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ZIF-Derived CuPt@Ag as Catalyst for Hydrogen Evolution Reaction

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Abstract:

In this study, ZIF-Cu and ZIF-Pt were synthesized from 2-methyl imidazole with Cu and Pt salts in the methanol medium. The synthesized ZIFs were annealed to produce a CuPt nanocatalyst in the tube furnace. The Cu: Pt (3:1) nanocatalyst slurry was deposited on silver deposited carbon rod electrode (CE). The hydrogen evolution reaction (HER) activities for the catalyst were measured in a 1 M KOH solution by using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The morphological structure and composition of CuPt@Ag have been studied by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX). It was observed that the prepared electrode surface had not only a homogeneous and porous structure but also nano-sized particles distributed on the surface. It has been observed that the current is increased from 5.22 mA cm^{-2} to 25.80 mA cm^{-2} under -1.55 V potential at CuPt@Ag electrode. The high current density shows that HER efficiency increases on the prepared catalyst.

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INTRODUCTION

With the continuously increasing population and emerging technology in the world, the energy demands increase with all needs [1-3]. The main energy source of the world is fossil fuels. Fossil fuel combustion products, especially CO_2 are one of the principal reasons for the greenhouse effect, which gives rise to severe damages to our environment. Another point of worry is that fossil fuel sources are limited [4].

Following today's technology, renewable and environmentally friendly energy types like wind energy and solar energy should be used instead of fossil fuels [3, 5]. However, the renewable energy source needs storage because of the fluctuation of them. This problem could solve the production of hydrogen from water. Hydrogen is produced from renewable energy sources. It is the best alternatives to fossil fuels [6-8]. Hydrogen is known as zero-emission fuel and is burned to fabricate water vapor. So the problem of environmental pollution and energy shortage can be solved out at the same time [9]. Although hydrogen production is the simplest method by water electrolysis, it is costly due to overloading in the system. Over potential can be reduced by producing with the catalytic cathode materials. The electrodes should be cheap, and it has been low overpotential. Therefore, the investigation for a cathode material with high catalytic efficiency, large surface area, low particle size and low over potential is continuing in the generation of hydrogen by electrolysis of water [10-13].

Catalytic efficiency is increasingly maximized due to the orbital filling of electrons in d orbitals [14, 15]. The combination of two d metals is known to limit the synergistic effect [16, 17]. For several years Pt, Rh, and Ru are highlighted as metals with great efficiency for hydrogen evolution reaction (HER) [8, 12, 18, 19]. Therefore, studies are currently underway on an inexpensive, effective cathode having a large surface area and high catalytic yield. Therefore, the studies have been conducted to obtain high performance from electrodes prepared with Low Pt loading [20]. However, Pt is not preferred in industrial processes due to its high price [21, 22]. So, it is very significant to obtain high efficiency by using less noble metals [23]. According to the literature, studies on electrodes such as Cu / Ni / NiZn-PtRu, mild steel / Ni / NiZn-Pt, and NiCoZn-Pt have shown that they are catalytically efficient [24-28]. In addition, it has been observed that deposition of little quantities of noble metals on NiZn significantly increases HER efficiency [26]. MOFs have been used as initiators to produce materials with porous and low particle sizes [29]. Zeolitic imidazolate frameworks (ZIFs) are considered as one of the sub-classes of Metal-organic frameworks (MOFs). (ZIF) is established with tetrahedral units formed by one transition metal cation and four imidazolate anions and used to produce nanoparticles [30].

The main purpose of this study is not only to produce an electrode with low over-potential by accumulating metals having a synergistic effect on it for hydrogen evolution reaction but also to produce a low cost, light, and cheap electrode with a high surface area. For this purpose, the carbon electrode was coated with high-activity Ag metal. ZIF structures produced with various metals such as Cu and Pt were annealed in a high temperature and nitrogen atmosphere to produce the catalyst. Cu and Pt nano catalysts were placed on the coated Ag surface. Electrochemical properties of the designed electrode to produce hydrogen were examined in an alkaline medium. According to our research, there are few studies on these materials.

EXPERIMENTAL PROCEDURE

Material and Methods

The chemicals were bought from Sigma-Aldrich Company and directly used. Electrodes and solutions were prepared freshly before each experiment.

