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Ag-Cu Nanoparticles as Cathodic Catalysts for an Anion Exchange Membrane Fuel Cell

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Abstract: In this work, the synthesis of bimetallic Ag and Cu particles on carbon vulcan (AgCu/C) is reported, synthesized by a simple galvanic displacement method using citrate tribasic hydrate as a co-reducing agent and a commercial material based on Cu/C as a template. The materials were characterized by several physicochemical techniques, including TGA, ICP-OES, XRD, SEM, and BET. The catalysts were evaluated as cathodic catalysts for the oxygen reduction reaction (ORR) and were used for the preparation of membrane electrode assemblies for evaluation in an Anion Exchange Membrane Fuel Cell (AEMFC). The results were compared with the commercial Ag/C and Cu/C catalysts; the bimetallic catalyst obtained a higher power density, which was attributed to a synergistic effect between Ag and Cu particles.



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Keywords: galvanic displacement; oxygen reduction; Ag-Cu nanoparticles; cathodic catalyst; membrane electrode assembly

1. Introduction

Under the current scheme for the electrical energy supply, the majority of the energy demand is addressed by fossil fuel-based systems, which exhibit some limitations, including the generation of greenhouse effect gases, air pollution, and the depletion of resources. Hence, there is a great interest in the transition to novel alternative electrical energies, replacing traditional fuels with alternative green energies, allowing the decarbonization of the environment and the diversification of the sources [1].

Energy storage and energy conversion devices are essential in the integration of renewable energies into the electrical distribution network that supplies the population's energy needs worldwide [2].

Among the devices that participate in both tasks (storage and conversion), fuel cells and electrolyzers can participate in the attenuation of the intermittency of renewable energies by supplying electricity during the deficit of the electrical energy of the distribution network or saving fuel during the surplus of the renewable electrical energy. The intermittency of the supply by renewable energy systems is one of the main disadvantages that prevent the integration of this technology, since this phenomenon reduces the reliability of the energy supply at any time for the users. On the other hand, renewable energies can be adjusted to any operational condition, from low to high demand [3,4].

The fuel cell technologies depend upon operation parameters such as the anion exchange membrane, temperature, catalysts, fuel, etc. Recently, the technology of the Anionic Exchange Membrane Fuel Cell (AEMFC) has gained attention from experts and scientists in the energy field since this technology is less dependent on Pt metal groups than the

Protonic Exchange Membrane Fuel Cell (PEMFC), and lower harsh conditions appear in alkaline media compared to acidic media [5,6].

Another key aspect of AEMFC is the wider variety of commercially available membranes compared to PEMFC, which is mostly limited to Nafion[®]-based membranes, increasing the cost of the technology [7].

When hydrogen is used as fuel at the AEMFC, the corresponding anodic and cathodic reactions are the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) at the anodic and cathodic compartments, respectively. The ORR has been reported as the rate-determining step of the AEMFC since it has a complex mechanism and a lower kinetic rate compared with the HOR. Under that argument, research focused on new affordable and active catalysts has been of interest to many investigation groups [2,8].

Mexico is the main producer of Ag in the world and is also ranked in the top ten of the main producers of Cu. This focuses on the strategy in the development of Ag- and Cu-based catalysts, which display desirable features such as high catalytic activity, excellent stability, and low cost, enabling a competitive framework for the development of catalysts for fuel cell technology and minimizing the dependence on foreign technology [9,10].

The global trend in the synthesis of methods for novel catalysts in the fuel cell has led to facile, fast, and reliable procedures that ensure a high area/volume ratio, avoiding the use of toxic and expensive organic solvents or additives that produce non-disposable byproducts. In that sense, the galvanic displacement method consists of the spontaneous deposition of a relatively noble metal by the stripping of a non-noble metal, where the electromotive force that drives the process is the potential of the half reactions. This simultaneous process (the stripping of the less noble metal and the deposition of the most noble metal) produces well-dispersed and highly porous structures without an external source of energy in a one-step procedure [11].

Recently, studies have been performed on AgCu alloy nanoparticles (NPs) as catalysts for ORR under alkaline conditions; here in AgCu loading, the metal composition was varied as Cu₃₀Ag₇₀, Cu₄₀Ag₆₀, and Cu₆₀Ag₄₀ NPs, improving the ORR catalytic activity with Cu₄₀Ag₆₀ NPs [12]. Feng et al. synthesized bimetallic AgCu nanosheets assembled in a flower-like structure by an electrodeposition method using cyclic voltammetry. The authors studied the ORR in alkaline media, demonstrating that the bimetallic AgCu catalyst is competitive with the commercial Pt/C-20% and superior to the monometallic Ag catalyst [13]. Kumar et al. synthesized bimetallic AgCu powders by using different strategies of combustion synthesis. The author reported changes in the adsorption of the oxygen molecule on the Cu nanoparticles due to the alloying with Ag; this fact exhibited an increase in the relative activity towards ORR in an alkaline medium [14]. Lee et al. investigated the catalytic performance of Ag, Cu, AgCu (core-shell), and AgCu (alloy) systems by studying the adsorption energy of oxygen and the activation energy of oxygen dissociation using the atomic orbital-based DMol package. The authors declared that AgCu (alloy) and Cu NPs exhibited strong adsorption energies and low activation-energy barriers [15]. Johnston et al. developed a catalyst based on AgCu metallic glass by pulsed laser deposition, exhibiting high electrocatalytic activity for ORR in 0.1 M KOH [16].

