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Communication

Methane to Methanol Conversion Using PEM Fuel Cell and PdAu/ATO Nanomaterials

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Abstract: This study investigates the use of Au-doped Pd anodic electrocatalysts on ATO support for the conversion of methane to methanol. The study involves cyclic voltammetry, in-situ Raman spectra, polarization curves, and FTIR analysis to determine the optimal composition of gold and palladium for enhancing the conversion process. The results demonstrate the potential for utilizing methane as a feedstock for producing sustainable energy sources. Pd₇₅Au₂₅/ATO electrode exhibited the highest OCP value, and Pd₅₀Au₅₀/ATO had the highest methanol production value at a potential of 0.05 V. Therefore, it can be concluded that an optimal composition of gold and palladium exists to enhance the conversion of methane to methanol. The findings contribute to the development of efficient and sustainable energy sources, highlighting the importance of exploring alternative ways to produce methanol.

Keywords: methane conversion; fuel cell; methanol; PEM; PdAu/ATO

1. Introduction

Methane is a widely available and inexpensive source of energy, but its combustion for energy production releases CO₂, contributing to climate change [1]. Therefore, researchers are exploring alternative methods to convert methane into chemicals like methanol, which can be utilized as a clean fuel and has diverse industrial applications [2]. Various techniques have been developed for methane conversion, including homogeneous and heterogeneous catalysis, photocatalysis [3], biocatalysis, plasma technologies, and electrochemical processes [4–7]. Among these, electrochemical processes have shown promise for converting methane into methanol under mild conditions and generating electricity [8–11].

To co-generate chemicals and electricity, one possible approach is to use a polymer electrolyte fuel cell as a reactor for converting methane into methanol and formates [11,12]. However, this conversion is challenging due to the high strength of the C-H bond in methane (434 kJ·mol⁻¹) and its low polarizability because of its regular tetrahedron conformation [13]. Therefore, the process involves oxidizing methane through a Non-Faradaic reaction, which activates methane using more reactive species generated by Faradaic processes, such as reactive oxygenated species (ROS) from water activation. The significance of water activation in transferring oxygen to hydrocarbon molecules to produce methanol has been emphasized by researchers [14–16].

To achieve this conversion, catalysts with specific characteristics are required. One of the key requirements is for the catalysts to have a bifunctional effect [17–19], that is, to be able to adsorb methane and activate water molecules. While transition metal oxides are commonly used catalysts, researchers have been exploring alternative catalysts, such as platinum and palladium, which have shown promising results in methane oxidation to methanol [11,20].

Palladium and gold supported on carbon materials, such as carbon nanotubes, activated carbon, and reduced graphene oxide [21,22], have been identified as effective catalysts for this process. Pd-Au nanoparticles have been used as active centers, and their catalytic activity can be improved by supporting them on functionalized carbon nanotubes [23]. In addition, gold's affinity for oxygen can facilitate the breakdown of hydrogen peroxide into OH•, which activates the C-H bond [21,24,25].

In the other hand, the oxygenated species produced can also attack the catalyst support, typically carbon, which affects the reactor's durability. Recent studies have explored the use of metallic oxides like TiO_2 and antimony-doped tin oxide (ATO) as catalyst support to improve catalyst stability [26,27]. In this context, researchers have investigated the conversion of methane to methanol in a polymer electrolyte fuel cell using Au-doped palladium anodic electrocatalysts in different proportions on ATO support. ATO was selected as the support because it favors the formation of reactive oxygenated species, has good electrical conduction, and corrosion resistance, making it a viable catalyst support option for the methane-to-methanol reaction.

2. Results

Figure 1 presents microscopy images and nanoparticle size distribution histograms for Au/ATO, Pd/ATO, and PdAu/ATO with varying ratios. The average nanoparticle size ranges from 12 to 19 nm, with the smallest size (12 nm) observed in Pd/ATO catalyst and the largest size (19 nm) observed in Pd₅₀Au₅₀/ATO catalyst. Additionally, the images show that the nanoparticles are not well-dispersed on the support and tend to agglomerate. The ATO support's ability has been observed in other catalytic materials in the literature [29,33–35].

