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Synthesis and performance of PdAu/ITO electrocatalysts in urea oxidation reaction

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ABSTRACT

PdAu electrocatalysts were prepared in different atomic compositions supported on ITO by sodium Borohydride process. XRD results show intense crystalline peaks related to ITO, which may mask the appearance of less crystalline Pd or Au phases. Transmission results indicate agglomeration of palladium and gold nanoparticles on the support, a phenomenon compatible with metal oxide supports. Cyclic voltammograms in the absence of urea display characteristics commonly observed for PdAu electrodes, with an increase in oxygenated species compared to pure Pd or Au. Voltammograms in the presence of urea showed oxidation processes and lower current values, indicating catalyst deactivation processes. PdAu 75:25 demonstrated higher power density values compared to other prepared electrocatalysts, suggesting a synergy between Pd and Au for urea oxidation reaction.

1. Introduction

In recent years, the demand for energy sources has increased significantly, driving the search for cleaner and more efficient alternatives. Proton Exchange Membrane (PEM) fuel cells have been proposed as one such alternative to fossil fuels, operating by oxidizing hydrogen at the anode and reducing oxygen at the cathode. However, hydrogen presents challenges in terms of storage and transportation, as it requires extreme conditions, raising safety concerns. To address these issues, liquid fuels have emerged as a more practical option. Among them, urea has gained attention due to its stability, non-flammability, and abundance, offering advantages over traditional hydrogen carriers such as ethanol, methane, and methanol [1].

Urea is considered a promising fuel for PEM fuel cells because it is widely available, cost-effective, and can be converted into nitrogen, carbon dioxide, and water through chemical reactions. Additionally, urea can be sourced from household waste, reducing waste and providing useful resources for agriculture. These attributes make urea an appealing option for sustainable energy production [2]. However, one key challenge in the development of direct urea fuel cells (DUFCs) is the slow reaction kinetics at the anode, which has limited the technology's broader adoption [3,4]. The performance of DUFCs is closely tied to the efficiency of the electrode materials used.

Traditionally, anode materials for DUFCs have been made from rare and precious metals like Ru, Pt, Au, and Pd. However, recent research suggests that nickel could improve urea oxidation reaction due to its high stability, abundance, and low cost [5,6]. Many studies on urea oxidation focus on nickel, but the potentials involved in urea oxidation reaction with nickel are quite high (>1.6 V versus the hydrogen reference electrode). At these high potentials, other reactions, such as urea electrolysis and oxygen evolution, can occur instead of urea oxidation. As a result, further studies involving noble metal catalysts are essential to fill gaps in the literature, which often present cyclic voltammetry results without reflecting the actual conditions within fuel cells [6–10].

Research on urea oxidation reaction in alkaline electrolyte has shown that platinum electrocatalysts outperform other pure metals. Notably, binary Pt electrocatalysts have demonstrated significant catalytic activity improvements. Gold is also of interest, as it shows considerable activity in alkaline media and is an effective catalyst for ethanol oxidation when alloyed with Pt or palladium. Palladium, being more abundant than platinum in the Earth's crust, has also proven effective in oxidizing ethanol and formic acid in alkaline conditions [11–13]. Carbon, commonly used as a catalyst support material, is prone to corrosion in alkaline environments.

To address potential corrosion issues, some metal oxides are used as supports, such as TiO_2, Antimony Tin Oxide (ATO), and Indium Tin Oxide (ITO), which would not be affected by phase changes. Among these candidates, ITO is particularly interesting because, in addition to