The HER efficiencies of electrodes were examined with electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements at ~298 K in an alkaline medium. Electrochemical measurements were investigated using Gamry interface 1000 potentiostat/galvanostat analyzer. Three electrode technique was used for these measurements. The prepared catalyst, the platinum with a 2.0 cm^2 total surface area, and the Ag/AgCl electrode were used as working electrode, the counter electrode, and the reference electrode, respectively. The working electrode was prepared in a cylindrical form with a length of 5 cm from a carbon rod. The whole surface of the carbon rod except the bottom side, which was used as working surface area (0.283 cm^2), was covered with polyester. Before electrochemical measurements, the surface of the electrode was abraded with 1200 grid emery paper. The cyclic voltammograms were taken for obtaining characteristic peaks of metal nanoparticles with 100 mV s^{-1} scan rate at (-1.00 V) - (0.80 V) versus Ag/AgCl. The EIS measurements were implemented between 10^5 Hz and 10^{-1} Hz at -1.45 V, -

1.50 V, and -1.55 V by applying an amplitude of 5 mV. Linear sweep voltammetry measurements were taken in between (-1.00 V) - (-1.80V) with a scan rate of 1.0 mV s^{-1}. Cathodic potentiodynamic polarization measurements were performed in the range of OCP to -1.80 V at a 1.0 mV s^{-1} scan rate. Morphology and size of samples were studied with SEM on FEI Quanta 650 Field Emission Sigma microscope equipped with an EDX.

Synthesis of CuPt@Ag Catalyst

Typically, as shown in the flow chart of Figure **1**, 1 mmol of salt (Cu or Pt) and 4 mmol of 2-methylimidazole were reacted in ethanol solution. The mixture was aged at room temperature for 24 hours without stirring. Respectively, purple-colored Cu^{2+} doped zeolitic imidazolate framework (ZIF-Cu) and yellow-colored Pt^{2+} doped zeolitic imidazolate framework (ZIF-Pt) were purified and dried under vacuum [30]. ZIF-Cu and ZIF-Pt were annealed with a heating rate of 4.4 °C min^{-1} at 800 °C under Ar for 2 h [32, 33]. To prepare binder ink, 2 mg of produced nano-sized metal mixture (Cu: Pt ratio is 3:1) was diluted with distilled water, ethanol, and %5 Nafion solution at a ratio of 370:90:40 as µL. The mixture was shaken for 30 minutes to obtain a homogeneous solution and put into the carbon electrode's surface. The 5 mM of silver nitrate and 0.3 M of sodium citrate dihydrate solutions were mixed for Ag deposition. The silver was electrochemically deposited on the ZIF coated carbon electrode applied 10 mA cm^{-2} current density for 240 s [31].

RESULTS AND DISCUSSIONS

The morphological and structural analysis of nano-catalysts coated carbon rods were examined with SEM - EDX. The scale bar is 500 nm for all micrographs. As can be seen from Figure **2**, ZIF-Cu (a) ZIF-Pt (b) Cu / nanocrystal polyhedrons (c) Pt/nanocrystal polyhedrons (d) highly porous mesh nanoparticles and nanocrystal polyhedron particle size is less than 100 nm. SEM-EDX results of CuPt@Ag (3:1 for Cu:Pt) catalyst are given in Figure **3**. It is seen from Figure **3a**, the nanoparticles were well dispersed on the porous network on the silver. According to the mapping result in Figure **3b**, the nanocatalysts have a coating linearly proportional with coating ratio on well-disturbed Ag particles and at the same time changed the small amount of CuPt@Ag electrode coated on the carbon rod. The weight composition of CuPt@Ag electrode from EDX measurement in Figure **3c** were 79.26% Cu, 19.16% Pt and 1.58% Ag.

The cyclic voltammograms of the catalyst are given in Figure **4**, taken at between the hydrogen and oxygen evolution potential range with 100 mV s^{-1} scan rate in alkaline medium, the electrochemical properties of the electrodes altered remarkably when the CE surface