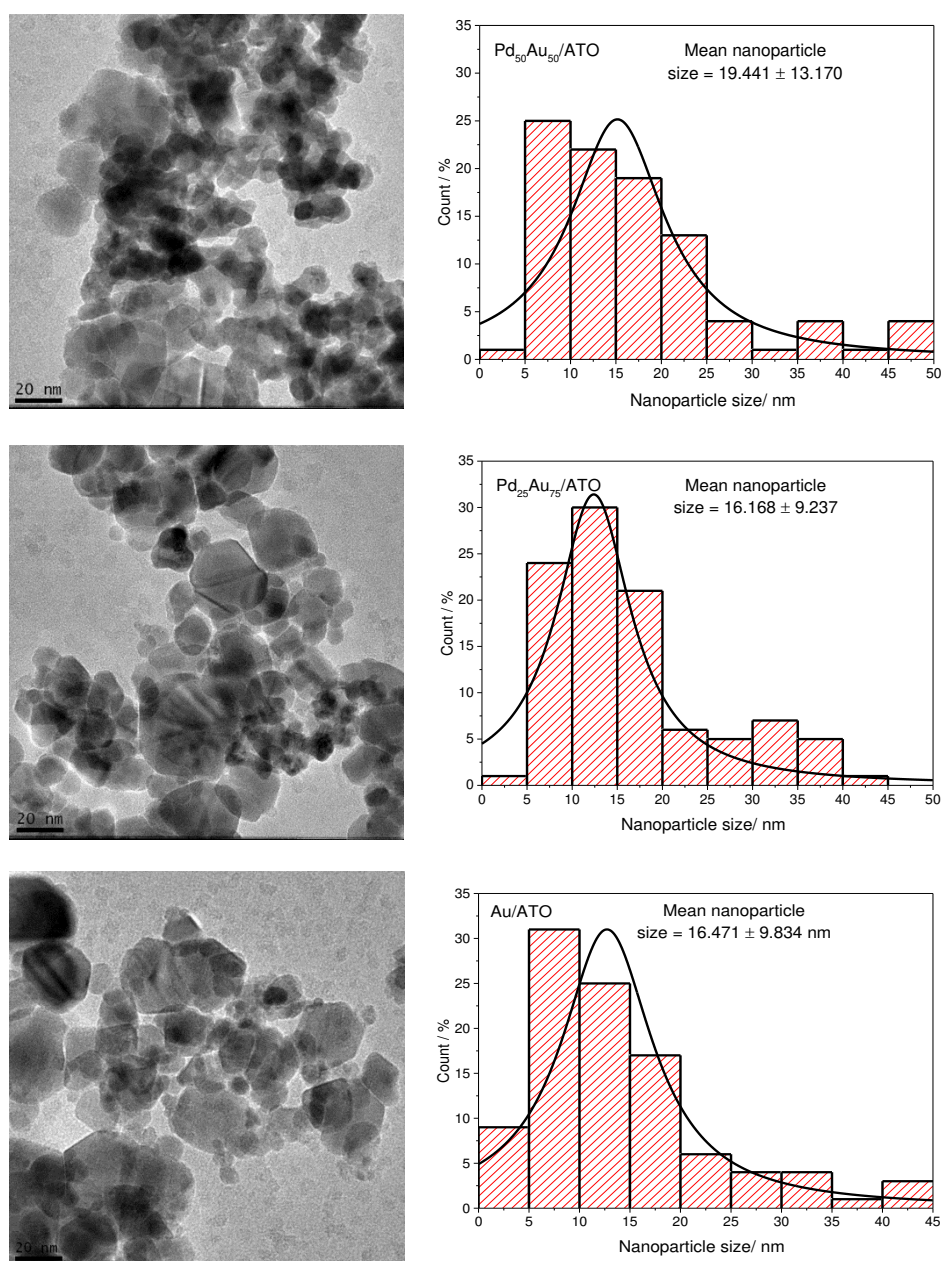


Figure 1. TEM micrograph and histograms of nanoparticle size distribution to Au/ATO, Pd/ATO and PdAu/ATO in different ratios.