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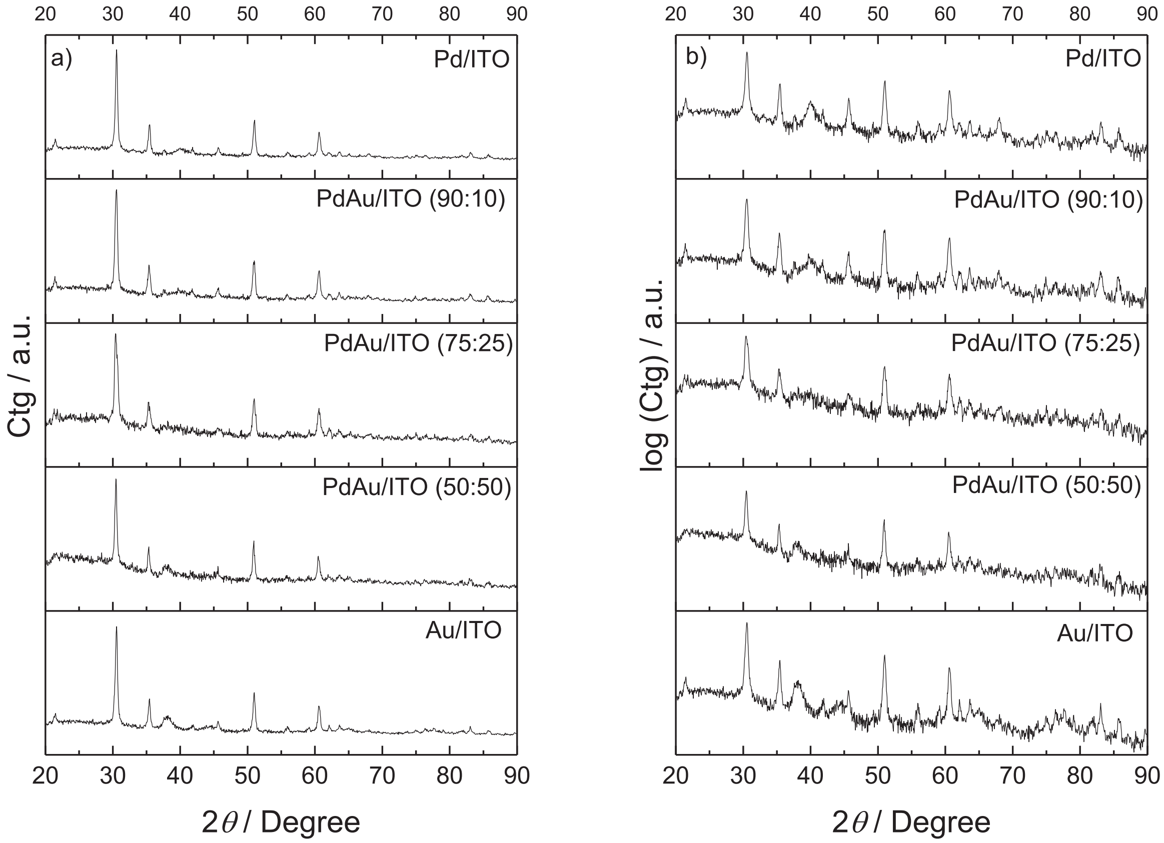

Fig. 1. a) X-ray diffractogram (XRD) pattern of Pd/ITO, PdAu/ITO (90:10), PdAu/ITO (75:25), and PdAu/ITO (50:50) and Au/ITO electrocatalysts. b) logarithm of the intensities from Fig. 1a).

serving as a support, it is also active in oxidation reactions in alkaline media [14].

In this study, we introduce a novel electrocatalyst composed of palladium-gold (PdAu) with varying atomic compositions, supported on indium tin oxide (ITO), for urea oxidation reaction. The PdAu/ITO electrocatalysts were prepared using a chemical reduction method with sodium borohydride. This approach not only enhances urea oxidation reaction efficiency but also demonstrates improved performance and stability of electrocatalysts in alkaline media.

2. Experimental

Indium tin oxide (ITO) was used as a support material for PdAu electrocatalysts, synthesized with atomic compositions of 90:10, 75:25, and 50:50 (Pd:Au) via a sodium borohydride reduction process. Chloroplatinic acid and gold chloride served as precursor agents for palladium and gold, respectively. Sodium Borohydride (NaBH4 – Aldrich) was used as a reducing agent and Vulcan Carbon (XC72) was the support. In the reduction step, the support and the metal sources were dissolved in a mixture of water/2-propanol 50/50 (v/v), later the solution content Sodium Borohydride in excess with 10 mL 0.01 mol. L-1 of KOH was added. The obtained catalysts were washed with water and dried at 70°C for 2 h with vacuum filtered.

Transmission electron microscopy (TEM) was performed using a JEOL JEM-2100 microscope operating at 200 keV, and histograms were constructed from measurements of 300 nanoparticles per electrocatalyst. X-ray diffraction (XRD) analysis was carried out on a Rigaku Miniflex II diffractometer using CuKα radiation ($\lambda = 1.5406$ Å) over the range of 20° to 90° at a scan rate of 2° min^{-1}.

