

## Research Article

# Electrooxidation Of Methanol On Ag, AgNi, And AgCo Catalysts Synthesized Using Combustion Method.

Yuda Afdhal, Anand Kumar, Ibrahim Abu Reesh, Christopher K. Russell, Jeffrey T. Miller, Mohammed Ali Saleh Saad, Mohammed J. Al-Marri .

University of Mainz, Mainz, Germany.

## Abstract

We synthesized silver-based electrocatalysts (Ag/C, AgCo/C, and AgNi/C) using solution combustion and evaluated their efficacy in the methanol oxidation reaction. Detailed structural and microscopic examination revealed the production of graphitic carbon and crystalline phases with substantial porosity in all three electrocatalysts. X-ray photoelectron spectroscopy (XPS) study revealed a high concentration of Ag<sub>2</sub>O (or Ag<sup>+</sup>) on AgNi/C, while AgCo/C had a high concentration of AgO (or Ag<sup>2+</sup>) on its surface. XPS study of C 1s revealed the largest concentrations of the sp<sup>2</sup> hybridized C-C bond on Ag/C, C-O on AgNi/C, and O-C-O bond on AgCo/C, respectively. X-ray absorption spectroscopy (XAS) study of Ag edges revealed similar bond lengths between AgCo and this means there is no Ag-M alloying. However, there was a considerable variation in particle sizes between AgNi and AgCo, measuring 2.5 and 6 nm, respectively. In methanol electrooxidation trials, AgNi/C electrocatalysts outperformed AgCo/C and Ag/C. Linear sweep voltammetry (LSV) studies revealed that AgNi/C outperformed other materials with an onset potential of 0.41 V. A 20-hour chronoamperometry experiment verified the better performance of the AgNi/C catalyst. This might be attributed to reduced particle size and Ag<sup>+</sup> stabilization on the catalytic surface.

## INTRODUCTION

The growing understanding of hazardous emissions from fossil fuels has led to a push for ecologically acceptable energy alternatives. The fuel cell is one such possibility that has recently become the subject of numerous studies.

It generates energy with minimal or no hazardous emissions, making it suitable for various technology applications including mobile phones, laptops, and vehicles. The direct methanol fuel cell (DMFC) has been extensively researched due to its favorable features such as low operating temperature, high energy density, environmental friendliness, and efficient energy conversion.<sup>1,2</sup>

However, for their practical operations, electrocatalysts are required on each of the electrodes (anode and cathode) to efficiently drive the anodic and cathodic reactions. For large-scale applications, a challenge arises in finding electrocatalysts that are not only of low cost, but that can also actively drive the reactions in fuel cells. Precious metals, such as platinum, are effective in promoting both anodic and cathodic reactions, including methanol oxidation reactions (MOR).<sup>3</sup> However, because platinum is scarce, expensive, and sensitive to poisoning by carbon monoxide at the anode, its usage for

large-scale applications has been significantly restricted.<sup>4-12</sup> Hence, the scientific community is posed with a challenge of developing a suitable and efficient catalyst for the widespread use of DMFCs.

Alternative materials, such as gold, palladium, silver, and rhodium nanoparticles (NPs), are reasonably abundant, display outstanding catalytic activity, and have a tendency to survive CO intermediate poisoning during MOR (13-16). However, due to their high surface energy and tiny size, metal NPs tend to agglomerate during reaction, resulting in a steady decrease in activity over time. Such occurrences can be avoided by anchoring metal NPs to carrier materials with high thermal conductivity, such as nanostructured carbons<sup>17,18</sup>, on which the growth of metal nanoparticles can be suppressed to achieve high stability of small particles via the heat sink effect.

Silver is one of the metals that has been examined for methanol oxidation and has shown encouraging results in terms of long-term stability and product selectivity.<sup>22</sup> Roshan et al. created an electrode material composed of silver nanoparticles (CuAg/Cu<sub>2</sub>O) on the surface of two-dimensional C-N nanosheets.<sup>23</sup> CuAg/Cu<sub>2</sub>O on C-N was decorated via the galvanic process, in which the sacrificial Cu and Cu<sub>2</sub>O atoms were replaced by

\*Corresponding Author: Yuda Afdhal, First Affiliated Hospital of Peking University, China.

Received: 10-Jan-2025, ; Editor Assigned: 11-Jan-2025 ; Reviewed: 26-Jan-2025, ; Published: 31-Jan-2025,

Citation: Yuda Afdhal. Electrooxidation of methanol on Ag, AgNi, and AgCo catalysts synthesized using combustion method. Journal of Energy Research. 2025 January; 1(1).

