Promoting Effect of Cu on Pd Applied to the Hydrazine Electro-Oxidation and Direct Hydrazine Fuel Cells

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Abstract: Use of liquid fuels in fuel cells is advantageous due to the easier and safer handling, transportation, and storage. Among the different options, hydrazine is of interest since the formation of highly poisoning carbonaceous species is avoided, in addition to its high energy density. In the search for more active direct hydrazine fuel cells (DHFC), this study analyzes the influence of Cu as an auxiliary metal on Pd. Three different PdxCu/C (x = 3, 1, and 0.33) catalysts were prepared by chemical reduction with NaBH4. The materials were physicochemically characterized by X-ray diffraction, energy-dispersive X-ray spectroscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy. Electrochemical analysis in a three-electrode glass cell and a single-cell DHFC was also carried out to study the impact on the electroactivity. Cu exerts a beneficial effect by reducing the adsorption energies of the adsorbed species and donating oxidized species for the completion of the hydrazine electro-oxidation, optimally balanced in the Pd1Cu/C (maximum power density of 180 mW cm−2). As a counterpoint, Cu slightly promotes the non-faradaic decomposition of hydrazine, seen by a larger H2 signal in mass spectroscopy in the anode exhaust at high current densities, which results in a slight loss in faradaic efficiency.

Keywords: electrocatalysis; alkaline; hydrazine electro-oxidation; palladium; copper; direct hydrazine fuel cells

1. Introduction

Fuel cells (FC) fed with liquid fuels are convenient alternatives to hydrogen. Advantages can be easily envisaged in terms of safer storage, handling, and transportation. Moreover, the already well-established oil and derivates infrastructure can be utilized [1–3]. Conventional liquid fuels used in FC are short-chain alcohols, especially methanol and ethanol, and, the shortest-chain organic acid, formic acid [4,5]. However, these fuels have serious limitations in electro-oxidation kinetics, due to the formation of strongly adsorbed carbonaceous species [6–8]. To overcome this shortcoming, non-carbon liquid fuels have been explored, among which hydrazine, sodium borohydride, ammonia, and borazane stand out, with similar or superior performances to those of carbon-based liquid fuel cells [1–3].

Hydrazine (N2H4) is an attractive non-C liquid fuel. Some strengths lie in its simple synthesis processes, which can be combined with the large-scale synthesis of ammonia [9], the low volatility compared to conventional C-based liquid fuels used in FC, non-flammability (in the hydrate form), and the feasible use in cold countries due to the low melting temperature [10]. Moreover, its electro-oxidation does not release greenhouse gases.
gases, exclusively forming N_2 gas, further avoiding the formation of the undesirable CO_ads species that severely poison the catalytic surface [11]. Hydrazine electro-oxidation reaction (HYEOR) is active in acidic and alkaline mediums. According to the thermodynamic data, the standard potential for HYEOR in alkali is −1.21 V vs. NHE, with a specific electrical capacity of 3.35 Ahg⁻¹. In combination with the oxygen reduction reaction, the standard cell potential difference corresponds to 1.56 V with an overall energy density of 5.36 Whg⁻¹ [12]. These theoretical bases comprise the advantages of the FC using hydrazine as fuel, in the so-called direct hydrazine fuel cells (DHFCs). Nevertheless, the challenge of developing high-performance HYEOR is very present in boosting the performance of DHFC.

Palladium is known to be a very active material for HYEOR and DHFCs in an alkaline medium [13–22], comparable to the reference Pt electrocatalyst [23]. Nevertheless, it is a very expensive noble metal with a limited abundance [24], which stimulates the search for alternatives to reduce the Pd loading. One approach is the addition of a second auxiliary non-noble metal [25,26] that promotes its specific activity, thus, permitting a decrease in the Pd loading. The synergic effects are attributed to the electronic alteration of Pd by the presence of the second metal (or oxide) and/or the bifunctional mechanism donating oxygenated species at low potentials [25]. One potential candidate is copper, an affordable and abundant material. In electrochemical terms, a previous work of this research group demonstrated the potential of Cu to promote the HYEOR activity of Pt, corroborated in a single-cell DHFC [27]. A recent study shows that CuPd alloy oxide is a promising material for HYEOR, as a result of the interaction between Cu and Pd, particularly in the oxide form [15]. PdCu-based electrocatalysts have been successfully used for alcohol oxidation, especially in an alkaline environment [28–34], based on the alteration of the adsorption energies (ligand effect) [35], and the donation of oxygenated species at earlier potentials (bifunctional effect) [36].