Not only the catalytic activity towards ORR is a key factor in AEMFC, but also the mechanism and the pathway are important factors since ORR is a sluggish process where oxygen reduction via four transferred electrons is a preferred route compared to the two electron transfer route, where the generated H₂O₂ promotes the degradation of either the membrane and/or the catalysts. Hence, the Koutecky-Levich and Tafel analyses permit the elucidation of thermodynamic and kinetic parameters [17].

In this work, a straightforward synthesis of AgCu/C catalysts is reported. Starting from a commercial template of Cu/C, the addition of Ag was carried out by the galvanic displacement method by using a co-reductor agent. This technique allows the production of a bimetallic catalyst while avoiding the waste of reagents and controlling the loading and deposition of Ag in one step. The catalysts were characterized by several physicochemical techniques, including TGA, XRD, BET, ICP-OES, and SEM. The catalytic activity of the ORR

as well as its performance as a cathodic catalyst in the AEMFC were evaluated. This work demonstrates that a simple and fast modification method increases the catalytic activity of commercial catalysts by using small quantities of metallic precursors, avoiding the use of expensive noble metals and difficult synthesis procedures.

2. Results and Discussion

2.1. Physicochemical Characterization

Figure 1A shows the micrographs for the Cu/C, Ag/C, and AgCu/C, where a high porosity structure with well dispersed small particles is observed in the monometallic catalysts (Cu/C and Ag/C). Additionally, small particles and few agglomerates are observed for the bimetallic AgCu/C catalyst, related to the Ag particles deposited on the support surface, since the galvanic displacement method assisted by co-reducing reagents promotes the formation of the agglomerates. It is important to point out that the Cu/C showed a specific surface area of $163.0 \text{ m}^2 \text{ g}^{-1}$. After the galvanic displacement of Ag assisted by sonication, the specific surface area decreased to $138.7 \text{ m}^2 \text{ g}^{-1}$. The decreasing surface area is attributed to the covering of the small particles of Ag in the porous structure, which are not located and are observed on all surfaces. Although the decreasing surface area of the bimetallic AgCu/C catalyst is an undesirable effect, the catalytic activity must be studied in order to verify the synergistic effect between the Ag and the residual Cu particles. Figure 1B shows the TEM images of the AgCu/C catalyst, where the spherical morphology of the metallic particles is shown. The micrographs exhibited a well-dispersed deposition of the particles onto the carbon surface.