Copyright © 2025 Yuda Afdhal. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Ag atoms. The C N/CuAg/Cu<sub>2</sub>O hybrid catalyst outperformed the C N/Cu/Cu<sub>2</sub>O electrocatalyst for methanol oxidation and had a higher selectivity for converting CO<sub>2</sub> into formate. The enhanced performance of CuAg catalyst during MOR could be because the silver surface forms weak oxygen bond while copper forms strong bond during oxidation reactions. The better preference in converting CO<sub>2</sub> to formate, on the other hand, could be ascribed to the suppression of side reaction, in particular hydrogen evolution. The reason may also be the generation of strain in CuAg alloy, which may prefer a reduced hydrogen coverage that minimizes copper's oxophilicity. Nickel's surface oxidation qualities make it a popular choice for electrocatalysts. It has been widely utilized to enhance anodic and cathodic reactions in chemical synthesis and water electrolysis. 24-27 Previous research has looked into the performance of nickel-containing electrocatalysts for alcohol oxidation. 28 Taraszewska and Roslonek investigated the performance of a glassy carbon/Ni(OH)<sub>2</sub> modified electrode for methanol oxidation. 29 It was discovered that most oxidizable organic substances oxidized at the same potential value, which corresponded exactly to the value at which the nickel anode surface oxidized. 28-32 Another investigation conducted by Van Effen and Evans included the oxidation of ethanol in a KOH solution. Higher valence nickel oxide was formed, which acted as a chemical oxidizing agent. 33 Cyclic voltammetry (CV) and alternating current impedance measurements corroborated this phenomenon. CV analysis permitted the discovery of a mediation pathway between higher oxides and organic compounds. Cobalt, another transition metal, is widely known for its catalytic activity in a variety of chemical processes. However, due to its poor electrocatalytic efficacy, it is rarely used as a primary electrocatalyst. Instead, it is utilized as a cocatalyst, such as platinum, to assist withstand CO poisoning of the active sites. Cobalt oxides (Co<sub>3</sub>O<sub>4</sub> and CoO) act as a catalyst.

In this study, we provide the MOR performance of three types of electrocatalysts produced via the solution combustion synthesis method: Ag, AgNi, and AgCo. The material systems were chosen based on the findings of studies that generated high-performance electrocatalysts by utilizing silver, nickel, and cobalt, as mentioned above. Using silver contributes to the development of electrocatalysts with long-term stability and improved product selectivity. The use of nickel in the material system takes advantage of its surface oxidation capabilities, and using cobalt as a co-metal can increase resistance to CO poisoning of the active sites while also forming more electroactive surface sites for MOR. Experimental results show that the silver in presence of Ni and Co perform relatively better than that of silver nanoparticles (NPs) by itself. The details of experimental methods; including synthesis conditions, structural characterizations and electrochemical methods used in this study are provided in the following section.

## EXPERIMENTAL

### Chemicals Silver Nitrate (AgNO<sub>3</sub>, 99%)

Chemicals Silver nitrate (AgNO<sub>3</sub>, 99%), cobalt(II) nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98 %), nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 97%), glycine (99.7%), isopropyl alcohol, and Nafion solution (5 wt.%) reagents were purchased from Sigma-Aldrich. Carbon black (VXC72) and Potassium hydroxide (KOH, 85%) were purchased from Cabot Corporation and Riedel-de Haen, respectively. Methanol (CH<sub>3</sub>OH, 99.8%) was purchased from BDH, AnalaR. Ultrapure water (Millipore, 18.2 MΩ cm) was utilized during the whole study. All the reagents were used without any further purification.

### Synthesis

Weighed AgNO<sub>3</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and glycine were added to a 250 mL beaker and mixed with 20 mL of deionized water. The beaker was then immersed in a sonic vibrator bath to create a homogeneous solution, and the beaker containing the reagents was placed on a hot plate at 250 degrees Celsius. As time passed, the solution evaporated, and the catalyst materials were obtained around 30 minutes later as a result of the combustion reaction by self-ignition that happened in the beaker. The resulting material was then pounded using a pestle and mortar before being sieved to produce uniform-sized particles. The preparation of the catalyst containing silver and cobalt were also performed using the same method. The molar ratios of the metal precursors in Ag-M samples were maintained at 1:1. Addition of glycine fuel to the mixture was determined based on a glycine to oxidizer ratio as formulated in literatures.<sup>31,32,38,41,42</sup>

### Characterization Techniques

The produced materials underwent X-ray diffraction (XRD) characterisation using a powder X-ray diffractometer (Rigaku MiniFlexII Desktop, Cu-Kα radiation, λ = 1.54056 Å). The JCPDS card numbers for the standard pattern of Ag, Ni, and Co<sub>3</sub>O<sub>4</sub> were 98-006-4997, 98-016-3354, and 98-004-2684, respectively. Transmission electron microscopy (TEM, TECNAI G2, F20 FEI) was used to examine the samples' morphology. The process entails ultrasonically dispersing a little amount of the sample in ethanol, then placing a few drops of the solution onto carbon-coated Cu-grids and allowing them to dry at ambient temperature. The elemental compositions and particle morphology of the samples were determined using an energy dispersive X-ray spectroscopy analyzer connected to a field-emission scanning electron microscope (SEM; Nova Nano 450, FEI). Analysis of the oxidation state of the elements in the samples was performed using X-ray photoelectron spectroscopy.