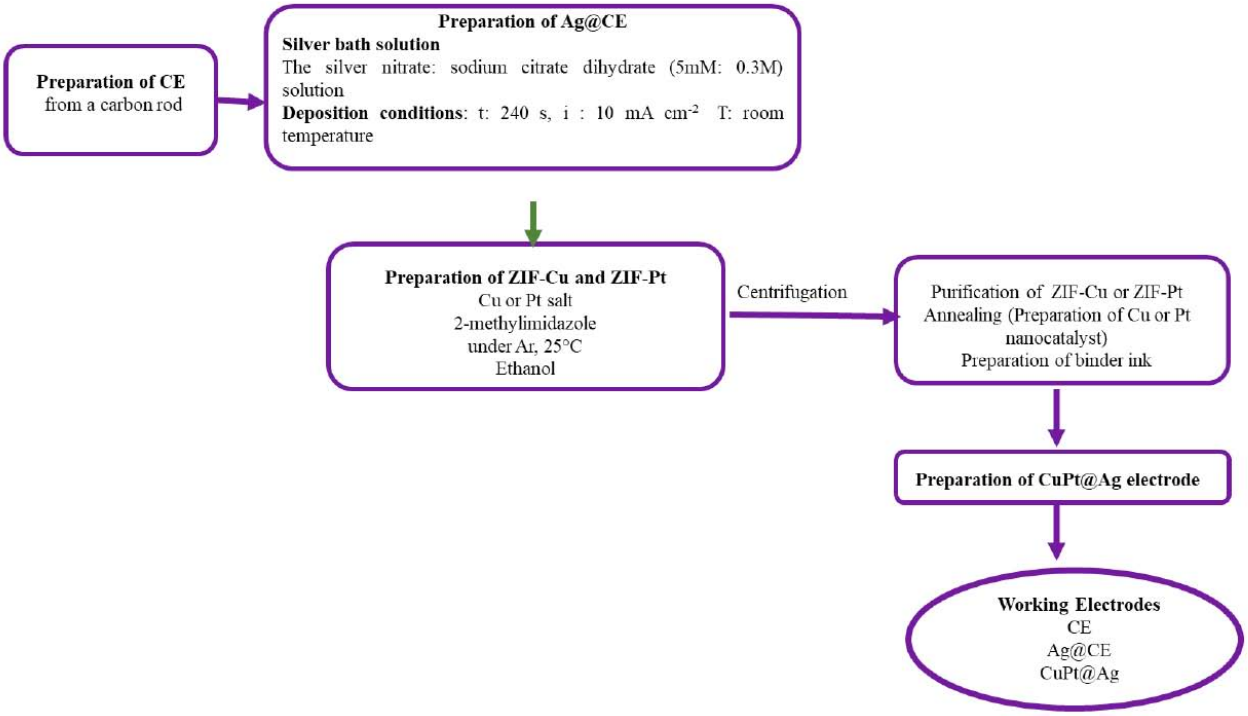

Figure 1: Flow chart of Nanocrystals Polyhedrons synthesized.