X-ray diffraction (XRD), as shown in Figure 2a, was utilized to characterize the chemical structures of a series of Pd/ATO, Au/ATO, and PdAu/ATO samples. The peaks observed at $2\theta \approx 26^\circ$, 33° , 38° , 51° , 54° , 62° , and 64° correspond to the characteristic diffraction peaks of $\text{SnO}_2 \cdot \text{Sb}_2\text{O}_5$ (JCPDS# 88-2348). The palladium and gold peaks appear discretely in comparison. Based on the diffraction pattern with intensity normalized by the logarithmic function (Figure 2b), it was possible to clearly observe the characteristic peaks of Pd and Au. The Pd-related peaks at $2\theta \approx 38^\circ$, 49° , and 66° are associated with the crystalline planes (111), (200), and (311), according to (JCPDS# 89-4897), which reveals a face-centered cubic (FCC) structure for Pd/ATO. The relative intensities of Pd and ATO are still discrete, even when normalized on a logarithmic scale, reflecting the smaller particle size compared to the other materials.

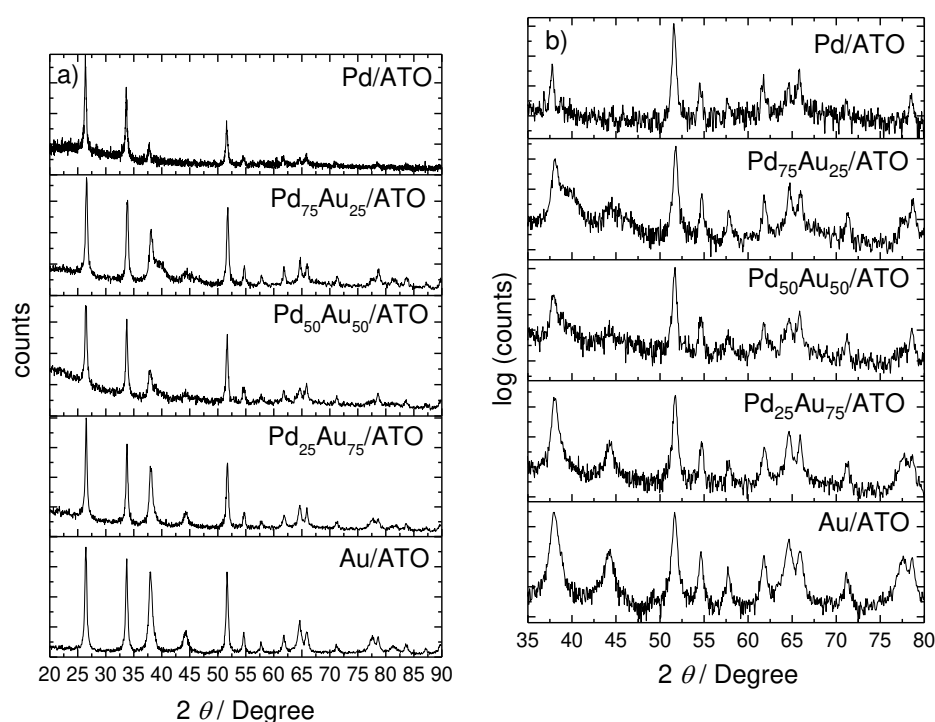


Figure 2. X-ray diffractogram (XRD) pattern of Au/ATO, Pd/ATO and PdAu/ATO in different ratios.

Two small reflection peaks were observed at $2\theta \approx 38.1^\circ$ and 44.4° , corresponding to the (1 1 1) and (2 0 0) planes of face-centered cubic-structure Au (JCPDS no. 89-3697). The peaks relative to the (2 2 0) and (3 1 1) planes at $2\theta \approx 64^\circ$ and 77° , respectively, appear convoluted with the peaks of Pd and tin oxide. It is noteworthy that the peak with the (3 1 1) plane stands out.

The cyclic voltammetry of PdAu materials, in different molar ratios in 1.0 mol L^{-1} NaOH aqueous solution (scan rate $v = 10 \text{ mV s}^{-1}$), was presented in Figure 3a. In the materials containing Pd, it is possible to observe in the region of -0.85 and -0.5 V the peaks corresponding to hydrogen adsorption and desorption [36], the Pd/ATO electrode presents the oxide reduction (-0.4 V), and oxide formation (0.05 V). The PdAu/ATO electrodes show a shift in the peak positions for the hydrogen adsorption-desorption, compared to Pd/ATO, which indicates the electronic modification of Pd atoms by Au [37].