## Electrode Procedures

The electrocatalytic performance of Ag/C, AgCo/C, and AgNi/C toward MOR was investigated using a three-cell PINE electrode bipotentiostat (Wave Driver 20) in a basic medium. To create the working electrode ink, combine 5 mg catalyst, 300  $\mu\text{l}$  isopropyl alcohol, and 30  $\mu\text{l}$  Nafion (a binder) in an ultrasonicator for 10 minutes. After creating the ink, carefully drop 5  $\mu\text{l}$  onto a 5 mm glassy carbon disc held by a Teflon mounting. Allow to dry at room temperature. A platinum coil supported by an epoxy rod served as a counter electrode, with a reference electrode of 4 M KCl-saturated Ag/AgCl. Before starting with the electrochemical measurements, the basic solution of 1 M KOH was fully purged with nitrogen to remove any unwanted gaseous impurities that may be present in the electrolyte. The pretreatment was performed on the working electrode to ensure that the surface of the electrode is stable and this involved conducting 100 oxidation-reduction cycles at 500 mV s<sup>-1</sup> scan rate.

## RESULTS AND DISCUSSION

Figure 2 shows the XRD pattern of the prepared Ag/C, AgNi/C, and AgCo/C samples. A shared characteristic signal at 26.1 for AgNi/C and AgCo/C indicates the presence of the (002) crystal plane of graphitic carbon in carbon nanotubes (CNTs). The three samples share four peaks at  $2\theta = 38.2, 44.3, 64.6,$  and  $77.6$ , which correspond to the silver metal (hkl) planes values of (111), (200), (220), and (311). The XRD investigation confirmed that the produced samples contain silver nanoparticles with a face-centered cubic (fcc) crystal structure. Displayed by the AgCo/C catalysts that correspond to the diffraction pattern of cubic Co<sub>3</sub>O<sub>4</sub>, 41,43 where some peaks are close to Ag and may have overlapped. With regards to the XRD pattern for AgNi/C there are diffraction peaks located at  $2\theta$  values of 45.8, 51.8, and 79 that correspond to the (111), (200), and (220) crystal planes of the face-centered cubic nickel particles, respectively. Furthermore, the low intensity peaks at  $2\theta$  values of 42.4, 44.3, 46.4, 53.2, and 69.1 correspond to the (010), (002), (011), (012), and (110) planes, indicating the hexagonal tight packed nickel structure. 42,44,45 The peaks of Ag(111) planes in the three samples show a shift in the value of  $2\theta$  to higher values, as demonstrated by AgNi/C and AgCo/C electrocatalysts. This shift could be due to the existence of lattice strain or changes in chemical composition caused by solid solution development. When an atom in a unit cell is replaced with another atom, such as through doping. Relatively greater displacement is observed for AgCo/C that signifies an improved combination of silver and cobalt atoms to produce alloys that behave as transition zones lead in to the formation of bimetal.46-48

## Electrochemical Analysis

Cyclic voltammetry (CV) was initially used to assess the electrocatalytic activity of bi-metallic AgNi/C and AgCo/C catalysts toward methanol electrooxidation in comparison to an electrocatalyst composed solely of silver supported on carbon. Figure 9 depicts the electrocatalysts' performance in a 1 M KOH solution prior to methanol addition in the presence of N<sub>2</sub> at a scan rate of 50 mV s<sup>-1</sup>. Polarization increased from 0.6 to +0.6 V in the anodic direction. The applied voltage was then reversed and directed to 0.6 V in the cathodic direction. The CV curve for Ag/C in Figure 9 displayed an upward (anodic) peak at around +0.27 V and a cathodic peak at approximately 0.01 V. AgCo/C, on the other hand, displayed an anodic peak at relatively greater potential of +0.29 V (and higher current density of ca. 2.02 mA cm<sup>-2</sup>) and cathodic peaks at about 0.31, +0.03, and +0.35 V. The anodic peak of AgNi/C can be observed at a higher potential value than that of Ag/C and AgCo/C catalysts (ca. +0.40 V) and cathodic peaks at +0.05 and +0.27 V. Figure 10A shows the CV of AgCo/C, AgNi/C, and Ag/C in a solution of 1 M KOH in the presence of nitrogen and 1 M methanol at 10 mV s<sup>-1</sup> scan rate. In the figure, it can be observed that the CV curve for Ag/C deposited on the glassy carbon electrode displayed an anodic peak at approximately +0.28 V and other small peaks at higher positive potential values, and a cathodic peak at approximately +0.03 V that could be ascribed to Ag<sub>2</sub>O and AgO formation, and AgO and Ag<sub>2</sub>O reduction in the mixture, respectively.54,55 In comparison to the CV curve of Ag/C in a KOH solution without methanol, these potential values of anodic and cathodic peaks are slightly higher. The CV curves for AgNi/C and AgCo/C in a mixture of KOH and CH<sub>3</sub>OH solution, besides, display their anodic peaks that signify silver oxide formation at approximately +0.3 V, but at lower current density values in comparison to that of Ag/C.