Based on these antecedents, this work aims at studying the promotional effect of Cu on Pd towards the HYEOR activity. For this, different PdₓCu/C (x = 3, 1, and 0.33) combinations were prepared by wet chemical reduction with sodium borohydride. The resultant materials were physically and morphologically characterized by energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) to gain physicochemical information to support the electrochemical results. Blank cyclic voltammograms (CV) to assess the electrochemical surface were carried out, followed by HYEOR voltammetries and chronoamperometries. Finally, single-cell DHFC tests were carried out to verify the actual performance of the electrocatalysts, accompanied by the monitoring of the formed HYEOR products. Accordingly, the efficiency of the materials was assessed.

2. Results and Discussion

The initial characterization begins with the estimation of the composition. Table 1 presents the total metal loading and atomic composition obtained from EDS, in addition to the comparison with the nominal composition. In general, metallic loadings are close to the nominal ones, except for Cu/C, in which the metallic loading is notably lower than the nominal one. Furthermore, the Pd proportion in the electrocatalysts is slightly larger than the nominal one. These observations can be explained in terms of the presence of copper oxides, whose anchorage on the carbon support might be partially hindered by the negative zeta potential of CuO in alkaline conditions [37] (catalysts were prepared at pH 12). Table 1 also collects the labels used for each bimetallic material hitherto.

Figure 1 shows the corresponding diffractograms of each material. As can be observed, PdC presents the typical face-centered cubic (fcc) diffraction peaks at 40.0°, 46.2°, 67.9°, 81.6°, and 86°, corresponding to the (111), (200), (220), (311), and (222) diffraction facets, respectively (JCPDS 46-1043). PdCu1C also presents these peaks, with a slight shift towards higher 2θ angles. This demonstrates the formation of a PdCu alloy. In the case of the PdCu2C, a decrease in the crystallinity is observed, along with a more intense shift towards higher angles, due to the incorporation of more Cu atoms into the Pd crystal lattice. Also,
peaks attributed to CuO (JCPDS 48-1548) start to emerge, especially those at 35.6 and 38.9°, corresponding to the (−111) and (200) diffraction planes, respectively. PdCu3C does not display the Pd fcc facets, very likely due to the formation of very small or amorphous Pd nanocrystals. Instead, the diffraction peaks of CuO stand out. Finally, CuC only presents the peaks associated with CuO at 35.6 and 38.9°, without any other evident crystalline orientation. From the XRD patterns, it can be inferred that, for the bimetallic materials, especially PdCu2C and PdCu3C, a large fraction of Cu deposited onto the carbon support is in the form of CuO.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metallic Loading</th>
<th>Pd:Cu Atomic Ratio</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>23</td>
<td>-</td>
<td>PdC</td>
</tr>
<tr>
<td>Pd3Cu/C</td>
<td>20</td>
<td>3.5 (nominal of 3)</td>
<td>PdCu1C</td>
</tr>
<tr>
<td>Pd1Cu/C</td>
<td>19</td>
<td>1.13 (nominal of 1)</td>
<td>PdCu2C</td>
</tr>
<tr>
<td>Pd0.33Cu/C</td>
<td>19</td>
<td>0.45 (nominal of 0.33)</td>
<td>PdCu3C</td>
</tr>
<tr>
<td>Cu/C</td>
<td>13</td>
<td>-</td>
<td>CuC</td>
</tr>
</tbody>
</table>

Table 1. Nominal and actual metal wt.% loading and Pd:Cu atomic ratio for the different electrocatalysts.

Figure 1. XRD patterns of the different electrocatalysts.