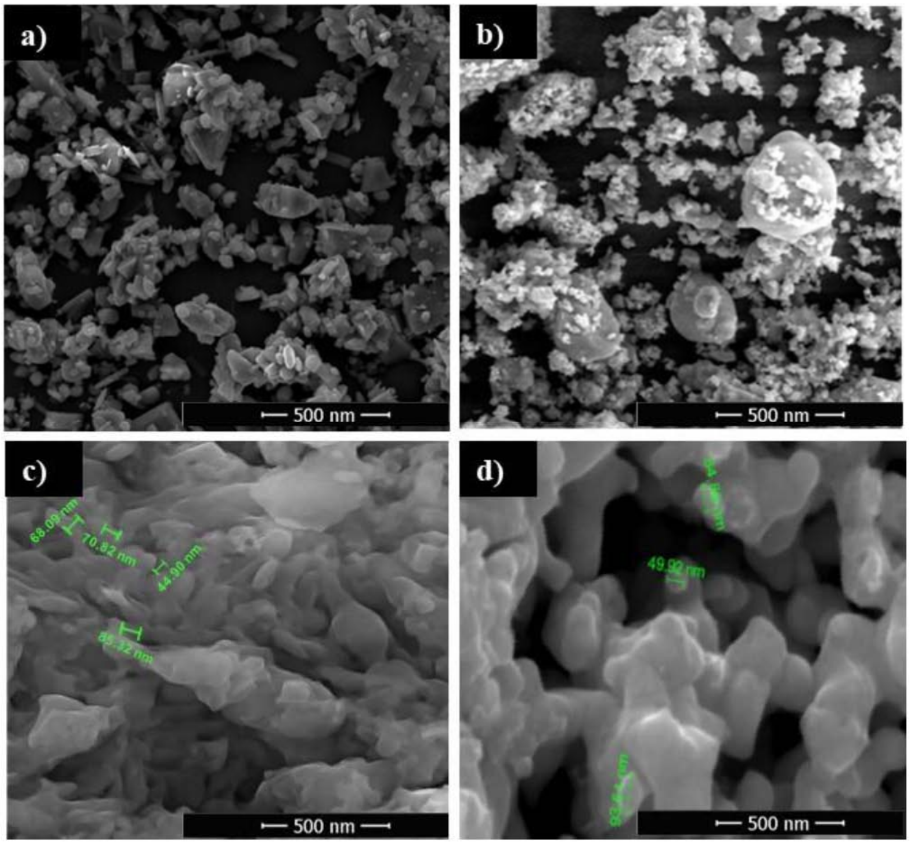

Figure 2: SEM images of ZIF-Cu (**a**) ZIF-Pt (**b**) Cu / nanocrystals polyhedrons (**c**) Pt / nanocrystals polyhedrons (**d**).

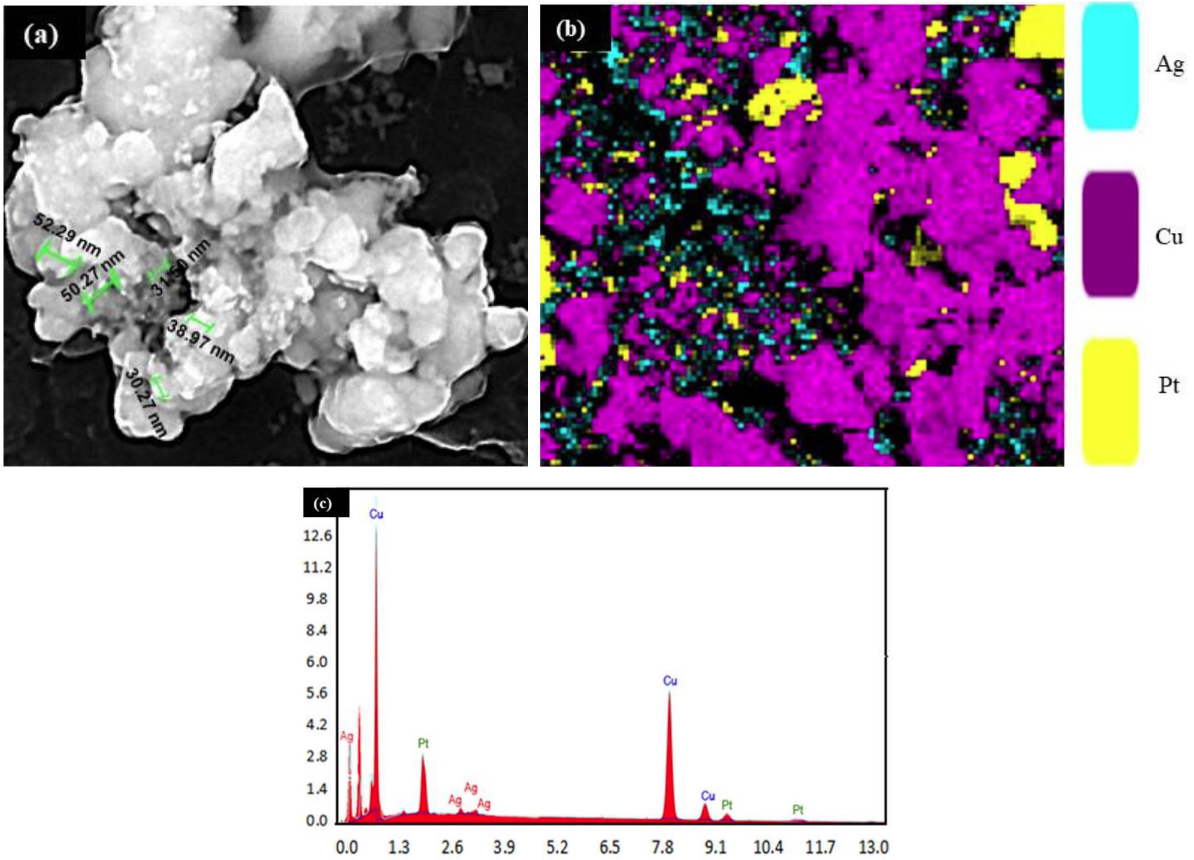

Figure 3: SEM image of CuPt@Ag surface (**a**) Mapping of CuPt@Ag surfaces (**b**) EDX result of CuPt@Ag surface (**c**).

was coated with metals. The CuPt@Ag electrode has the highest current density in the voltammogram and is the suitable electrode for HER.