Electrochemical studies were conducted using a three-electrode setup connected to a PGSTAT 302N potentiostat/galvanostat (Metrohm Autolab B.V.). The working electrode was prepared by depositing a thin porous layer of the catalytic material onto a vitreous carbon substrate. The catalytic layer was formed from a colloidal suspension containing 8.00 mg of the electrocatalyst precursor, 600.0 μL of deionized water (resistivity > 18.2 MΩ·cm at 298.15 K), 400.0 μL of anhydrous isopropanol (99.9 % purity), and 15.0 μL of Nafion® solution (D-520 dispersion, 5 % w/w in lower aliphatic alcohols and water). The suspension was homogenized using ultrasonication for 30 min, then deposited onto the carbon substrate and dried. An Ag/AgCl electrode (3.0 mol L^{-1} KCl) was used as the reference, and a platinum plate electrode (surface area: 2.00 cm^{2}) served as the counter electrode. The electrolyte solution was 1.0 mol L^{-1} NaOH and 1.0 mol L^{-1} NaOH + 1.0 mol L^{-1} urea. Cyclic voltammetry was performed at a scan rate of 10.0 mV s^{-1} within a potential window of −0.85 V to +0.30 V (vs. Ag/AgCl). Voltammetric measurements were taken in the presence and absence of urea.

Direct urea fuel cell performance was evaluated using PdAu/ITO as the anode and Pt/C as the cathode. The cell configuration consisted of carbon-cloth electrode substrates treated with Teflon (W0S1011 Fuel Cell Store), and a Nafion® 117 membrane as the electrolyte. The anode and cathode were thermally pressed onto the Nafion® membrane at 125°C for 300 s 225 kgf cm^{-2}. Each anode electrode contained 1.0 mg Pd cm^{-2}, and the cathode contained 1.0 mg Pt cm^{-2}. The urea solution was fed at a flow rate of 1.0 mL min^{-1}, while oxygen was supplied at 200 mL min^{-1}. Polarization curves were recorded at room temperature in the presence of 1.0 M urea and 1.0 M NaOH, using the PGSTAT 302 N potentiostat/galvanostat to assess the electrochemical performance of the fuel cell. The method for preparing the diffuser layer and the catalytic layer was developed in our laboratory.