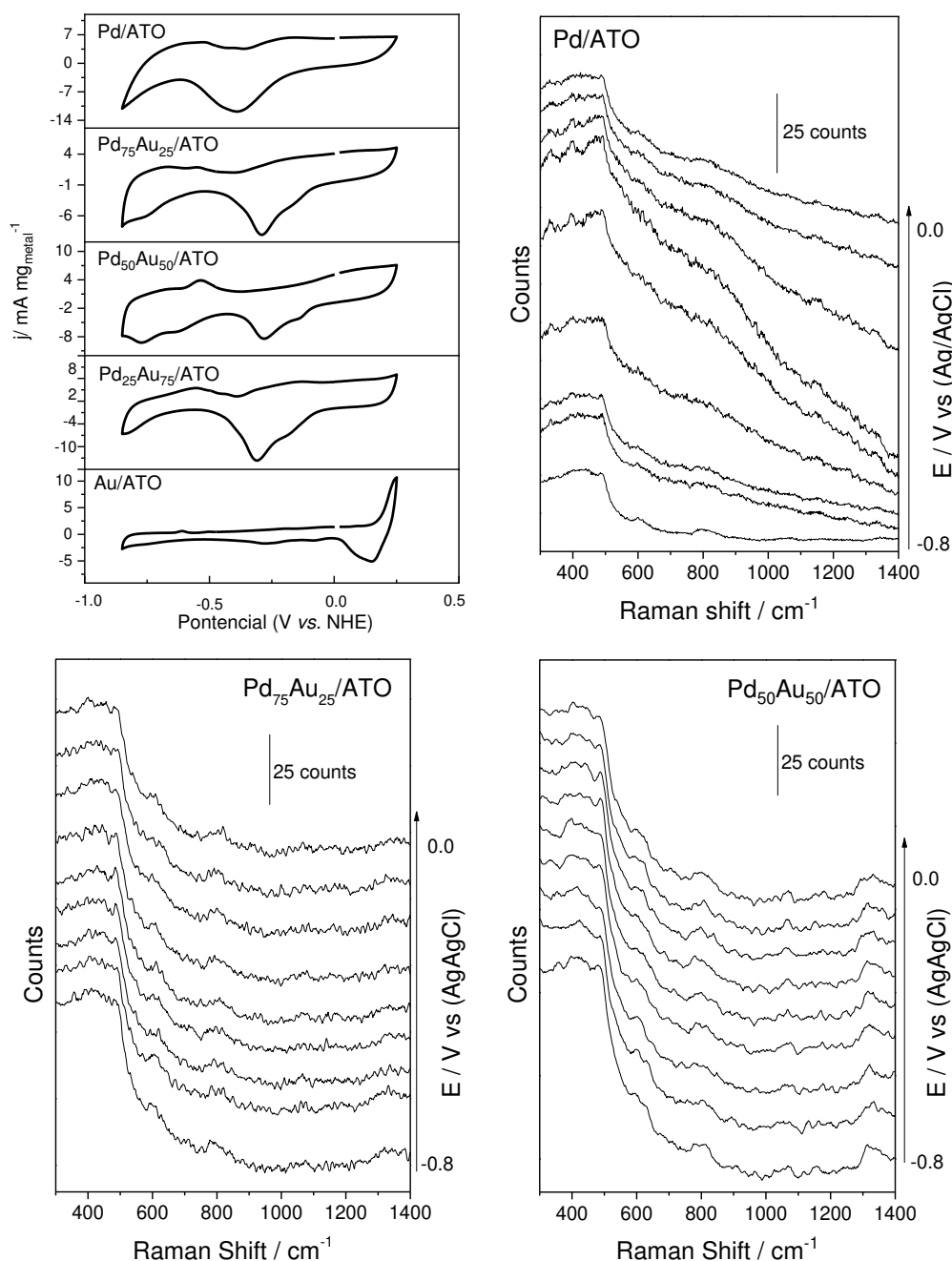


Figure 3. a) Cyclic Voltammetry (CV) of Au/ATO, Pd/ATO and PdAu/ATO in different ratios (scan rate $v = 10 \text{ mV s}^{-1}$) in 1 mol L^{-1} NaOH aqueous solution. b-f) Spectra of in-situ Raman-assisted electrochemical measurements collected at different potentials in NaOH 1.0 mol L^{-1} .