The average Pd crystallite size (d\textsubscript{XRD}) can be estimated from Scherrer’s Equation (1) for PdC, PdCu1C, and PdCu2C, where the Pd fcc crystal structure is more nitid. The parameter K is a particle-shape-dependent constant (0.9 for spherical particles), λ is the wavelength of the incident radiation (Cu K\textsubscript{α}), θ is the angle of the (hkl) peak, and β(2θ) is the width in radians of the diffraction peak at half height. Vegard’s law can be also applied to the PdCu1C and PdCu2C electrocatalysts (Equation (2) [38]), where \( a_{\text{PdCu}} \) represents the lattice parameter of the bimetallic material, \( a_{\text{Pd}} \) is the lattice parameter of Pd (0.3890 nm), \( a_{\text{Cu}} \) is the lattice parameter of Cu (0.3610 nm), and \( x_{\text{Cu}} \) is the Cu fraction in the PdCu alloy. Equation (3) can be used to estimate the Cu alloyed with Pd, where \( \text{Cu}_{\text{alloyed}} \) is the fraction of Cu in the alloy to the total amount of Cu, and Cu/Pd is the actual atomic ratio between the two metals.
Table 2 collects the corresponding average crystallite size, the fraction of Cu in the alloy composition \( \text{Pt}_{1-x} \text{Cu}_x \), and the fraction of total Cu integrated into the alloy. As can be seen, Cu partially alloys with Pd, forming a solid solution containing 15% of Cu for PdCu1/C and 19% for PdCu2/C. The slight increase in the fraction of Cu in the alloy in the PdCu2C compared to PdCu1C, despite doubling the amount of Cu in the overall formulation, is noticeable. The catalyst preparation in a medium containing water may somehow limit the formation of the PdCu solid solution in favor of the hydrolysis and consequent formation of the copper oxide. This also reflects on the reduced fraction of alloyed Cu for the PdCu1C. Finally, the addition of Cu to the catalyst formulation reduces the crystallite size. This phenomenon was already observed for PtCu electrocatalysts [27], and could be attributed to a protective effect of the negatively surface-charged CuO particles, which could limit the growth of the metallic crystals.

\[
\begin{align*}
\frac{d_{\text{XRD}}}{\text{nm}} &= \frac{K \lambda}{\beta_2 \cos \theta} \\
\alpha_{\text{PdCu}} &= x_{\text{Cu}}a_{\text{Pd}} + (1 - x_{\text{Cu}})a_{\text{Pd}} \\
\text{Cu}_{\text{alloyed}} &= \frac{x_{\text{Cu}}}{(1 - x_{\text{Cu}})}
\end{align*}
\]  

Table 2. Nominal and actual metal wt.% loading and Pd:Cu atomic ratio for the different electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( d_{\text{XRD}} ) (nm)</th>
<th>( d_{\text{TEM}} ) (nm)</th>
<th>Lattice Parameter (nm)</th>
<th>Alloy Composition</th>
<th>( \text{Cu}_{\text{alloyed}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdC</td>
<td>4.3</td>
<td>6.4</td>
<td>0.3890</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PdCu1C</td>
<td>3.0</td>
<td>5.3</td>
<td>0.3856</td>
<td>( \text{Pd}<em>{85}\text{Cu}</em>{15} )</td>
<td>0.59</td>
</tr>
<tr>
<td>PdCu2C</td>
<td>2.7</td>
<td>5.0</td>
<td>0.3845</td>
<td>( \text{Pd}<em>{81}\text{Cu}</em>{19} )</td>
<td>0.26</td>
</tr>
<tr>
<td>PdCu3C</td>
<td>–</td>
<td>4.8</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Figure 2 shows the TEM images of the catalysts. As can be seen, in the case of the PdC, small nanoparticles are combined with agglomerates, whereas the bimetallic materials present smaller particle sizes, due to the aforementioned protective role of copper. The CuC material displays almost imperceptible CuO nanoparticles. Table 2 collects the corresponding average particle size from the TEM images.

