nanostructure construction on zinc foil: the concept from an ionic liquid precursor aqueous solution, Chem. Commun. (2009) 6273.
- [22] K. Sopian, W.R. Wan Daud, Challenges and future developments in proton exchange membrane fuel cells, Renew. Energy 31 (2006) 719.
- [23] H. Xu, H. Zhang, H. Wang, D.Y.C. Leung, L. Zhang, J. Cao, K. Jiao, J. Xuan, Counterflow formic acid microfluidic fuel cell with high fuel utilization exceeding 90%, Appl. Energy 160 (2015) 930.
- [24] E. Kjeang, N. Djilali, D. Sinton, Microfluidic fuel cells: A review, J. Power Sources 186 (2009) 353.
- [25] L. An, T.S. Zhao, J.B. Xu, A bi-functional cathode structure for alkaline-acid direct ethanol fuel cells, Int. J. Hydrogen Energy 36 (2011) 13089.

- [26] X. Lu, J. Xuan, D.Y.C. Leung, H. Zhou, J. Li, H. Wang, H. Wang, A switchable pHdifferential unitized regenerative fuel cell with high performance, J. Power Sources 314 (2016) 76.
- [27] B. Chen, D.Y.C. Leung, J. Xuan, H. Wang, A mixed-pH dual-electrolyte microfluidic aluminum-air cell with high performance, Appl. Energy, 10.1016/j. apenergy,2015.10.029 (in press).
- [28] E. Ortiz-Ortega, M.-A. Goulet, J.W. Lee, M. Guerra-Balcázar, N. Arjona, E. Kjeang, J. Ledesma-García, L.G. Arriaga, A nanofluidic direct formic acid fuel cell with a combined flow-through and air-breathing electrode for high performance, Lab Chip 14 (2014) 4596.
- [29] N. Bicak, A new ionic liquid: 2-hydroxy ethylammonium formate, J. Mol. Liq. 116 (2005) 15.
- [30] Z. Zhang, L. Xin, K. Sun, W. Li, Pd-Ni electrocatalysts for efficient ethanol oxidation reaction in alkaline electrolyte, Int, J. Hydrogen Energy 36 (2011) 12686.
- [31] X. Duan, J. Ma, J. Lian, W. Zheng, The art of using ionic liquids in the synthesis of inorganic nanomaterials, CrystEngComm 16 (2014) 2550.
- [32] Z. Ma, J. Yu, S. Dai, Preparation of Inorganic Materials Using Ionic Liquids, Adv. Mater. 22 (2010) 261.
- [33] M. Wang, W. Liu, C. Huang, Investigation of PdNiO/C catalyst for methanol electrooxidation, Int. J. Hydrogen Energy 34 (2009) 2758.
- [34] D.B. Kim, H.-J. Chun, Y.K. Lee, Preparation of Pt/NiO-C electrocatalyst and heattreatment effect on its electrocatalytic performance for methanol oxidation, Int. J. Hydrogen Energy 35 (2010) 313.
- [35] Y. Zhao, X. Yang, J. Tian, F. Wang, L. Zhan, Methanol electro-oxidation on Ni@Pd core-shell nanoparticles supported on multi-walled carbon nanotubes in alkaline media, Int. J. Hydrogen Energy 35 (2010) 3249.
- [36] R. Pattabiraman, Electrochemical investigations on carbon supported palladium catalysts, Appl. Catal. A 153 (1997) 9.
- [37] T. Suzuki, T. Yamada, K. Itaya, In Situ Electrochemical Scanning Tunneling Microscopy of Ni(111), Ni(100), and Sulfur-Modified Ni(100) in Acidic Solution, J. Phys. Chem. 100 (1996) 8954.
- [38] B.B. Nayak, S. Vitta, A.K. Nigam, D. Bahadur, Ni and Ni-nickel oxide nanoparticles with different shapes and a core-shell structure, Thin solid Films 505 (2006) 109.
- [39] W. Chen, Y. Zhang, X. Wei, Catalytic performances of PdNi/MWCNT for electrooxidations of methanol and ethanol in alkaline media, Int, J. Hydrogen Energy 40 (2015) 1154.
- [40] J.A.D. del Rosario, J.D. Ocon, H. Jeon, Y. Yi, J.K. Lee, J.Y. Lee, Enhancing Role of Nickel in the Nickel-Palladium Bilayer for Electrocatalytic Oxidation of Ethanol in Alkaline Media, J.Phys. Chem. C 118 (2014) 22473.
- [41] A. Dutta, J. Datta, Energy efficient role of Ni/NiO in PdNi nano catalyst used in alkaline DEFC, J. Mater. Chem. A 2 (2014) 3237.