In order to complement and expand the observations from cyclic voltammetry, in-situ Raman spectra of the Pd-Au materials were measured (Figure 3b). In all spectra, the characteristic bands of SnO_2 are observed at approximately 486 , 602 , and $780\text{--}793 \text{ cm}^{-1}$, corresponding to the active bands of SnO_2 Eg, A_{1g}, and B_{2g}, respectively [38,39]. Additionally, a band centred at 639 cm^{-1} , corresponding to the bending of the PdO-H bond [40], indicates the oxidation of Pd as a function of potential in the Pd/ATO catalyst.

For all materials containing gold, it is possible to observe a feature at potentials less negative than -0.4 V , which is assigned to the Au-O stretching vibration of Au oxide and appears at approximately 559 cm^{-1} [41], and this potential is shift for more negative with gold content increases. At 635 cm^{-1} is referent to the Au-O and Au-OOH vibrations [42], and this bands decreases with

addition of Pd. The band observed at 602 cm^{-1} in SnO_2 was overlapping with this band, while distinct bands were observed at 794 , 974 , and 1166 cm^{-1} , which can be attributed to Nafion [43].

The polarization curves (Figure 4) of the partial oxidation of methane in a polymer electrolyte reactor and the measured open circuit potential (OCP) values range between 0.3 and 0.5 V , which are comparable to those reported in other literature [3,29]. The $\text{Pd}_{75}\text{Au}_{25}/\text{ATO}$ electrode exhibits the highest OCP value, while the Au/ATO electrode has the lowest, indicating that the synergy between Pd and Au increases the OCP value compared to that of Pd or Au alone. The Au/ATO and $\text{Pd}_{25}\text{Au}_{75}/\text{ATO}$ electrodes have the same OCP value, but the power density of $\text{Pd}_{25}\text{Au}_{75}/\text{ATO}$ is 0.9 mW/cm^2 , which is higher than that of Au/ATO (0.49 mW/cm^2). This suggests that the addition of Au to Pd/ATO reduces the resistivity of the material.