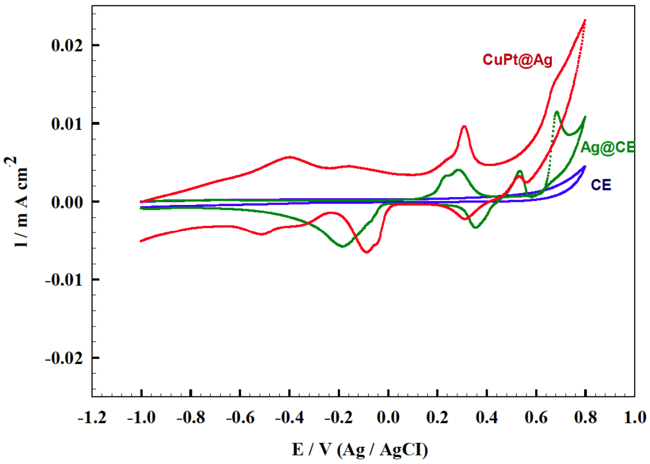

Figure 4: The cyclic voltammograms of CE, Ag@CE, and CuPt@Ag recorded in 1.0 M KOH solution at 298 K, scan rate: 100 mV s^{-1}.

As it can be seen from the linear sweep voltammetry curves in Figure **5**, the current density increases at Ag @ CE and CuPt @ Ag catalyst compared to the carbon rod. According to Figure **5** and Table **1**, CuPt@Ag provides the highest current density. The synergistic effect of Cu, Pt, and Ag leads to the formation of active sites at the CuPt@Ag electrode surface, thereby reducing the overpotential for hydrogen reduction and increasing the current density of hydrogen evolution.

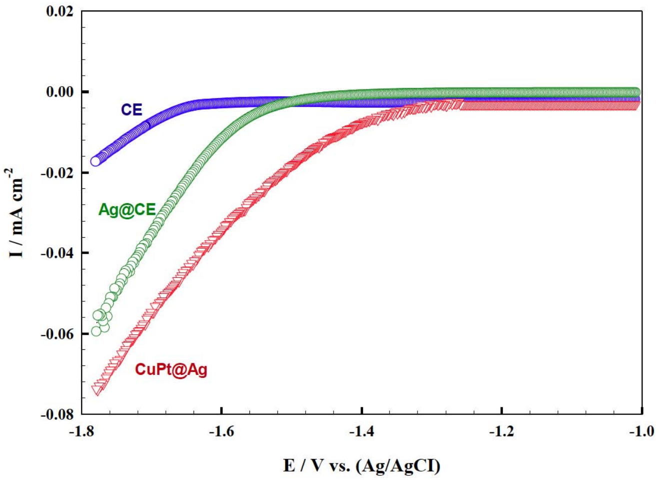

Figure 5: Linear sweep voltammetry curves of CE, Ag@CE and CuPt@Ag in 1 M KOH.

Table 1: Hydrogen Evolition Current Densities of Electrodes at -1.45V, -1.50V,- 1.55V

Electrode	$i_{-1.45V}$ /mA cm^{-2}	$i_{-1.50V}$ /mA cm^{-2}	$i_{-1.55V}$ /mA cm^{-2}
CE	0.15	2.42	2.52
Ag@CE	0.22	2.45	5.22
CuPt@Ag	1.51	18.00	25.80