3. Results and discussions

Fig. 1a shows the X-ray diffractograms obtained for the Au/ITO, Pd/

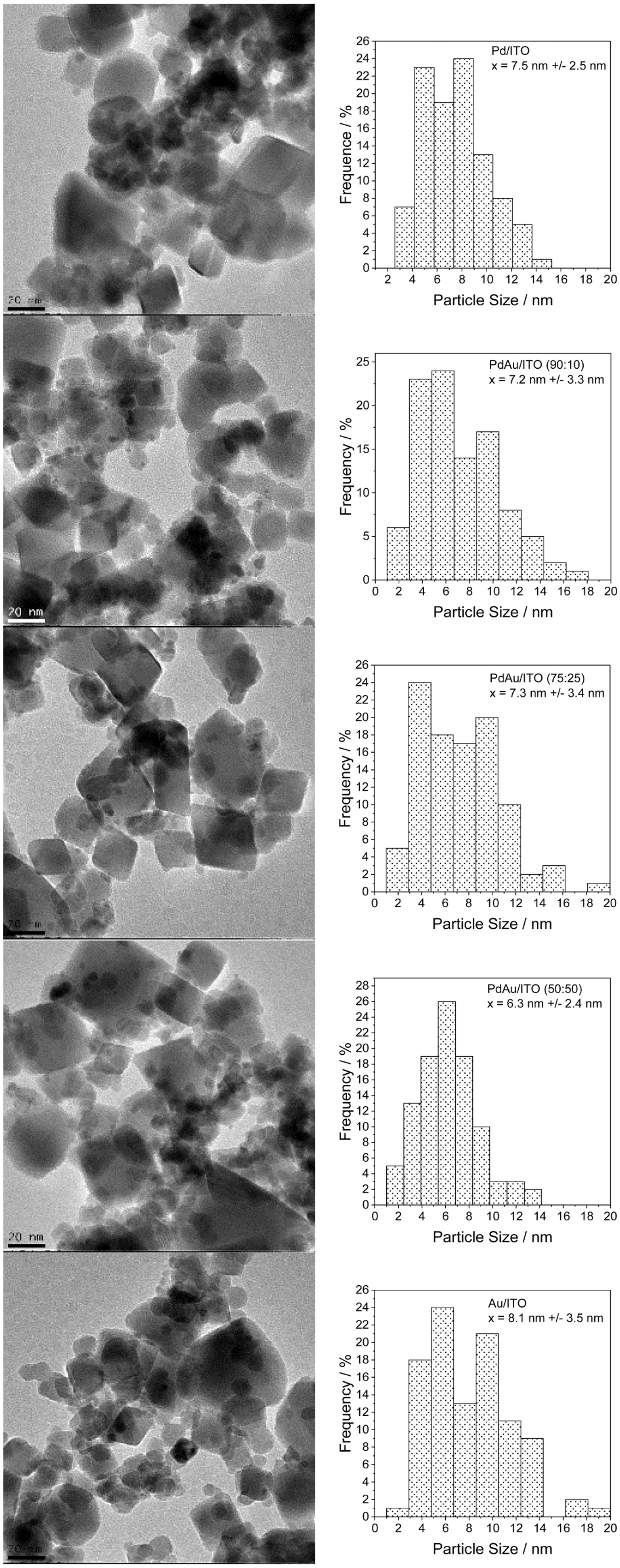

Fig. 2. TEM Micrograph Images and Particle Size Distribution Histograms for Pd/ITO, PdAu/ITO (90:10), PdAu/ITO (75:25), and PdAu/ITO (50:50) and Au/ITO electrocatalysts.

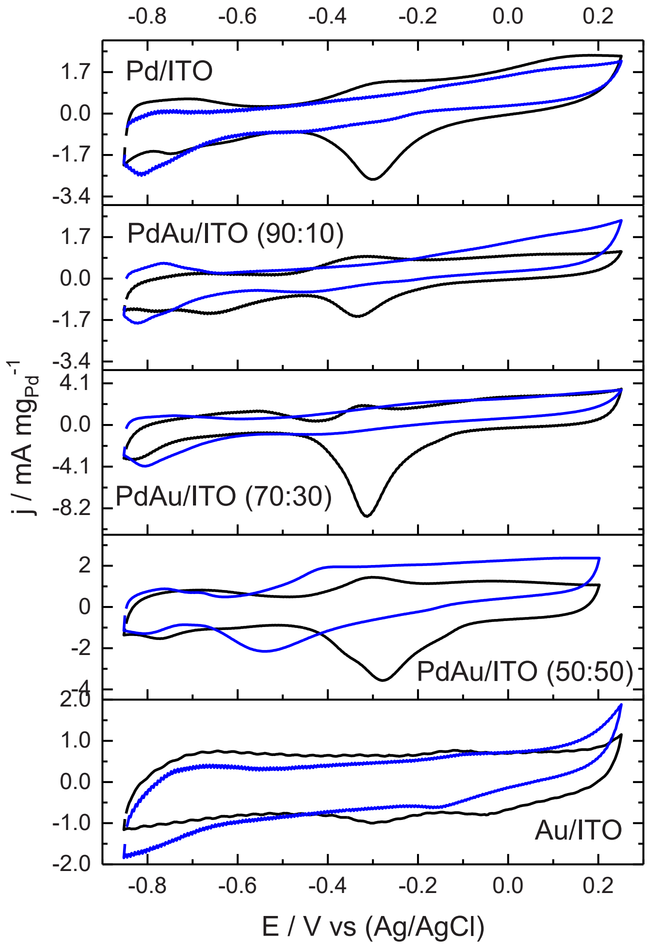

Fig. 3. Cyclic voltammetry in 1 mol/L of NaOH for Au/ITO, Pd/ITO, PdAu/ITO (90:10), PdAu/ITO (75:25), and PdAu/ITO (50:50) catalysts prepared via sodium borohydride reduction in the absence (black) and in presence of urea 1 mol L-1 (blue) in solution at 10 mv s^{-1}.

ITO, PdAu/ITO (90:10), PdAu/ITO (75:25), and PdAu/ITO (50:50) electrocatalysts prepared via sodium borohydride reduction. The pattern obtained for all materials is predominantly that of ITO (JCPDS #89-4598), with 2θ = 31°, 36°, 45° 51°, 55° and 60° corresponding to the (222), (400), (440), and (622) planes, respectively [15]. To observe the peaks related to the noble metals, it was necessary to take the logarithm of the intensities from the original diffractograms (Fig. 1b).