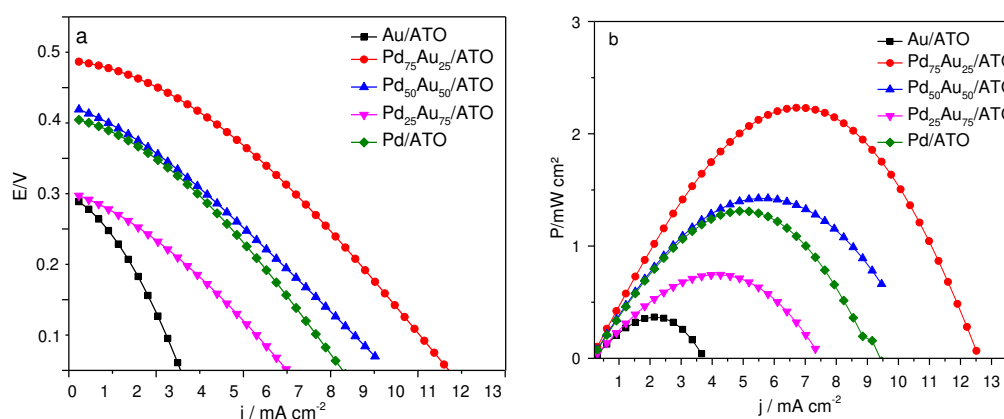
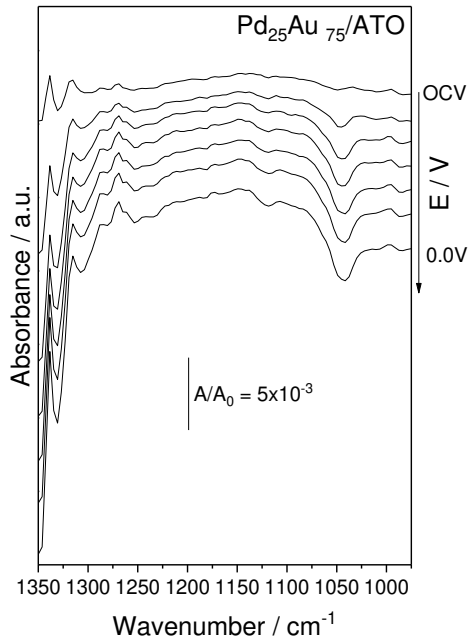
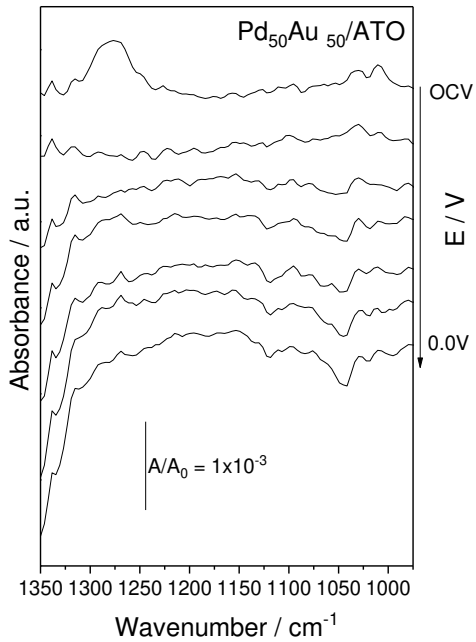
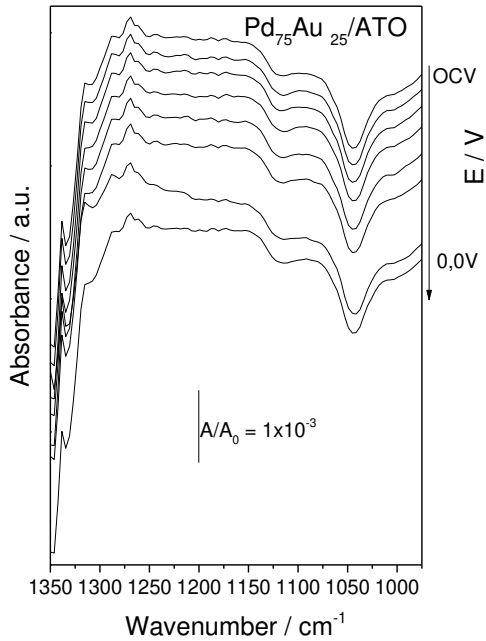
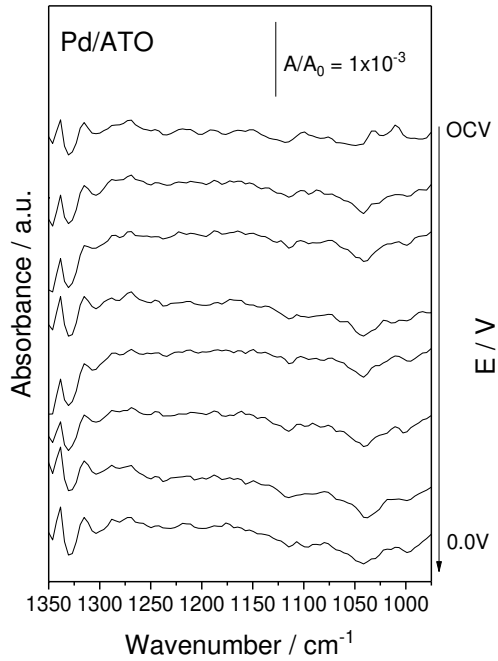


Figure 4. a) Polarisation curves ATO supported PdAu materials in different compositions. b) Power Density curves.

The FTIR analysis (Figure 5), displays the spectra of aliquots collected from the reactor effluent every 100 mV for 5 minutes in a $1.0\text{ mol L}^{-1}\text{ NaOH}$ solution, with a methane flow rate adjusted to 100 mL min^{-1} for all catalysts. The obtained spectra exhibit a characteristic methane band at $\sim 1304\text{ cm}^{-1}$, corresponding to CH_4 dissolving in water [44,45]. Methanol formation can be identified by specific bands that appear at 1033 , 1077 , and 1082 cm^{-1} [46], although they are subtle and present in all materials. Additionally, a band centred at $\sim 1342\text{ cm}^{-1}$ corresponding to the $\nu(\text{COO})$ of formate in the solution [47] is visible in all materials. This band may indicate that the process is leading to more oxidized products of methane than methanol.