The EIS measurements were applied at the overpotentials in the hydrogen evolution region to investigate HER activity. The obtained Nyquist plots at potentials of -1.45 V, 1.50 V, - 1.55 V are fitted with Gamry Echem analyst software and these are shown in Figure **6**. According to Figure **6**, it is seen that the highest hydrogen output (c) is at -1.55 V. Electrical equivalent circuit models in Figure **7** can be proposed to accurately determine the properties of the high and low-frequency regions and to gain information about the processes occurring at the electrode/electrolyte interface and the electrode surface [34]. In addition, electrical circuit parameters are given in Table **2**. Capacitance for electrical equivalent circuits represents double-layer capacitance (C_{dl}). The deviation in the ideal capacitor occurs in connection with the constant phase element (CPE). The CPE can provide information about the condition like homogeneity, roughness, and degree of multi-crystallinity of the electrode surface [35, 36]. The electrical equivalent circuits are given in Figure **7** include Rs, CPE_1, CPE_2, and n. Rp indicates the polarization resistance that includes charge transfer resistance Rct and is given in Table **2** as the sum of the R_1 and R_2. CPE_1 and CPE_2 are related to constant phase elements of the high and low-frequency loops. n is the phase shift (0 <n <1), which can give information about the homogeneity of surface. Polarization resistance (Rp) is expressed as $R_{ct}+R_f$. The resistance of the carbon electrode is comparatively high as can be found from the Nyquist plot. A catalytic surface was created with the Cu and Pt nanoparticles on the Ag coated carbon electrode, and the charge transfer resistance decreased. It can be obviously seen in Table **2** that the CPE values of the CuPt@Ag cathode are significantly higher than that seen for the CE and Ag@CE cathode. These high values indicate that the nanocatalyst coatings on the electrode increase the electrochemical activity [25, 37, 38]. According to Table **2** Rp value of the CE is considerably higher than Ag@CE and CuPt@Ag at the overpotential of -1.55 V vs Ag/AgCl. At the same time, the CuPt@Ag electrode has the lowest Rp value vs. Ag/AgCl. This suggests that noble metal addition may further enhance the intrinsic catalytic activity on hydrogen evolution performance [27, 38].

The hydrogen gas evolved in the hydrogen evolution experiments performed on 10 mA cm^{-2} current density