In Fig. 1b, the Pd/ITO, PdAu/ITO (90:10), and PdAu/ITO (75:25) materials exhibit the characteristic peaks of palladium at 39° and 67°, with the peak definition decreasing as the Pd content (JCPDS # 89–4897) in the materials decreases. For PdAu/ITO (50:50), these peaks are almost imperceptible. Nandenha et al. [16] showed for Pd electrocatalysts peaks about 2θ ≈ 40º, 47º, 68º, 82º and 87º associated, respectively, to (111), (200), (220), (311) and (222) planes of Pd (JCPDS # 89-4897) with face-centered cubic (FCC) structure, for gold, as evidenced by the convolution of the peak corresponding to the 222 plane of ITO, centered around ~36°, with the peak corresponding to the 222 plane of gold (JCPDS #01–1172) at 38°.

Fig. 2 illustrates the transmission electron microscopy (TEM) images and their respective histograms for the Au/ITO, Pd/ITO, PdAu/ITO (90:10), PdAu/ITO (75:25), and PdAu/ITO (50:50) electrocatalysts prepared via sodium borohydride reduction.

The broad size distribution of particles, approximately ~7.5 nm, was observed in the Pd/ITO catalyst, with the largest size (8.17 nm) found in Au/ITO the catalyst. This variability in particle size suggests differences in the nucleation and growth processes during synthesis. The

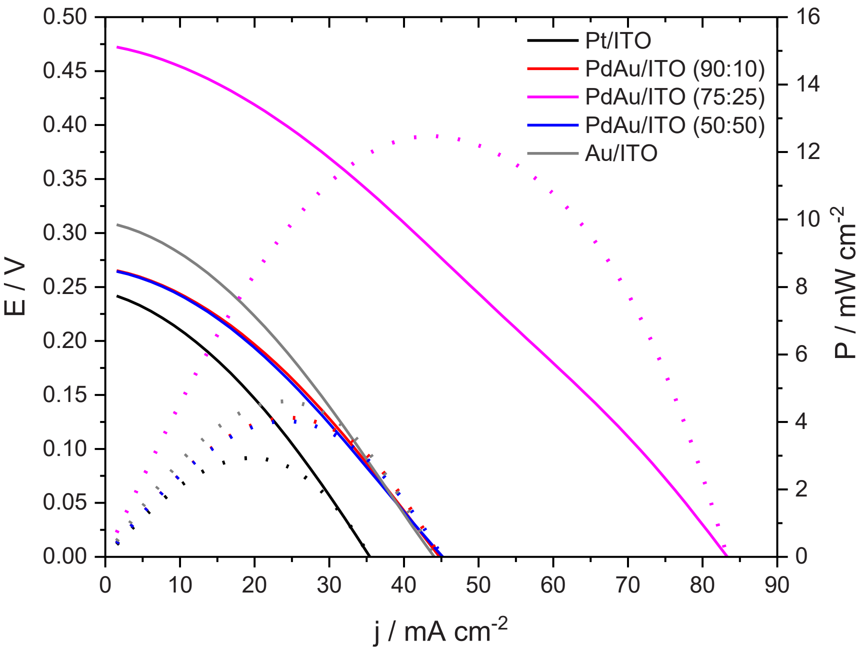

Fig. 4. Direct urea fuel cell experiments for Au/ITO, Pd/ITO, PdAu/ITO (90:10), PdAu/ITO (75:25), and PdAu/ITO (50:50) electrocatalysts. Flow = 1 mL min 1 of a 1 mol solution of NaOH in the presence of 1.0 mol L 1 of urea. The cathode was maintained under an oxygen flow of 150 mL min 1. Cell operating room temperature. Humidifier bottle temperature = 85 ∘C.

aggregation of nanoparticles often indicates a tendency for particles to coalesce, which can be influenced by factors such as the deposition method, the nature of the support material, and the interaction between the catalyst particles and the metal oxide substrate. The presence of agglomerated nanoparticles is particularly significant in the context of metal oxide supports, as these supports can influence the distribution and dispersion of the active catalyst particles. In materials richer in Pd, the nanoparticles are poorly dispersed on the support [17–19], likely because palladium ions tend to deposit in locations that result in a greater decrease in surface free energy, leading to a more stable system and promoting the formation of crystals at edges and defects.