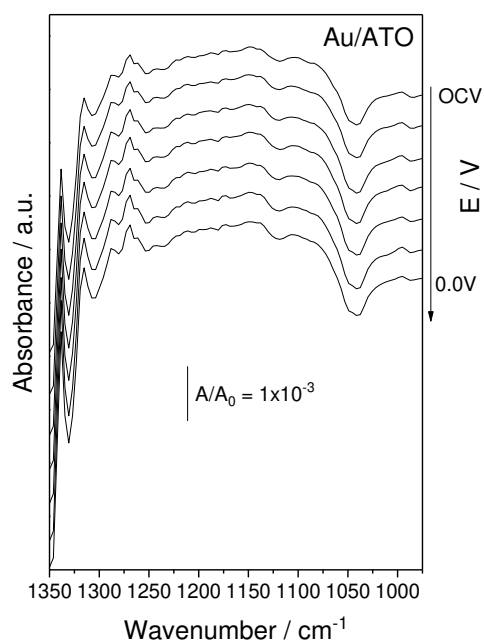


Figure 5. Spectra of FTIR aliquots collected from the reactor effluent every 100 mV for 5 min in NaOH 1.0 mol L⁻¹ with methane flow adjusted to 100 mL min⁻¹ for all catalysts.

The collected effluent from the reactor was also used to quantify the methanol produced by HPLC, and this value was converted and reported as the rate of reaction (eq. 1).

$$r = ([\text{methanol}]) / (V \cdot \text{time}) \quad (1)$$

Figure 6 reports the rate of reaction for palladium- and gold-based materials. The data show that Pd₅₀Au₅₀/ATO has the highest methanol production value at a potential of -0.05 V, outperforming all other materials and potentials. These results indicate that an optimal composition of gold and palladium exists to enhance the conversion of methane to methanol. The combination of gold's oxophilic nature [21,22], which facilitates water activation, with PdO's carbophilic ability [11], and the balance between the two types of sites, favors the pathway of methane conversion to methanol.

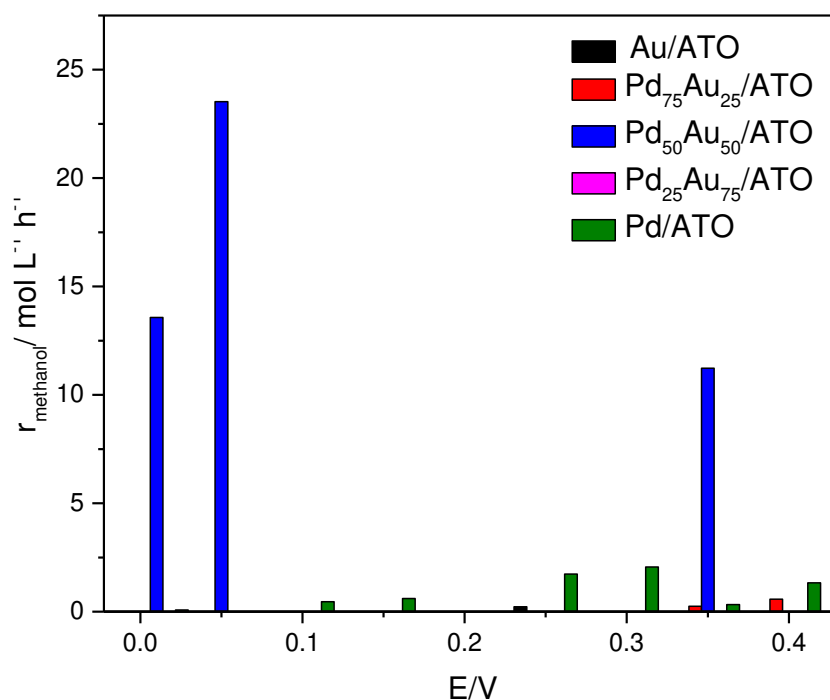


Figure 6. Rate reaction of Au/ATO, Pd/ATO and PdAu/ATO in different potentials.