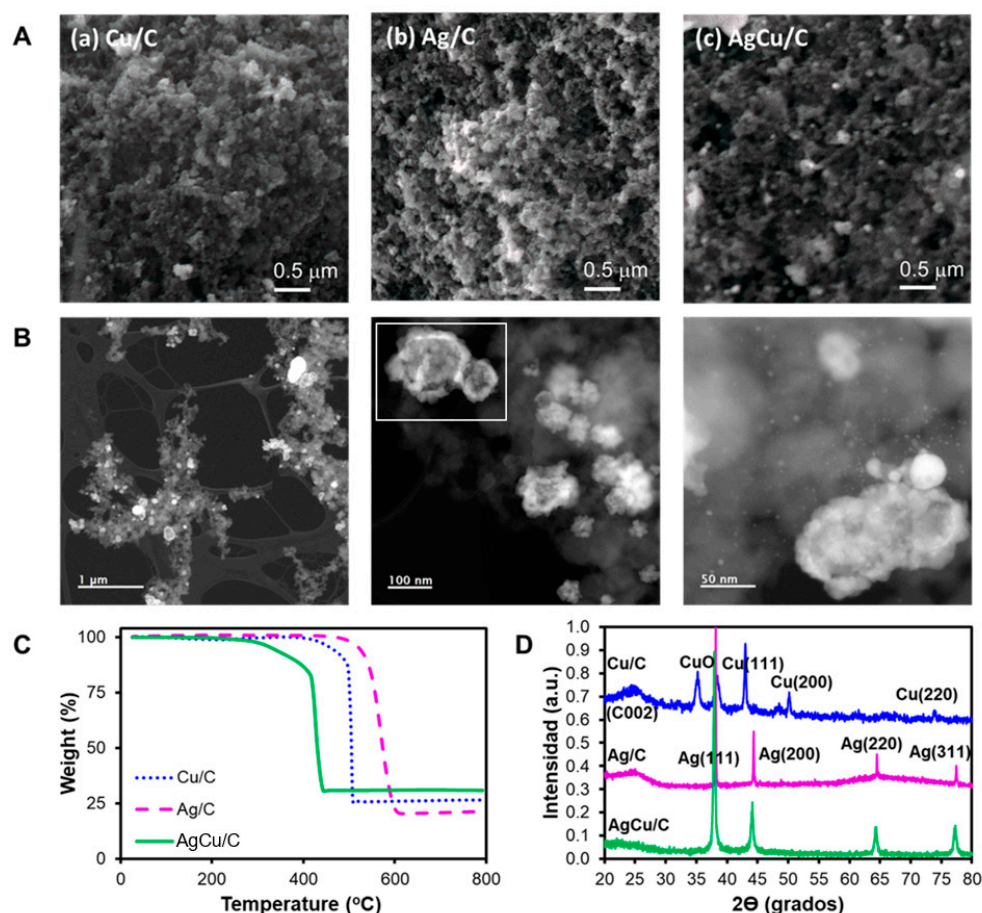


Figure 1. (A) SEM images of (a) Cu/C, (b) Ag/C, and (c) AgCu/C; (B) TEM images of AgCu/C; (C) Thermogravimetric analysis; and (D) Diffraction of patterns of Cu/C, Ag/C, and AgCu/C catalysts.

Figure 1C exhibits the thermogravimetric analysis performed on the three catalysts. It is important to note that the thermal degradation of the bimetallic catalyst (AgCu/C) takes place at a lower temperature than that of the monometallic catalysts (Cu/C and Ag/C), which is attributed to the well-dispersed particles and higher metal loading since the metallic particles behave as ignition points for the carbonaceous support. The remaining weight percentages measured at 650 °C were 26.29%, 23.78%, and 32.00% for Cu/C, Ag/C, and AgCu/C, respectively. These remaining weight percentages are related to the metallic oxides after the combustion of the carbonaceous support. From the ICP-OES, the composition of Cu and Ag in the bimetallic catalyst AgCu/C was estimated, observing a remaining 1.92% of Cu from the original template, which indicates that the Cu was dissolved, while 27.84% of Ag is deposited onto the surface support.

Figure 1D shows the XRD patterns for the three catalysts, where the peak related to the support is observed at 25°. The typical peaks for Cu/C are located at 36°, 44°, and 50°, related to CuO, Cu (1 1 1), and Cu (2 0 0). On the other hand, the peaks for Ag/C are located at 38°, 43°, and 65°, related to Ag (1 1 1), Ag (2 0 0), and Ag (2 2 0). As expected, the bimetallic catalyst exhibited almost the same peaks as the commercial Ag/C, with minor displacement attributed to modifications in the planes of the crystal due to strain effects, where the peaks attributed to the diffraction plane of Cu crystals do not appear, which agrees with findings in ICP-OES analysis [18].

2.2. Electrochemical Characterization

Figure 2a shows the cyclic voltammograms obtained for AgCu/C, Ag/C, and Cu/C catalysts. Two broad peaks located at 1.0 V (cathodic) and 1.4 V (anodic) take place for Ag/C, while the cathodic and anodic peaks are located at 0.5 V and 0.9 V, respectively, for Cu/C. The bimetallic catalyst AgCu/C showed the same cathodic peak with slight displacement, evidencing the interactions between Ag and Cu particles since the cathodic peak is located at 0.85 V. This phenomenon is attributed to an electronic effect (d-band) when the Ag interacts with Cu, where a change in the adsorption energy of the oxygen species is observed. On the other hand, the anodic peaks in the AgCu/C catalysts are observed at the same potentials in comparison to monometallic catalysts; however, the higher current density in the anodic peaks for the bimetallic catalyst is associated with the presence of the respective metallic oxides on the surface of the catalysts.

Polarization curves under hydrodynamic conditions are shown in Figure 2b–d for Cu/C, Ag/C, and AgCu/C. Here, it can be observed that the cathodic current increases as the rotation rate increases, which is typical for mass-transport-controlled systems. In the polarization curves, three regions are identified: (i) the kinetic region, where the current density depends upon the potential; (ii) the mixed region; and (iii) the mass-transport region, where the current density is independent of the potential but depends upon the rotating rate of the electrode. Moreover, the cathodic peak shown in Figure 2a appears for the Ag/C and AgCu/C catalysts, with higher intensity for the bimetallic catalyst, even with a lower specific surface area than the monometallic Cu/C, as determined by BET analysis. It is important to note that the bimetallic catalyst reached a higher current density and a more positive $E_{1/2}$, which is attributed to enhanced catalytic activity for AgCu/C compared to the monometallic catalysts. According to the volcano plot, the catalytic activity in the ORR for Ag is higher than Cu, and the free energy of the intermediates (ΔE_o) is more positive, indicating a weak bonding of the oxygen to the active sites, facilitating the ORR [19].