Fig. 3 presents the voltammograms of PdAu materials supported on ITO, both with and without urea. It is observed that, in the absence of urea, the profile is similar to that of comparable materials supported on carbon [20], featuring the hydrogen adsorption and desorption region on Pd (−0.85 to −0.55 V). This region shows a decrease in both definition and intensity with the increasing gold content in the composition. Additionally, a broadening of the PdO reduction peak is noted, attributed to the convolution with the ITO reduction process. This effect is particularly prominent in the PdAu/ITO (50:50) and Au/ITO materials.

The addition of urea to the solution alters the profile of all the materials. In the Pd-rich materials (Pd/ITO, PdAu/ITO (90:10), and PdAu/ITO (75:25), the oxidation and reduction peaks are suppressed, and there is an increase in the definition of the hydrogen adsorption and desorption region, which may indicate a strong urea adsorption process. However, in the case of PdAu/ITO (50:50) and Au/ITO, urea oxidation reaction profile becomes evident, and a decrease in the peak definition is observed, along with a slope in the voltammogram, suggesting an increase in the electrochemistry system's resistivity. The cyclic voltammetry results show that urea can, to some extent, adsorb onto palladium sites in palladium-rich electrocatalysts. This can be observed by the increase in current in the hydrogen adsorption region, while gold could aid in water activation at higher potential values.

Yoon et al. [8] demonstrated that urea oxidation reaction on nickel in an alkaline medium leads to the formation of carbonates, which deactivates the electrocatalyst and reduces its active surface area. A potential alternative is the use of noble metals such as Pd or Pt, which could enhance urea oxidation, as observed in the voltammograms of Pd- and Au-based materials on ITO.

Fig. 4 shows the current density/voltage and current density/power density plots for the direct urea fuel cells with Au/ITO, Pd/ITO, PdAu/ITO (90:10), PdAu/ITO (75:25), and PdAu/ITO (50:50). anode electrocatalysts.

The PdAu/ITO (75:25) electrocatalyst exhibited the highest open circuit potential (0.47 V) compared to the other prepared electrocatalysts, which showed approximately 0.32 V for Au/ITO, 0.27 V for PdAu/ITO (90:10), 0.27 V for PdAu/ITO (50:50), and 0.24 V for Pd/ITO. The maximum power density was also observed for the PdAu/ITO (75:25) electrocatalyst, indicating a beneficial effect of adding gold to palladium. This enhanced performance can be attributed to the synergy between the elements in the electrocatalyst, likely due to electronic effects and a bifunctional mechanism. In cyclic voltammetry, a shift in the oxide reduction peaks was observed, which could be explained by the formation of an alloy between Pd and Au, as no such process was observed for pure gold in the studied potential range. The bifunctional mechanism may also be supported by the increased presence of oxygenated species in the PdAu catalysts.

The expected potentials for urea oxidation reaction in fuel cells should be around 1.0 V. values lower than this suggest that the catalysts are poisoned under the cell's operating conditions. Another possible mechanism could involve the activation of water and the potential formation of reactive oxygen species, which may contribute to the partial oxidation of urea. The activation of water can also result in the formation of hydroxyl radicals. These radicals can react with conventional supports, leading to corrosion, then one way to address this issue is the use of ITO, which is a material that improves the corrosion resistance of the electrocatalyst.

Therefore, the power densities observed in urea-fed fuel cells could arise from intermediates formed by these species. Nandenha et al. [21] demonstrated that a solid membrane reactor-PEM fuel cell can utilize reactive oxygen species for the partial oxidation of low-reactivity hydrocarbons, transforming them into alcohols and other more reactive products, and in this case can be the key to explain the urea oxidation.

Enas et al. [22] has attributed the performance drop in urea-fueled direct fuel cells to the formation of carbonates at the anode, which may act as a contaminant for the electrocatalyst. They also concluded that non-noble metals can lead to anode poisoning and require the development of new strategies; however, the use of non-noble metals facilitates commercialization. They further concluded that working with an anode in an alkaline electrolyte and a cathode in an acidic electrolyte enhances reactions and increases the open circuit potential.