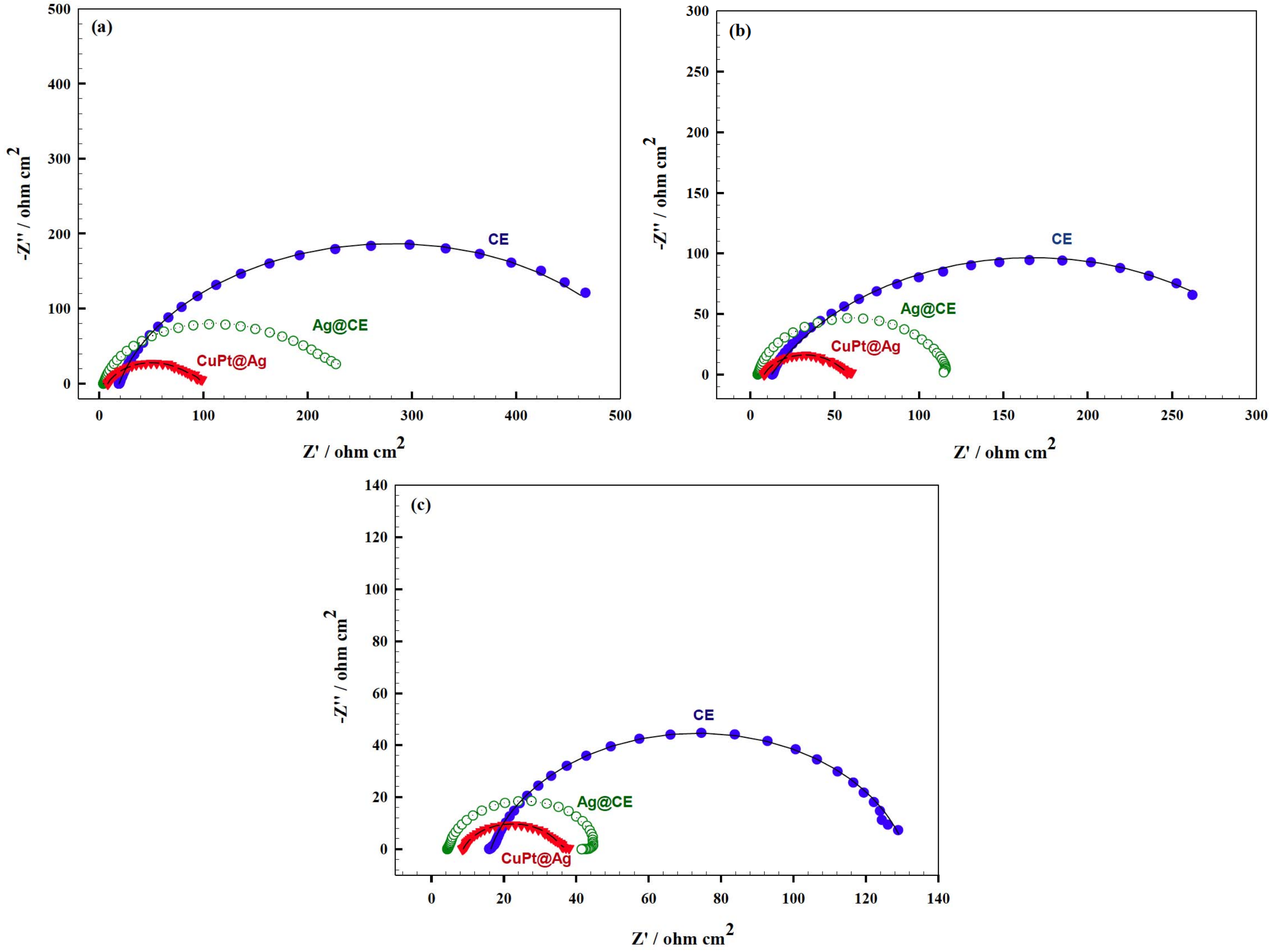

Figure 6: Nyquist plots of CE, Ag@CE and CuPt@Ag electrodes at -1.45 V (**a**) -1.50 V (**b**) -1.55V (**c**) in 1 M KOH.

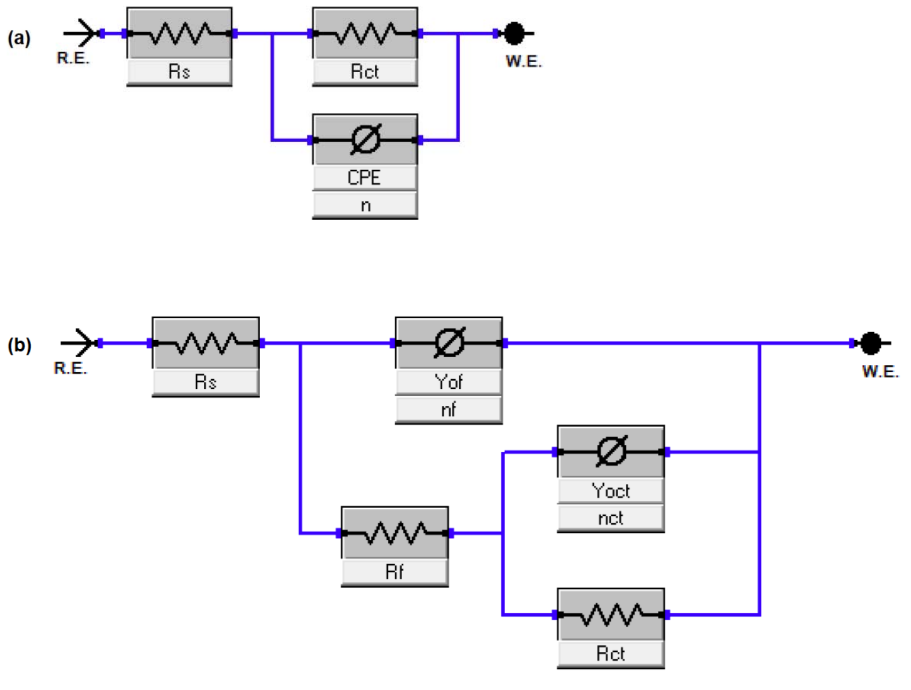

Figure 7: Electrical equivalent circuit diagrams for graphite (**a**) and CuPt@Ag(**b**) cathodes.

Table 2: Electrochemical Parameters Determined from the EIS Data

Electrode	Potential vs Ag/AgCl(V)	R_s (Ωcm^2)	R_P (Ωcm^2)	n_{ct}	n_f	CPE_1 $Y^o_{ct}\times10^{-6}\ \Omega^{-1}s^ncm^{-2}$	CPE_2 $Y^o_f\times10^{-6}\Omega^{-1}s^ncm^{-2}$
CE	-1.45	5.37	143.5	0.812	0.004	819.4	13.43
	-1.50	3.59	87.73	0.718	-	1285.0	10.24
	-1.55	4.64	32.38	0.842	-	679.2	-
Ag@CE	-1.45	1.16	63.31	1.000	0.856	7453.0	372
	-1.50	1.27	31.75	0.883	0.883	287.6	16.43
	-1.55	1.27	11.61	0.940	0.950	215.7	42.25
CuPt@Ag	-1.45	2.30	25.63	0.745	0.999	65550	722.9
	-1.50	2.34	13.94	1.000	0.748	735	774
	-1.55	2.49	8.10	0.975	0.776	575	689

for an hour with a two-electrode system was collected in the inverted burette. Hydrogen volumes are given in Figure **8** promoted the current-potential curves and EIS results. The CE, Ag@CE and CuPt@Ag catalyst provide 21.2 mL cm^{-2}, 30.4 mL cm^{-2} and 50.9 mL cm^{-2} hydrogen volume, respectively**.** Based on these results, it can be said that a low quantity of CuPt on the Ag coated carbon cathode has well catalytic activity in the hydrogen evolution reaction. The highest hydrogen volume for CuPt@Ag catalyst can compete with the literature [39-40].