Figure 3 shows the main information that can be withdrawn from the XPS spectra. These are shown in the Supplementary Material (Figure S1). The surface atomic composition is presented in Figure 3a, whereas the “bulk” (EDS) vs. surface (XPS) Pd/Cu atomic ratio is displayed in Figure 3b, and the ratio between the oxidation state of each metal, along with the Pd 5d_{5/2} binding energy, is presented in Figure 3c. As can be observed, the surface composition shows the expected growth in the proportion of Pd/Cu as the loading of Cu increases. One interesting feature is the enrichment in the Pd of the surface compared to the “bulk” composition. One possible explanation is a galvanic replacement effect of Pd onto some Cu nanoparticles formed during the reduction process, leading to an enriched Pd surface [39]. This effect could be expected to be more intense the higher the Pd/Cu ratio is, as indeed is observed in the experimental results (Figure 3b). The oxidation state of the outermost atoms reveals (Figure 3c), in the case of Pd, a predominance of PdO. The superficial Cu is almost completely in the form of CuO, with a reduced percentage of Cu\(^0\)/Cu\(_2\)O (5.8% for PdCu1C and 1.4% for PdCu2C). Some reasons behind this could be the labile nature of Cu to oxidize in the air environment, the presence of water in the reduction medium, inducing the formation of CuO, and, also, the mentioned galvanic displacement that could further stimulate the formation of superficial CuO. Finally, a very important result relies on the binding energy of the Pd 3d\(_{3/2}\), which decreases for the bimetallic material, with a minimum for the PdCu2C. Such a downshift of the binding
energy evidences the electronic effect of Cu on the outermost Pd atomic layers, whose effect is discussed in the electrochemical performance.

Figure 2. Cont.
Figure 2. TEM images of the different electrocatalysts: (a) PdC; (b) PdCu1C; (c) PdCu2C; (d) PdCu3C; and (e) CuC ((a2–e2) correspond with higher magnification micrographs compared to (a1–e1)).

Figure 3. (a) Surface atomic composition of the different catalysts; (b) surface vs. bulk Pd/Cu atomic ratio for the bimetallic materials; and (c) proportion of the oxidation state of each metal and Pd 3d_{5/2} of each catalyst and Pd 3d_{5/2} binding energy for the Pd-based catalysts.
Blank CVs are presented in Figure S2. In overall terms, PdCu1C and PdCu2C display similar shapes to PdC. Only the PdCu2C shows a current increase in the region of formation of PdO ($\approx -0.05$ V vs. MMO), attributed to the interference coming from the formation of Cu(II) species (Cu$_2$O and Cu(OH)$_2$). As expected, PdCu3C shows a more intense peak in the combined PdO/CuO formation region. In the anodic scan, CuC shows a first tiny peak associated with the Cu$_2$O formation and a second intense one attributed to the formation of CuO/Cu(OH)$_2$. Given that the blank voltammogram of Cu does not show a relevant signal in the cathodic scan associated with the reduction of CuO, we tentatively used the PdO reduction peak to estimate the electrochemically active surface area (EASA, Table S1) to be used for normalization of the HYEOR voltammograms, aiming at minimizing any eventual particle size effect.

Figure 4a,b show the corresponding HYEOR linear sweep voltammetry (LSV) profiles. As can be observed, Cu promotes the HYEOR activity compared to the monometallic PdC. The beneficial role of Cu can be explained in terms of the electronic effect that Cu exerts on Pd. The decrease in the binding energy is associated with a transfer of electrons from Cu to Pd, due to the higher electronegativity of Pd (2.2) compared to Cu (1.9), as observed in the literature [40–42]. The filling of the Pd 3d band reduces the adsorption energy of any eventual species onto the surface Pd sites [42–44], favoring the dissociative adsorption steps of hydrazine onto Pd to form the active H$_{ads}$ and N$_2$H$_4$$_{ads}$ species for the complete hydrazine electro-oxidation [17,45] (electronic effect). Furthermore, the complete oxidation in the alkaline medium requires OH$_{ads}$ species, which could be further provided by the oxidized Cu surface in the bimetallic material (bifunctional mechanism). The most balanced composition combining the electronic and bifunctional effects corresponds to the almost equiatomic PdCu2C. The EASA normalized curves (Figure 4b), in which the intrinsic electrochemical activity can be better seen, also confirm the best performance of the PdCu2C. As can be observed, the inclusion of Cu promotes the HYEOR activity, with an optimum value for the PdCu2C (almost equiatomic composition). The intensity of the electronic and bifunctional effects is smaller in the PdCu1C, whereas the excess of Cu (CuO) in the PdCu3C hinders the electrochemical activity. Also, the chronoamperometric curves, shown in Figure S3, corroborate the promotional effect of Cu onto Pd, as well as the largest activity of the PdCu2C catalyst.