4. Conclusion

The Au, Pd, and PdAu electrocatalysts supported on ITO for urea fuel cells demonstrate that the addition of gold to palladium significantly improves electrochemical performance. X-ray diffraction analysis revealed characteristic peaks of palladium and gold, suggesting the formation of a PdAu alloy. Additionally, transmission electron microscopy indicated that palladium-rich materials exhibit greater agglomeration. In electrochemical experiments, a change in the voltammogram profile was observed compared to the blank, however, there was no significant increase in current values, suggesting the formation of strongly adsorbed intermediates, which may indicate that urea oxidation is either partial or occurs through the formation of reactive oxygenated species.

Among the studied materials, the PdAu/ITO (75:25) electrocatalyst stood out with the highest open circuit potential (0.47 V) and the highest power density, highlighting a synergistic effect between the two metals. This effect can be attributed to the bifunctional mechanism, enhanced by the generation of reactive oxygen species, which facilitates urea oxidation. Therefore, the combination of palladium and gold shows promise for application in urea fuel cells, offering improved performance.

CRediT authorship contribution statement

Victória A. Maia: Methodology. **Rodrigo F.B. de Souza:** Writing – review & editing. **Isabely M. G. Abreu:** Investigation. **Almir Oliveira Neto:** Writing – original draft, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] I.L. Lera, S. Khasnabis, L.M. Wangatia, O.E. Femi, P.C. Ramamurthy, An innovative catalyst of PdNiP nanosphere deposited PEDOT:PSS/rGO hybrid material as an efficient electrocatalyst for alkaline urea oxidation, Polym. Bull. 80 (2023) 1265–1283, https://doi.org/10.1007/s00289-022-04100-w.

[2] V. Vedharathinam, G.G. Botte, Understanding the electro-catalytic oxidation mechanism of urea on nickel electrodes in alkaline medium, Electrochim. Acta 81 (2012) 292–300, https://doi.org/10.1016/j.electacta.2012.07.007.

[3] Y.M.T.A. Putri, J. Gunlazuardi, Y. Yulizar, R. Wibowo, Y. Einaga, T.A. Ivandini, Recent progress in direct urea fuel cell, Open Chem. 19 (2021) 1116–1133, https://doi.org/10.1515/chem-2021-0100.

[4] W. Shi, R. Ding, X. Li, Q. Xu, E. Liu, Enhanced performance and electrocatalytic kinetics of Ni-Mo/graphene nanocatalysts towards alkaline urea oxidation reaction, Electrochim. Acta 242 (2017) 247–259, https://doi.org/10.1016/j.electacta.2017.05.002.

[5] J. Miao, Q.-L. Hong, P. Zhang, Z.-F. Ren, A.-C. Zhao, Y.-H. Li, P.-F. Wang, Y. Chen, Self-supported Pt nanoparticles-NiFeP nanosheets arrays nanohybrid with hydrophilic surface towards urea electrolysis, Appl. Surf. Sci. 652 (2024) 159276, https://doi.org/10.1016/j.apsusc.2023.159276.

[6] M. Taha, Y.A. Attia, S.S. Medany, Enhanced electrocatalytic activity of graphitic carbon nitride-supported Ni/NiO microflower structures for urea electro-oxidation, J. Chem. Technol. Biotechnol. 99 (2024) 509–521, https://doi.org/10.1002/jctb.7553.

[7] X. Yin, K. Zhu, K. Ye, J. Yan, D. Cao, D. Zhang, J. Yao, G. Wang, FeNi supported on carbon sponge for efficient urea oxidation in direct urea fuel cell, J. Colloid Interface Sci. 654 (2024) 36–45, https://doi.org/10.1016/j.jcis.2023.10.011.

[8] J. Yoon, D. Lee, Y.N. Lee, Y.S. Yoon, D.-J. Kim, Solid solution palladium-nickel bimetallic anode catalysts by co-sputtering for direct urea fuel cells (DUFC), J. Power Sources 431 (2019) 259–264, https://doi.org/10.1016/j.jpowsour.2019.05.059.

[9] K. Yang, L. Hao, Y. Hou, J. Zhang, J.-H. Yang, Summary and application of Ni-based catalysts for electrocatalytic urea oxidation, Int. J. Hydrogen Energy 51 (2024) 966–981, https://doi.org/10.1016/j.ijhydene.2023.10.279.

[10] Y. Ma, C. Ma, Y. Wang, K. Wang, Advanced nickel-based catalysts for urea oxidation reaction: challenges and developments, Catalysts (2022).