A comparative linear voltammogram of the catalysts at 1600 rpm can be seen in Figure 3a, which was performed to evaluate the performance of the ORR catalytic activity of the catalysts, demonstrating a higher current density value with AgCu/C catalyst compared with Ag/C and Cu/C catalysts; additionally, a lower overpotential is observed by the bimetallic catalyst, which is associated with a lower activation energy for the ORR. Figure 3b shows the Koutecky-Levich plots for AgCu/C, Ag/C, and Cu/C, where the three catalysts exhibited similar behavior and the slope was lower than the theoretical slope for

four electrons transferred. From this fact, the number of electrons transferred in the ORR is higher, resulting in other reactions that take place, such as water reduction. Besides, it is important to point out that K-L considers a smooth surface of the electrodes, which is a wide difference from the real conditions since the catalytic inks deposited produce a highly rough, thin film of the catalyst, and theoretical slopes consider the geometric area of the RDE. Figures S1–S3 show the K-L analysis performed at different potential values in the mass transference limiting condition for the three catalysts Cu/C, Ag/C, and AgCu/C, respectively, where there is no significant difference in the catalytic parameters among the potential conditions studied. Figure 3c shows the Tafel plot, where there are two different regions identified with different Tafel slope values: (i) the low overpotential region, where the Tafel slope exhibited values close to 60 mV dec^{-1} , and (ii) the high overpotential region, where the Tafel slope is around 120 mV dec^{-1} . AgCu/C, Ag/C, and Cu/C exhibited Tafel slope values at the high overpotential region of 124, 138, and 123 mV dec^{-1} , respectively.

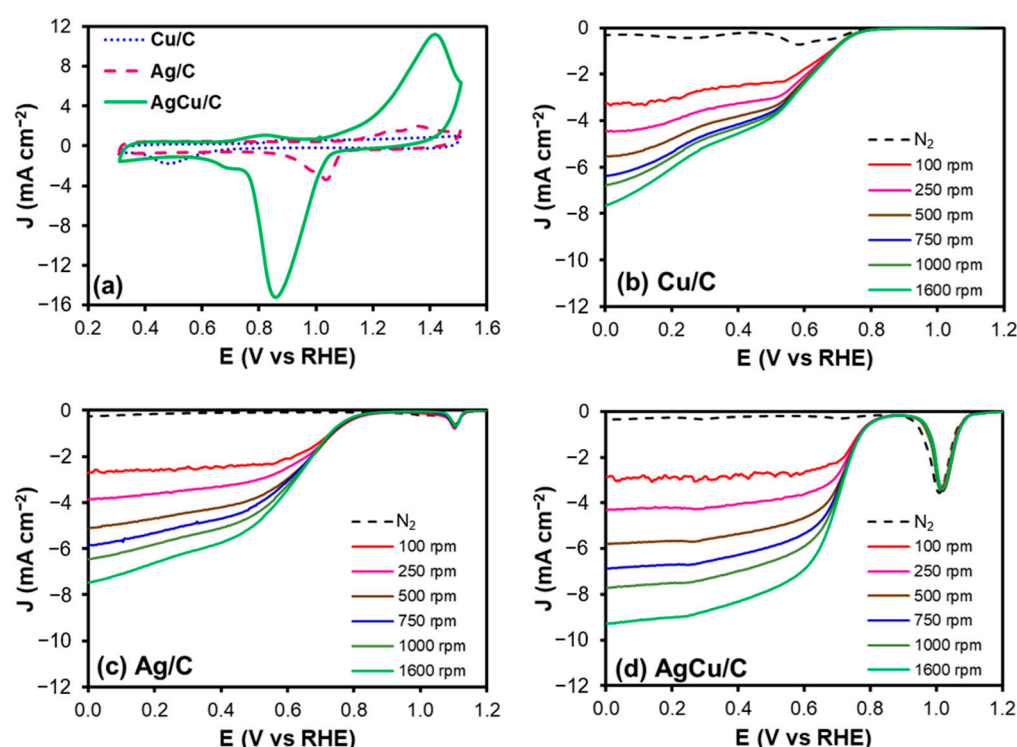


Figure 2. (a) Cyclic voltammograms of synthesized catalysts in N_2 -saturated 0.1 M KOH at a scan rate of 100 mV s^{-1} . Linear voltammograms of the catalysts in O_2 -saturated 0.1 M KOH at a scan rate of 10 mV s^{-1} and with ω different rotation rates for (b) Cu/C, (c) Ag/C, and (d) AgCu/C.

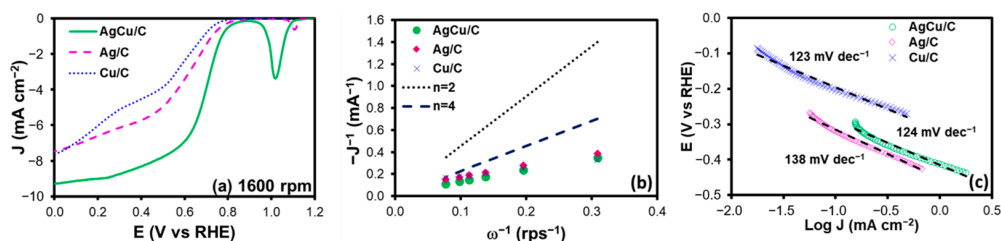


Figure 3. (a) Linear voltammograms of the catalysts in 0.1 M KOH , saturated with oxygen at a scan rate of 10 mV s^{-1} and rotation rate of 1600 rpm ; (b) Koutecky-Levich plots for ORR at 0.2 V vs. RHE , derived from RDE measurements; and (c) Tafel slope analysis for the ORR.