![Figure 4](image_url)

**Figure 4.** HYEOR linear sweep voltammograms profiles of the catalysts in 1 mol L$^{-1}$ N$_2$H$_4$ and 1 mol L$^{-1}$ KOH normalized to: (a) mass of Pd; and (b) EASA of Pd.

Figure 5 shows the polarization curves (Figure 5a the cell voltage and Figure 5b the power density) for the DHFC operation at 60 °C. The polarization curves and the
power density confirm the tendencies observed in the three-electrode glass cell studies. The PdCu2C electrocatalyst emerges as the most adequate Pd:Cu ratio (maximum power density of 180 mW cm\(^{-2}\) vs. 95 mW cm\(^{-2}\) for PdC), where the electronic effect is more intense, thus, favoring the HYEOR, combined with a large fraction of surface copper oxide that assists in providing the required oxygenated species. The large fraction of CuO on the surface of the PdCu3C limits the performance to the point of having a smaller maximum power density compared to PdC. CuC, despite the expected lower activity, can achieve a maximum power density of approximately 30 mW cm\(^{-2}\), confirming the possibility of using non-noble metals for DHFC.

![Figure 5](image)

**Figure 5.** (a) Cell voltage and; (b) power density curves for the different electrocatalysts in a DHFC at 60 °C (anode: 1 mol L\(^{-1}\) hydrazine and 4 mol L\(^{-1}\) KOH, cathode: 30 mL min\(^{-1}\) O\(_2\); electrolyte: KOH-doped polybenzimidazole).

One important aspect of DHFC is the study of parasitic parallel reactions coming from the hydrazine decomposition, displayed in reactions four and five (reaction six is the HYEOR). Figure 6 shows the corresponding \(m/z\) signals of N\(_2\), NH\(_3\), and H\(_2\) from the mass spectrometer coupled to the DHFC. As expected, the most notable signal corresponds to N\(_2\) from the hydrazine (electro)-oxidation. The signal intensity proportionally increases the higher the current density. Despite the fact that the \(m/z = 28\) signal could be majorly attributed to N\(_2\), it cannot be neglected as a minor contribution coming from the CO produced by the carbon corrosion, as observed by Maillard et al. [46]. The authors reported the corrosion of the carbon support, mostly in the metal/carbon interface from the combination of the carboxylic groups of the carbon support and the H-groups in the metal surface, despite operating at low anode potential. To verify the parallel reaction 5, the signal of NH\(_3\) is monitored, with no apparent change, indicating that the N\(_2\)H\(_4\) decomposition to NH\(_3\) does not happen in this system. In the case of hydrogen, the signal does not vary except for the experiment at 400 mA cm\(^{-2}\), where hydrogen is detected.

\[
\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 2\text{H}_2 \quad (4)
\]

\[
3\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{NH}_3 \quad (5)
\]

\[
\text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + 4\text{e}^- \quad (6)
\]
Figure 6. Mass spectra of the anode exhaust for N₂ (m/z = 28), NH₃ (m/z = 17) and H₂ (m/z = 2) for different current densities (first column corresponds to PdC and the second column to PdCu2C).
Such non-faradaic hydrogen comes from reaction 4, from the hydrazine decomposition. The surge of this hydrogen at high current density could be considered unexpected, since we may think that the non-faradaic routes should be favored in open circuit voltage or low current density conditions. One tentative explanation lies in the HYEOR mechanism in the alkaline medium, described by Korovin and Yanchuk [17], where $H_{ads}$ species are formed. In the electrochemical route, these $H_{ads}$ react with $OH^-/OH_{ads}$ to form $H_2O$ as the final product. At high current densities, the $H_{ads}$ coverage could be expected to be large, which may not only induce the electrochemical pathway, but also the non-faradaic route with the formation of $H_2$ by the combination of two adjacent $H_{ads}$. It is interesting to note that the addition of copper leads to a slight increase in the detected amount of $H_2$. One possible reason is the electronic effect induced by Cu, which reduces the adsorption strength of the adsorbed species. This may favor the recombination of $H_{ads}$ to form the $H_2$ molecule.