## CONCLUSIONS

Three types of Ag-based electrocatalysts were synthesized utilizing the solution combustion synthesis method. The XRD examination revealed the presence of graphitic carbon in carbon nanotubes in all three electrocatalysts. Detailed investigation using XRD, XAS, and XPS reveals that the majority of the electrocatalysts are not alloyed, with discrete phases of silver and nickel/cobalt oxides, whereas surface alloying is confirmed, revealing metals in varying oxidation states. SEM micro images confirmed the presence of a well-porous structure on the surface of the electrocatalysts, and TEM analysis determined the elemental phase distribution of silver in the electrocatalysts, particularly the distribution of Ag nanoparticles with nickel (in AgNi/C) and cobalt nanoparticles (in AgCo/C), a characteristic that was further analyzed using XPS.

The electrocatalytic performance of Ag-M electrocatalysts (AgNi/C and AgCo/C) was compared to an Ag-only catalyst based on carbon. Based on CV, LSV, and CA studies, AgNi/C was found to be the most active and stable catalyst for MOR compared to AgCo/C and Ag/C. When examined using CA, the AgNi/C displayed the highest current density with comparatively slower decay among the three electrocatalysts, showing its potential for long-term, sustainable employment in methanol oxidation.

## REFERENCES

1. Heinzl A, Barragan VM. Review of the state-of-the-art of the methanol crossover in direct methanol fuel cells. *J Power Sources*. 1999;84:70-74. doi:10.1016/S0378-7753(99)00302-X
2. Eberle U, Müller B, Von Helmolt R. Fuel cell electric vehicles and hydrogen infrastructure: status 2012. *Energy Environ Sci*. 2012;5:8780-8798. doi:10.1039/c2ee22596d
3. Matin MA, Saad MAHS, Kumar A, Al-Marri MJ, Mansour SA. Effect of fuel content on the electrocatalytic methanol oxidation performance of Pt/ZnO nanoparticles synthesized by solution combustion. *Appl Surf Sci*. 2019;492:73-81. doi:10.1016/j.apsusc.2019.06.213
4. Matin MA, Lee E, Kim H, Yoon WS, Kwon YU. Rational syntheses of core-shell Fe@(PtRu) nanoparticle electrocatalysts for the methanol oxidation reaction with complete suppression of CO-poisoning and highly enhanced activity. *J Mater Chem A*. 2015;3:17154-17164. doi:10.1039/c5ta03809j
5. Nassr ABAA, Bron M. Microwave-assisted ethanol reduction as a new method for the preparation of highly active and stable CNT-supported PtRu electrocatalysts for methanol oxidation. *ChemCatChem*. 2013;5:1472-1480. doi:10.1002/cctc.201200742
6. Meher SK, Rao GR. Polymer-assisted hydrothermal synthesis of highly reducible shuttle-shaped CeO<sub>2</sub>: microstructural effect on promoting Pt/C for methanol electrooxidation. *ACS Catal*. 2012;2:2795-2809. doi:10.1021/cs300473e
7. Wang W, Huang Q, Liu J, Zou Z, Li Z, Yang H. One-step synthesis of carbon-supported Pd-Pt alloy electrocatalysts for methanol tolerant oxygen reduction. *Electrochem Commun*. 2008;10:1396-1399. doi:10.1016/j.elecom.2008.07.018
8. Jiang X, Gür TM, Prinz FB, Bent SF. Sputtered Pt-Ru alloys as catalysts for highly concentrated methanol oxidation. *J Electrochem Soc*. 2010;157:B314. doi:10.1149/1.3273081
9. Eid K, Ahmad YH, AlQaradawi SY, Allam NK. Rational design of porous binary Pt-based nanodendrites as efficient catalysts for direct glucose fuel cells over a wide pH range. *Catal Sci Technol*. 2017;7:2819-2827. doi:10.1039/c7cy00860k
10. Liu Z, Ling XY, Guo B, Hong L, Lee JY. Pt and PtRu nanoparticles deposited on single-wall carbon nanotubes for methanol electro-oxidation. *J Power Sources*. 2007;167:272-280. doi:10.1016/j.jpowsour.2007.02.044.