Considering the negligible differences found between the Tafel slope values of the AgCu/C and Cu/C, it can be stated that the order reaction is the same; hence, no changes are appreciated in the RDS, but the slightly higher Tafel slope values for the Ag/C are associated with a higher activation energy in this catalyst. Table 1 summarizes all the parameters determined by the Koutecky-Levich and Tafel analyses. According to the parameters, it can be stated that all catalysts exhibit a charge transference coefficient near symmetry (0.5). Overall, the best kinetic parameters were observed for AgCu/C, since higher current density (J values showed at potential value of 0.2 V, $J_{0.2}$ V), higher $E_{1/2}$ (lower activation energy), and higher kinetic current density (J_k) were observed.

Table 1. Kinetic and mechanistic parameters of the catalysts towards RRO.

Catalyst	$E_{1/2}$ (V vs. RHE)	$J_{0.2}$ V (mA cm ⁻²)	J_k (mA cm ⁻²)	Tafel Slope (mV dec ⁻¹)	α	J_0 (mA cm ⁻²)	Ref.
Cu/C	0.56	−6.0	9.1	123	0.48	2.57	This work
Ag/C	0.60	−6.6	13.6	138	0.43	0.52	This work
AgCu/C	0.69	−9.0	29.2	124	0.47	0.47	This work
Ag	0.73	−4.5 ^a	-	113	-	-	[12]
Cu ₃₀ Ag ₇₀	0.76	−5.0 ^a	-	85	-	-	[12]
Cu ₄₀ Ag ₆₀	0.76	−5.3 ^a	-	84	-	-	[12]
Cu ₆₀ Ag ₄₀	0.76	−5.5 ^a	-	78	-	-	[12]
Ag	0.75	−4.3 ^b	−0.55	101	-	-	[13]
AgCu	0.82	−4.5 ^b	−1.35	70	-	-	[13]
Cu	0.33	−5.3 ^c	-	-	-	-	[20]
Ag	0.73	−5.8 ^c	0.38	90	-	-	[20]
Ag ₅₀ Cu ₅₀	0.70	−6.0 ^c	0.40	45	-	-	[20]
Ag/C	0.62	−3.0 ^d	-	−81	-	-	[21]
n-Cu/NC	0.83	−5.5	-	55	-	-	[22]
Ag/C	0.67	−5.6 ^e	-	112	-	-	[23]

^a J at 0.5 V vs. RHE. ^b J at 0.4 V vs. RHE and 20 mV s⁻¹. ^c J at 20 mV s⁻¹. ^d J at 1800 rpm. ^e J at 2 mV s⁻¹ and 0.1 M NaOH.

2.3. Single Fuel Cell Testing

2.3.1. Structure and Thickness of the Cathodic Catalytic Layer

In order to measure the thickness of the catalytic layer in the diffusers of MEA, SEM analysis was performed. Figure 4 shows micrographs for MEA evaluated in a fuel cell, where Figure 4a,c exhibited the catalytic layer impregnated on the diffuser for AgCu/C and Ag/C, respectively. The thickness of the catalytic layer obtained values of 5.5 μ m for AgCu/C and 6.1 μ m for Ag/C, showed in the Figure 4b,d, respectively.

2.3.2. Performance of the Cathodic Electrocatalyst in the AEMFC

Figure 5 shows the single fuel cell performance of the commercial catalysts Cu/C, Ag/C, and the synthesized bimetallic AgCu/C catalyst. It is important to point out that the OCP is practically the same value for the three catalysts (around 0.82 V), which is relatively lower than the OCP value of noble metals, such as Pt/C (around 1.0 V); however, the catalyst loading of the studied MEAs was 0.5 mg cm⁻², which is a catalyst loading up to six times lower than other reports [24–27]. The activation polarization followed a decreasing order for Cu/C > Ag/C > AgCu/C, where the observed potentials at a current density of 10 mA cm⁻² were 0.575 V, 0.637 V, and 0.704 V, respectively, demonstrating that the bimetallic catalyst exhibits a lower polarization connected to a lower activation energy than the monometallic

catalysts, probably due to electronic or geometric effects [15]. This fact is in agreement with the previous results in the polarization curves at hydrodynamic conditions.