Thus, based on the combination of the physicochemical and electrochemical characterizations, it is evident that Cu exerts several beneficial effects that, nevertheless, must be adequately balanced: (1) an electronic effect that accelerates the HYEOR due to the weaker adsorption of the species formed during the HYEOR; (2) a likely bifunctional effect, providing the oxygenated species required in the HYEOR; and (3) an apparent protective role, allowing the obtainment of smaller nanoparticles the higher the Cu loading. The most equilibrated summation of these three effects is achieved for PdCu2C (almost equiatomic composition).

3. Materials and Methods

The electrocatalysts PdC, CuC, PdCu1C, PdCu2C, and PdCu3C (nominal metal loading of 20 wt.%) were prepared by chemical reduction with borohydride (NaBH$_4$, Neon, Suzano, Brazil), using K$_2$PdCl$_4$ (Sigma Aldrich, São Paulo, Brazil) and CuCl$_2$·2H$_2$O (Synth) as metal sources, 2-propanol (Synth, Diadema, São Paulo) and ultra-pure water (Milli-Q, Millipore) as solvents, and carbon black (Vulcan XC-72R, Cabot Corp., Alpharetta, GA, USA) as support. In all the cases, a mass of 250 mg of 20 wt.% metal on carbon was prepared. For this, the required amounts of precursors, K$_2$PdCl$_4$ and CuCl$_2$, were accordingly weighted and dissolved in 100 mL of a mixture formed by water and isopropanol in an 80:20 volume proportion. Next, carbon was added and ultrasonicated to be homogeneously dispersed in the reaction medium. The final preparation step is the chemical reduction of the precursors with NaBH$_4$, added in a 5:1 (molar basis) excess referred to as metallic loading. The borohydride is dissolved in 5 mL of a NaOH solution with the pH fixed at 12, to minimize its hydrolysis. Finally, the obtained solid was filtered, washed with ultra-pure water, and dried at 70 °C for 2 h.

The Pd:Cu atomic ratios of electrocatalysts were measured by energy-dispersive X-ray (EDX, Peabody, MA, USA) analysis using a JEOL 2100 scanning electron microscope with a 15 keV electron beam. X-ray diffraction analyses were performed in a Bruker model D8 Focus diffractometer using Cu K$_\alpha$ radiation ($\lambda$ = 0.15406 nm). The diffractograms were recorded with 2θ angles in the range of 20 to 90° (0.05° step, 0.5° min$^{-1}$).

TEM analysis was performed using a JEM 2100 microscope operating (Tokyo, Japan) at 200 kV with a point-to-point resolution of 0.19 Å. The particle size distribution was estimated from observations of at least 300 particles in different images. The average particle size, $D$, was calculated according to Equation (7), where $n_i$ represents the number of particles of diameter $D_i$. The sample holder was composed of a gold grid covered by Lacey carbon (EMS).

$$D = \frac{\sum n_i D_i}{\sum n_i}$$ (7)

XPS measurements were carried out using a Physical Electronics (PHI) 5800-01 spectrometer (Chanhassen, MN, USA). A monochromatic AlK$_\alpha$ X-ray source was used at a power of 350 W. Spectra were obtained with pass energies of 58.7 eV for elemental analysis and 11.75 eV for determination of the oxidation states. The pressure in the analysis chamber
of the spectrometer was $10^{-9}$ Torr during measurements. The Ag 3d$_{5/2}$ peak of an Ag foil was used, after argon sputtering, to check the calibration of the binding energy scale. Quantitative evaluation of each peak was performed by dividing the integrated peak area by atomic sensitivity factors, which were calculated from the ionization cross-sections, the mean free electron escape depth, and the measured transmission functions of the spectrometer. XPS data were interpreted by using the online library of oxidation states implemented in PHI MultiPak 6.1 software (Chanhassen, MN, USA, 1999) and the PHI Handbook of X-ray photoelectron spectroscopy.