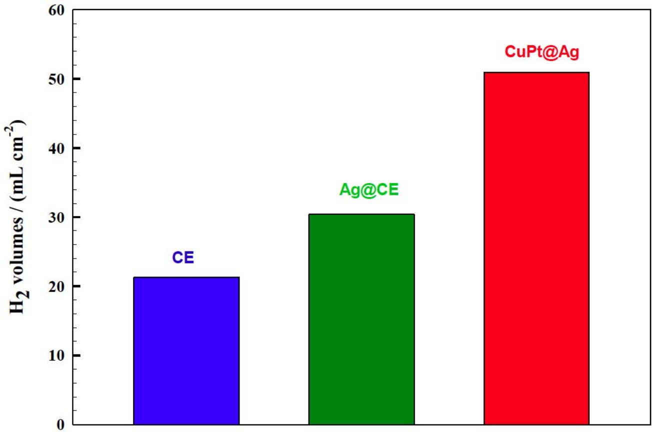

Figure 8: Hydrogen volumes of CE (🟦), Ag@CE (🟩), and CuPt@Ag (🟥) electrodes in 1 M KOH for 30 min.

The cathodic polarization curves of CuPt@Ag given in Figure **9** for the endurance test were obtained at 24, 48, and 72 hours. The results show that the catalyst efficiency and hydrogen evolution overpotential were not changed, while the duration period increase. This proved the long-time stability of the catalyst. According to these curves, the current density increases due to the separation of oxide derivatives from the surface [41]. The prepared cathode shows durability and catalytic activity during the long-time electrolysis.

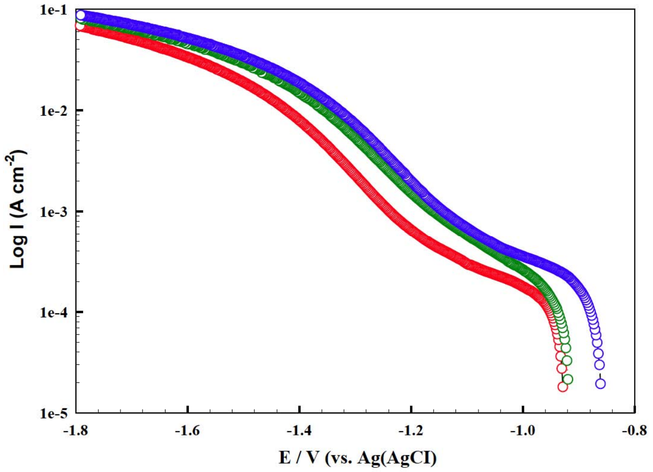

Figure 9: Cathodic current-potential curves of CuPt@Ag electrode after 24 hours (●),48 hours (●), 72 hours (●).

CONCLUSIONS

The following conclusion is drawn from the study:

- The SEM images show that the CuPt@Ag electrode having the active surface area has an advantage for the diffusion of the interiors of the ions. At the same time, SEM images show that the catalyst is homogeneously dispersed on the surface of the CuPt@Ag electrode and the particle size is less than 100 nm.

- The characteristic peak of metals has been seen in cyclic voltammograms. Characteristic peaks of metals were larger and wider compared to carbon electrodes.

- It is seen from the polarization plots that the synthesized catalyst has a lower overpotential for the HER and has a -25.80 mA cm^{-2} current density value at -1.55 V. This indicates that the amount of Cu, Pt, and the relatively low Ag has a synergistic effect.

- The EIS results show that the charge transfer resistance of the CuPt@Ag electrode has decreased to 26.4 Ω. One semicircle has been seen in the Nyquist plots of Ag@CE and CuPt@Ag cathode at potentials of -1.45, -1.50 V, -1.55 V.

- Since CuPt@Ag has a low over-potential and is a cheap electrode, it may be utilized in water electrolysis in industrial.

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