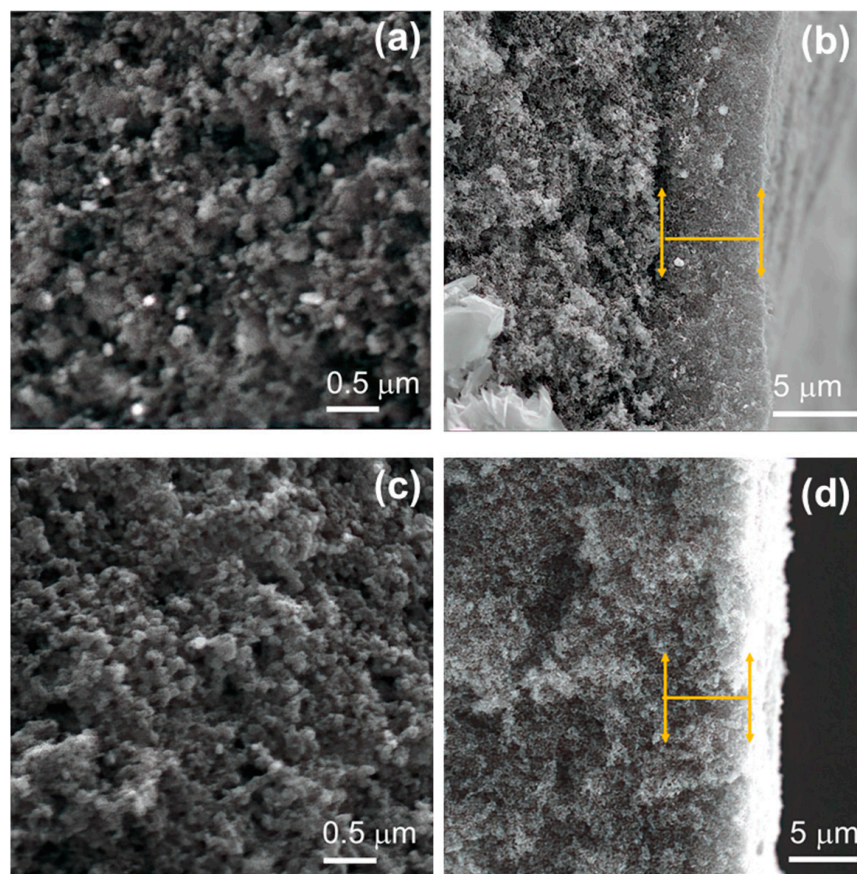


Figure 4. SEM images of the modified diffuser surface (a,c) and transversal section thickness (b,d) for AgCu/C (upper) and Ag/C (lower), respectively. Yellow arrows indicate the catalytic layer thickness of the diffusers.

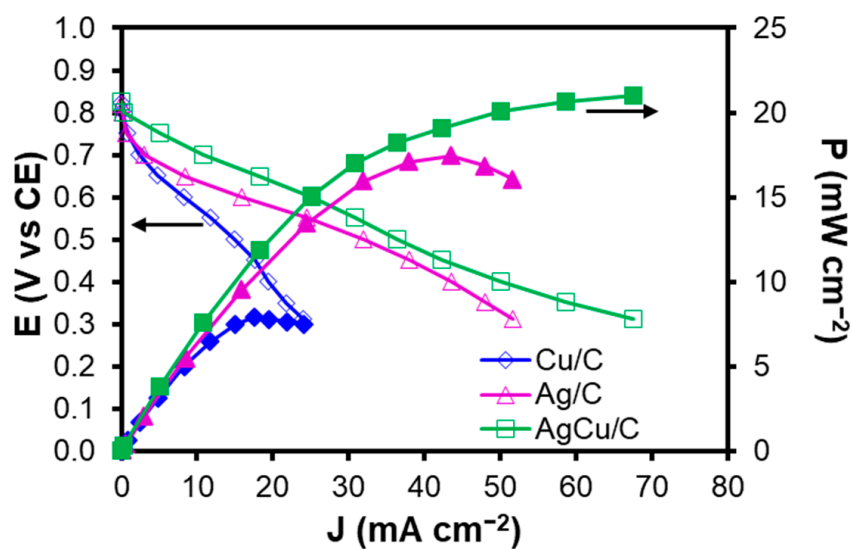


Figure 5. Single-cell performance of MEAs with different cathode catalysts: Cu/C, Ag/C, and AgCu/C at 60 °C (H₂/O₂, back pressure 10 psig). Empty markers represent the polarization curves (J vs. E, primary Y-axis), while Filled marker represent the power density curves (J vs. P, secondary Y-axis).

Similarly, the ohmic polarization is more evident for the monometallic catalysts than the bimetallic synthesized catalysts. This fact contributes to a rapidly decreasing potential for the monometallic catalysts, while AgCu/C exhibited an attenuated potential diminution, which is probably attributed to a thinner catalytic layer thickness in AgCu/C than Ag/C.

The concentration polarization is characterized by water accumulation, where the water molecules interfere in the mass transport of the gases through the catalytic layer, decreasing the reaction rates at the anode and the cathode [28]. Finally, the power density peaks were 8.0 mW cm^{-2} , 17.4 mW cm^{-2} , and 21.0 mW cm^{-2} for Cu/C, Ag/C, and AgCu/C. From these results, it can be inferred that Ag exhibited higher catalytic activity than Cu. Moreover, the addition of Ag to Cu/C to obtain AgCu/C enhances the catalytic activity by up to 20% due to geometric or electronic factors.

3. Materials and Methods

3.1. Reagents

Silver nitrate (AgNO_3 , $\geq 99\%$), sodium citrate tribasic hydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot x\text{H}_2\text{O}$, 99%), and Nafion[®] 117 solution (5%) were purchased from Sigma-Aldrich (Darmstadt, Germany). Commercial Cu/C (20 wt%) and Ag/C (20 wt%) catalysts were acquired from Fuel Cell Store[®] (Bryan, TX, USA). Isopropanol ($\text{C}_3\text{H}_8\text{O}$, 99%) and potassium hydroxide (KOH) were acquired from FAGALAB (Sinaloa, Mexico). Oxygen (O_2 , 99.5%) and nitrogen (N_2 , 99.999%) gases were supplied by Infra (Edo. de Mexico, Mexico). Acetone ($\text{C}_3\text{H}_6\text{O}$, 99.7%) and ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99%) were purchased from Fermont (Edo. de Mexico, Mexico). All chemicals were used as received. All aqueous solutions were prepared with Milli-Q water (18 M Ω , Millipore (Darmstadt, Germany)).