[11] E.H. Fontes, C.E.D. Ramos, C.A. Ottoni, R.F.B. de Souza, E. Antolini, A.O. Neto, Glycerol dehydrogenation steps on Au/C surface in alkaline medium: an in-situ ATR-FTIR approach, Renew. Energy 167 (2021) 954–959, https://doi.org/10.1016/j.renene.2020.12.026.

[12] J. Nandenha, C.E.D. Ramos, S.G. da Silva, R.F.B. de Souza, E.H. Fontes, C.A. Ottoni, A.O. Neto, Borohydride reduction method for PdIn/C electrocatalysts synthesis towards glycerol electrooxidation under alkaline condition, Electroanalysis 33 (2021) 1115–1120, https://doi.org/10.1002/elan.202060322.

[13] S.G. da Silva, J.C.M. Silva, G.S. Buzzo, A.O. Neto, M.H.M.T. Assumpção, Use of PtAu/C electrocatalysts toward formate oxidation: electrochemical and fuel cell considerations, Mater. Renew. Sustain. Energy 5 (2016) 15, https://doi.org/10.1007/s40243-016-0079-8.

[14] R.S. Henrique, R.F.B. De Souza, J.C.M. Silva, J.M.S. Ayoub, R.M. Piasentin, M. Linardi, E.V. Spinacé, M.C. Santos, A.O. Neto, Preparation of Pt/C-In2O3.SnO2 electrocatalysts by borohydride reduction process for ethanol electro-oxidation, Int. J. Electrochem. Sci. 7 (2012) 2036–2046, https://doi.org/10.1016/S1452-3981(23)13861-2.

[15] R.S. Henrique, R.F.B. De Souza, J.C.M. Silva, J.M.S. Ayoub, R.M. Piasentin, M. Linardi, E.V. Spinacé, M.C. Santos, A.O. Neto, Preparation of Pt/C-In 2O 3.SnO 2 electrocatalysts by borohydride reduction process for ethanol electro-oxidation, Int. J. Electrochem. Sci. 7 (2012) 2036–2046.

[16] J. Nandenha, R.F.B. De Souza, M.H.M.T. Assumpção, E.V. Spinacé, A.O. Neto, Preparation of PdAu/C-Sb2O5·SnO2 electrocatalysts by borohydride reduction process for direct formic acid fuel cell, Ionics 19 (2013) 1207–1213, https://doi.org/10.1007/s11581-013-0955-5.

[17] J.F. Coelho, I.M. Gutierrez, N.G.P. Filho, P.J. Zambiazi, A.O. Neto, R.F.B. de Souza, PdxNiy/TiO2 electrocatalysts for converting methane to methanol in an electrolytic polymeric reactor - fuel cell type (PER-FC), Methane 2 (2023) 137–147, https://doi.org/10.3390/methane2020011.

[18] Y.Q. Liang, Z.D. Cui, S.L. Zhu, Y. Liu, X.J. Yang, Silver nanoparticles supported on TiO2 nanotubes as active catalysts for ethanol oxidation, J. Catal. 278 (2011) 276–287, https://doi.org/10.1016/j.jcat.2010.12.011.

[19] J. Yuan, J.J. Zhang, M.P. Yang, W.J. Meng, H. Wang, J.X. Lu, CuO nanoparticles supported on TiO with high efficiency for CO electrochemical reduction to ethanol, Catalysts 8 (2018), https://doi.org/10.3390/catal8040171.

[20] C.A. Ottoni, S.G. da Silva, R.F.B. De Souza, A.O. Neto, Glycerol oxidation reaction using PdAu/C electrocatalysts, Ionics 22 (2016) 1167–1175, https://doi.org/10.1007/s11581-015-1631-8.

[21] F. de Moura Souza, R.F.B. de Souza, B.L. Batista, M.C. dos Santos, F.C. Fonseca, A. O. Neto, J. Nandenha, Methane activation at low temperature in an acidic electrolyte using PdAu/C, PdCu/C, and PdTiO2/C electrocatalysts for PEMFC, Res. Chem. Intermed. 46 (2020) 2481–2496, https://doi.org/10.1007/s11164-020-04102-1.

[22] E.T. Sayed, T. Eisa, H.O. Mohamed, M.A. Abdelkareem, A. Allagui, H. Alawadhi, K.-J. Chae, Direct urea fuel cells: challenges and opportunities, J. Power Sources 417 (2019) 159–175, https://doi.org/10.1016/j.jpowsour.2018.12.024.