The electrochemical measurements were carried out in a three-electrode cell using a platinized Pt gauze as the counter electrode, an Hg/HgO/KOH electrode as the reference electrode, and a reticulated vitreous carbon (RVC) working electrode (area of 0.785 cm$^2$), using a £-Autolab (model Type III) potentiostat/galvanostat coupled to a personal computer with the general-purpose electrochemical system (GPES) software. Electrochemical studies of the electrocatalysts were performed using the ultra-thin coating technique. A mass of 1 mg of the electrocatalyst was dispersed in 1 mL of 2-propanol with 10 µL of Nafion® emulsion (5 wt.% in a mixture of aliphatic alcohols, IonPower (New Castle, DE, USA). The mixture was sonicated for 10 min; then, with the aid of a chromatographic syringe, 20 µL of the dispersion was transferred to the surface of the previously polished RVC electrode. Cyclic voltammetry measurements were performed in a 1.0 mol L$^{-1}$ KOH solution at a scan rate of 10 mV s$^{-1}$. The study of HYEOR was performed at room temperature by LSV (same scan rate) and chronoamperometry (for 30 min) at 0.024 V versus Hg/HgO in a solution of 1.0 mol L$^{-1}$ hydrazine and 1.0 mol L$^{-1}$ KOH. The results were normalized to the mass of Pd, and, as described in the Supplementary Material, to the EASA.

For the single-cell DHFC tests, the electrodes were first prepared by brush-painting a catalytic slurry onto a carbon cloth (Zoltek PX30, Bridgeton, MO, USA) diffusion layer. The ink was prepared by mixing the required mass of the catalyst, the Nafion® emulsion (a mass of 10 wt.% of the catalyst mass), and 2-propanol as the solvent and dispersing agent. In the anode, the prepared Pd-based materials were used as anodes, completing a Pd loading of 0.5 mg cm$^{-2}$, whereas in the cathode, 20 wt.% Pt/C (BASF) using a Pt loading of 1 mg cm$^{-2}$. The polymeric membrane was a KOH-doped polybenzimidazole membrane (Dapozol from Danish Power Systems, Lyngby, Denmark), immersed in 4 mol L$^{-1}$ for one week to guarantee its impregnation. Electrical performances were determined from polarization and power density curves at 60 °C. The fuel was delivered at 1 mL min$^{-1}$ through the anode and pure oxygen flow was regulated at 30 mL min$^{-1}$ for the cathode. The exhaust products were monitored with the aid of a mass spectrometer (MS, Dymaxion MS, Ametek, Newark, NJ, USA). The liquid solution was returned to a completely sealed fuel reservoir, which was constantly purged with a soft stream of argon. This gas was used to drag the formed exhaust gases to the MS. The chosen mass/charge rations ($m/z$) were 28 for N$_2$ (N$_2^+$), 17 for NH$_3$ (NH$_3^+$), and 2 for H$_2$ (H$_2^+$). A scheme of the experimental setup is shown in Figure S4.

4. Conclusions

This study demonstrates that Cu, in an adequate proportion, can exert a positive effect on Pd for HYEOR. First, its presence, to some extent, is capable of limiting the growth of the Pd nanoparticles, resulting in a decrease in the average particle size of the bimetallic materials compared to PdC. Also, Cu inserts itself within the crystal structure of Pd, forming an alloy. This directly impacts the electronic properties of Pd, reducing the adsorption strength of the adsorbed species, and, finally, the most external layer of Cu is in the form of oxide. Thus, it becomes a source of oxygenated species to complete the HYEOR. The most equilibrated Pd:Cu ratio is attained for the PdCu2C (1.13), in which the electronic effect is the most intense without a too large fraction of copper oxide. Such effects reflect on the maximum performance of this material in the DHFC, almost doubling the monometallic PdC. As a counterpoint, the addition of Cu at high current densities slightly
induces the non-faradaic production of H₂, very likely from the recombination of H⁺ads species produced in the initial stages of the HYEOR.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12121639/s1, Figure S1: XPS spectra of the different electrocatalysts in the regions of Pd 3d and Cu 2p; Figure S2. Blank cyclic voltamograms of the catalysts in 1 mol L⁻¹ KOH; Figure S3. HYEOR chronocoulometric curves for the different electrocatalysts in 1 mol L⁻¹ N₂H₄ and 1 mol L⁻¹ KOH at 0.024 V vs. MMO; Figure S4. Experimental setup used to detect the HYEOR products; Table S1. EASA of the different electrocatalysts. References [47–49] are cited in Supplementary Materials.


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**Data Availability Statement:** The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**