- [42] P.K. Shen, C.W. Xu, Alcohol oxidation on nanocrystalline oxide Pd/C promoted electrocatalysts, Electrochem. Commun. 8 (2006) 184.
- [43] N. Arjona, M. Guerra-Balcázar, L. Ortiz-Frade, G. Osorio-Monreal, L. Álvarez-Contreras, J. Ledesma-García, L.G. Arriaga, Electrocatalytic activity of welldefined and homogeneous cubic-shaped Pd nanoparticles, J. Mater. Chem. A 1 (2013) 15524.
- [44] N. Hoshi, K. Kida, M. Nakamura, M. Nakada, K. Osada, Structural Effects of Electrochemical Oxidation of Formic Acid on Single Crystal Electrodes of Palladium, J. Phys. Chem. B 110 (2006) 12480.
- [45] C.A. López-Rico, J. Galindo-de-la-Rosa, J. Ledesma-García, L.G. Arriaga, M. Guerra-Balcázar, N. Arjona, Effect of pH in a Pd-based ethanol membraneless air breathing nanofluidic fuel cell with flow-through electrodes, J. Phys. Conf. Ser. 660 (2015) 012056.
- [46] A. Napoleao Geraldes, D. Furtunato da Silva, J.C. Martins da Silva, O.A. de Sá, E. Vitório Spinacé, A. Oliveira Neto, M. Coelho dos Santos, Palladium and palladium-tin supported on multi wall carbon nanotubes or carbon for alkaline direct ethanol fuel cell, J.Power Sources 275 (2015) 189.
- [47] S.Y. Shen, T.S. Zhao, J.B. Xu, Y.S. Li, Synthesis of PdNi catalysts for the oxidation of ethanol in alkaline direct ethanol fuel cells, J. Power Sources 195 (2010) 1001.
- [48] J. Goel, S. Basu, Effect of support materials on the performance of direct ethanol fuel cell anode catalyst, Int, J. Hydrogen Energy 39 (2014) 15956.
- [49] E.R. Choban, L.J. Markoski, A. Wieckoswki, P.J.A. Kenis, Microfluidic fuel cell based on laminar flow, J. Power Sources 128 (2004) 54.
- [50] R.S. Jayashree, L. Gancs, E.R. Choban, A. Primak, D. Natarajan, L.J. Markoski, P.J. A. Kenis, Air-Breathing Laminar Flow-Based Microfluidic Fuel Cell, J. Am. Chem. Soc. 127 (2005) 16758.
- [51] S.A. Mousavi Shaegh, N.-T. Nguyen, S.H. Chan, Air-breathing microfluidic fuel cell with fuel reservoir, J. Power Sources 209 (2012) 312.
- [52] J. Maya-Cornejo, E. Ortiz-Ortega, L. Álvarez-Contreras, N. Arjona, M. Guerra-Balcázar, J. Ledesma-García, L.G. Arriaga, Copper-palladium core-shell as an anode in a multi-fuel membraneless nanofluidic fuel cell: toward a new era of small energy conversion devices, Chem Commun. 51 (2015) 2536.
- [53] B. Zhang, D.-D. Ye, J. Li, X. Zhu, Q. Liao, Air-breathing microfluidic fuel cells with a cylinder anode operating in acidic and alkaline media, Electrochim. Acta 177 (2015) 264.
- [54] E.R. Choban, J.S. Spendelow, L. Gancs, A. Wieckowski, P.J.A. Kenis, Membraneless laminar flow-based micro fuel cells operating in alkaline, acidic, and acidic/alkaline media, Electrochim. Acta 50 (2005) 5390.
- [55] E. Kjeang, A.G. Brolo, D.A. Harrington, N. Djilali, D. Sinton, Hydrogen Peroxide as an Oxidant for Microfluidic Fuel Cells, J. Electrochem. Soc. 154 (2007) B1220.
- [56] A.E. Sanli, A. Aytac, Response to Disselkamp: Direct peroxide/peroxide fuel cell as a novel type fuel cell, Int. J. Hydrogen Energy 36 (2011) 869.

- [57] S. Hasegawa, K. Shimotani, K. Kishi, H. Watanabe, Electricity Generation from Decomposition of Hydrogen Peroxide, Electrochem. Solid-state Lett. 8 (2005) A119.
- [58] E. Ortiz-Ortega, M.P. Gurrola, L.G. Arriaga, J. Ledesma-García, A bendable and compact device for low-power application, J. Phys. Conf. Ser 660 (2015) 012054.
- [59] F.R. Brushett, R.S. Jayashree, W.-P. Zhou, P.J.A. Kenis, Investigation of fuel and media flexible laminar flow-based fuel cells, Electrochim. Acta 54 (2009) 7099.