3.2. Synthesis of the Nanomaterial AgCu/C

The AgCu/C catalyst was obtained by the galvanic displacement method described in a previous report by using a commercial material as a template based on Cu/C (20 wt%, Fuel Cell Store[®]) [29]. The Cu/C template was dispersed in 100 mL of water DI in a beaker under sonication. Afterward, an aqueous solution of 20 mM AgNO_3 was prepared and diluted to 100 mL in a volumetric flask. Both solutions were mixed, and galvanic displacement of the Cu by the Ag^+ ions was carried out assisted by an ultrasonic probe (Sonics, model Vibra Cell 750, Newtown, CT, USA) at 53% of the maximum intensity (maximum power intensity 750 W) at 60 Hz for 5 min, applying a 1:1 on/off pulse. Then, 10 mL of an aqueous solution containing 23 mM of sodium citrate tribasic hydrate was added to the mixed solution and stirred for 2 h at room temperature. Finally, the remaining solution was filtered, rinsed with water, methanol, and acetone, and dried at 100°C for 24 h.

3.3. Physicochemical Characterization

The TA Instrument-Q500 (New Castle, DE, USA) was used in order to perform thermogravimetric analysis; the thermogravimetric curves were recorded in a temperature range of 30°C to 800°C , using a heating rate of $20^\circ\text{C min}^{-1}$ under air atmosphere.

AutosorbIQ Quantachrome (Boynton Beach, FL, USA) was employed for the measurement of the specific surface area of the catalysts.

X-ray diffraction patterns were obtained by using a D8 Advance X-ray Diffraction Bruker diffractometer (Billerica, MA, USA) with Cu K α radiation ($1.5404 \text{ \AA}$). The samples were scanned with a step of 0.01 and 2 s of collection per step.

Perkin Elmer Optima 8300 (Waltham, MA, USA) was used in order to determine the composition and stability of the catalysts using Ar plasma in axial mode. The plasma conditions were 15.0 L min^{-1} , 0.20 L min^{-1} , and 0.55 L min^{-1} for the gas, auxiliary, and nebulizer flows, respectively; the radiofrequency and the sample flow rate were 1300 W and 1.5 L min^{-1} . The wavelengths for Ag and Cu were 328.068 nm and 327.393 nm, respectively.

TESCAN VEGA 3 (Kohoutovice, Czech Republic) with a Bruker 125 eV detector operated at 20 kV was used to obtain SEM micrographs and elemental analysis of the structure of the membrane electrode assemblies (MEAs) prepared with the catalysts.

The morphology of AgCu/C was observed using the technique of Transmission Electron Microscopy (TEM) on a JEOL 2200FS (Tokyo, Japan) equipped with a spherical aberration corrector in probe mode.

3.4. Oxygen Reduction Reaction Activity

3.4.1. Cell Description and Working Electrode Preparation

In order to perform the electrochemical measurements, the ORR catalytic activity was conducted in a conventional three-electrode electrochemical cell setup consisting of a glassy carbon rotating disk electrode (GCRDE, geometric area 0.1963 cm²) as the working electrode, a Hg/HgO/1.0 M NaOH as the reference electrode, and a Pt coil as the counter electrode. The surface of the GCRDE was polished with an alumina (0.05 µm) slurry, soaked with DI water, and dried before the modification with the catalytic inks.

Catalytic inks were prepared with 2 mg of each nanomaterial (Cu/C, Ag/C, or Ag-Cu/C) dispersed in 550 µL of ethanol and 150 µL of Nafion[®] (5 wt%). The solutions were sonicated for 10 min in order to obtain a uniform suspension. The working electrode was prepared by depositing 40 µL of the catalytic ink, dropping it on GCRDE, and drying at room temperature. The modified GCRDE was attached to a PINE research-controlled ring-disk electrode system rotator model AFMSRCE in order to perform the electrochemical evaluation of the catalysts.

3.4.2. Electrochemical Measurements

Cyclic voltammetry was recorded in 0.1 M KOH electrolyte in the potential range of 0.3 V to 1.5 V vs. RHE at a scan rate of 100 mV s^{−1} at room temperature. The three-electrode electrochemical cell aforementioned was connected to a potentiostat/galvanostat Biologic VMP-300. In this study, all potential values of the electrochemical evaluations were referred to the Reversible Hydrogen Electrode (RHE).

Polarization curves were performed by linear sweep voltammetry at a sweep rate of 10 mV s^{−1} in order to study the ORR catalytic activity in the potential range of 1.4 V to −0.3 V vs. RHE in a solution of 0.1 M KOH. The electrolyte solution was saturated with nitrogen gas for 10 min; afterwards, the electrolyte was saturated with oxygen gas for 20 min, and the polarization curves were performed under hydrodynamic conditions (rotation rates of 100, 250, 500, 750, 1000, and 1600 rpm).