4. Materials and Methods

The PdAu/ATO materials were prepared using the sodium borohydride reduction method [28] in different ratios. Each material was prepared by mixing a solution of ultrapure water and isopropanol (50/50 v/v) with a specific amount of ATO support ($\text{Sb}_2\text{O}_5 \cdot \text{SnO}_2$ Aldrich) in an ultrasonic bath for 15 minutes. Then, 20% of metallic precursors $\text{Pd}(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$ (Aldrich) and $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$ (Aldrich) in different ratios were added. In this medium, NaBH_4 (Aldrich) was added to a 10 mL 0.01 mol L^{-1} NaOH solution with an excess of 5:1 in relation to the metals, and stirring was maintained for 30 minutes. The resulting material was washed and filtered with 4 L of ultrapure water.

The morphology of PdAu/ATO (nanoparticle size and general aspects) was investigated using Transmission Electronical Microscopy (TEM) JEOL JEM-2100, operated at 200 keV. For the histogram and the calculation of the average size, 300 nanoparticles of each catalyst were calculated using the ImageJ software package. The crystalline structure of materials was analysed using a diffractometer (Rigaku – Miniflex II) at $\text{Cu}/\alpha \lambda = 0.154 \text{ nm}$, with 2θ ranging from 20 to 90°, with scan speed of 2° min⁻¹, operating at 40 kV. The analysed XRD standards were compared with JCPDS (Joint Committee on Powder Diffraction).

The electrochemical experiments were observed by cyclic voltammetry (CV) performed on a three-electrode cell, connected to a potentiostat/galvanostat (PGSTAT 302 N, Autolab®) with the PdAu/ATO as working electrode, a 2 cm² Pt plate as the counter electrode and, a commercial Ag/AgCl electrode (3.0 mol L^{-1} solution) as the reference electrode, all in a single compartment cell. The Raman in-situ was analysed using a Raman Micro Raman spectrometer – Horiba, with 785 nm laser and same single compartment cell used in CV experiments.

A PEM fuel cell unit was used in this work, similar to the used in previous studies [29,30]. Five different membrane electrode assemblies (MEAs) of anode/electrolyte/cathode were constructed. The different 1 mg per cm² of metals (Pd: Au) as anode, a membrane of Nafion® 117 (DuPont®) treated with KOH as electrolyte, and 1 mg of Pt/C – BASF (20% w/w) as cathode. The ink contains the catalyst with 30% by mass of a solution of Nafion® D-520 (Aldrich) and isopropanol. The anodes were prepared by brushing the ink on carbon cloth treated with PTFE [31,32]. The conditions of fuel cell were fed with a mixture of methane (100 mL min⁻¹) and NaOH 1 mol L^{-1} at (1 mL min⁻¹) supply at

the anode, while in cathode is supplied with humidified O₂ bottle at temperature of 85 °C with a flow rate of 400 mL min⁻¹. The temperature measurement in the cell was 45°C. For the application of currents and potentials to the cell, a potentiostat/galvanostat (PGSTAT 302 N, Autolab®) was used.

The reaction products are collected from the reactor every for 5 min in the open circuit potential (OCP) to 0.0 V and analysed by infrared (IR) spectroscopy performed on a Nicolett® 6700 with ATR Miracle (Pike) accessory and diamond/ZnSe crystal and a detector of MCT, and a high-performance liquid chromatography (HPLC) (YL9100) with a UV/Vis detector made at 225 nm, with flow of 0.8 mL min⁻¹ of 50% water 40% acetonitrile and 10% buffer solution in an isocratic run on a C18 (Phenomenex Luna 5 µm, 250 X 4.6 nm). The calibration curve presents the following linear equation: peak area = 0.29574 + 0.00979 [methanol] and presents r² = 0.994.

5. Conclusions

This study examined the conversion of methane to methanol in a polymer electrolyte fuel cell using Au-doped palladium anodic electrocatalysts in different proportions on ATO support. The cyclic voltammetry and in-situ Raman spectra of the Pd-Au materials were measured to observe the electronic modification of Pd atoms by Au. The polarization curves of the partial oxidation of methane in a polymer electrolyte reactor and the measured open circuit potential values were also studied. The results showed that the Pd₇₅Au₂₅/ATO electrode exhibited the highest OCP value, and Pd₅₀Au₅₀/ATO had the highest methanol production value at a potential of 0.05 V. Therefore, it can be concluded that an optimal composition of gold and palladium exists to enhance the conversion of methane to methanol. This study contributes to the development of efficient and sustainable energy sources by utilizing methane, a potent greenhouse gas, as a feedstock for producing methanol.

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