ORR in alkaline conditions shows a sluggish mechanism that involves two pathways: (i) via the four e[−] route, where the reduction of O₂ directly produces four OH[−] and (ii) via the two e[−] route with the formation of HO₂[−] [30]. Koutecky-Levich analysis can be used to elucidate the mechanism of ORR, as shown in Equation (1) [31,32]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{0.20nFD_{O_2}^{2/3}\theta^{-1/6}C_{O_2}} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \quad (1)$$

where j is the measured current density, j_k is the kinetic current density, B is the Levich slope, D_{O_2} is the oxygen diffusion coefficient in alkaline media (1.9×10^{-5} cm² s^{−1}), θ is the kinematic viscosity of KOH solution (0.01 cm² s^{−1}), C_{O_2} is the concentration of dissolved oxygen in the solution (1.2×10^{-6} mol cm^{−3}), and ω is the rotation rate in rpm. The number of electrons (n) involved in the ORR per oxygen molecule was obtained using the K-L plot slope of j^{-1} vs. $\omega^{-1/2}$ [33].

Tafel analysis provides information about the rate-determining step (RDS) of the electrochemical process as well as kinetic parameters of the catalysts, such as the exchange current density (j_0), as shown in Equation (2):

$$\eta = \frac{RT}{\alpha F} \ln(j_0) - \frac{RT}{\alpha F} \ln(j) \quad (2)$$

where η is the overpotential (V), R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), α is the charge transference coefficient, and F is the Faraday constant ($96,485 \text{ C mol}^{-1}$). It has been reported that a Tafel slope value around 120 V dec^{-1} is obtained when the RDS is the first discharge step or upon consumption of the MOOH species with high coverage of MOO^- . Higher Tafel slope values are associated with a high potential to increase the reaction rate [34].

3.5. Hydrogen Fuel Cell

MEA Preparation and Fuel Cell Test

MEAs were prepared by applying the catalyst ink (catalyst with a solution of water, Nafion[®] solution 5 wt%, and ethanol) onto the Gas Diffusion Layers (GDL) with a metal loading on the GDL of 0.5 mg cm^{-2} and an active area of 9 cm^2 . The nanomaterials synthesized in this work were evaluated as the cathodic electrode, and commercial Pt/C was used as an anodic electrode in all the prepared MEAs. The MEA sandwich arrangement of cathode-membrane-anode was hot-pressed at 130°C and 1.5 tons using a commercial IONOMR[®] membrane.

The fuel cell tests were performed using a potentiostat/galvanostat Solartron model 1287 upgraded with a 20 A booster; the ohmic resistance of the MEAs was measured by a Solartron model 1290; and an Impedance/Gain-phase analyzer by a Solartron model 1260.

The MEAs prepared were characterized by hand-crafted fuel cell hardware using oxygen at the cathodic compartment and hydrogen at the anodic compartment; the operating pressure of both gases was 10 psig at 60°C . A potentiodynamic polarization was performed from the open circuit potential (OCP) to 0.1 V with a scan rate of 2 mV s^{-1} . All results were performed in duplicate for each sample.

The electrochemical Impedance Spectroscopy (EIS) technique was used to obtain the ohmic resistance in the frequency range of 100 kHz to 0.1 Hz with an amplitude of 10 mV at 0 V DC and 10 steps dec^{-1} .

4. Conclusions

A bimetallic AgCu/C catalyst has been synthesized by a simple one-step procedure by depositing Ag ions in a Cu/C template using a galvanic displacement method assisted by a co-reducing reagent. The Cu was almost totally replaced, generating a few agglomerates. The catalytic activity towards ORR of AgCu/C was evaluated and compared against Ag/C and Au/C, where the bimetallic catalyst exhibits better performance values.

The catalysts were also evaluated in AEMFC, where the bimetallic catalyst showed lower polarization values than Ag/C and Cu/C, reaching 21 mW cm^{-2} , more than 20% of the power density of Ag/C, which is attributed to a geometric or electronic factor derived from the interaction of Ag and Cu.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13071050/s1>, Figure S1: Koutecky-Levich plots for ORR at different potentials values (vs. RHE) of Cu/C catalyst. Experimental K-L equations at different potentials are inset for this catalyst; Figure S2: Koutecky-Levich plots for ORR at different potentials values (vs. RHE) of Ag/C catalyst. Experimental K-L equations at different potentials are inset for this catalyst; Figure S3: Koutecky-Levich plots for ORR at different potentials values (vs. RHE) of AgCu/C catalyst. Experimental K-L equations at different potentials are inset for this catalyst.

Author Contributions: M.B.-G. wrote the manuscript; S.G.P.-F. and M.B.-G. performed the experiments in a half cell and analyzed the data; J.R.F.-H. and T.R.-C. performed fuel cell experiments; M.I.S.-G. performed ICP-OES analyses and reviewed the manuscript; B.T.-N. performed SEM and XRD analyses; C.S.-C. and E.A.R.-S. experimental; R.M.F.-N. resources and funding acquisition. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The datasets used to support the findings are included in the Supplementary Materials and within the paper.

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

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