

Original Research

## Fabrication of CuO-Decorated Fe<sub>2</sub>O<sub>3</sub> Nanoparticles as Efficient and Durable Electrocatalyst for Oxygen Evolution Reaction

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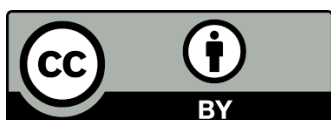
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### Abstract

The electrochemical water oxidation application of CuO@Fe<sub>2</sub>O<sub>3</sub> materials as potential catalysts is being reported for the first time. A series of CuO@Fe<sub>2</sub>O<sub>3</sub> with different molar ratios of CuO (5, 7, 10, 12, and 15%) was fabricated through precipitation followed by the impregnation method. Structural and electrochemical studies were carried out by using different analytical platforms, including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDS), Cyclic voltammetry (CV), Linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS). Synthesized materials were used as catalytic supports for electrochemical water splitting in alkaline media. The XRD pattern confirmed the formation of rhombohedral crystal structure in all CuO@Fe<sub>2</sub>O<sub>3</sub> nanomaterials, and FTIR



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analysis showed the phase purity and metal oxygen bond formation below  $800\text{ cm}^{-1}$ . The electrochemical explorations showed that when  $\text{Fe}_2\text{O}_3$  was combined with  $\text{CuO}$ , the electrocatalytic activity towards oxygen evolution reaction (OER) was improved in all compositions. OER catalysis indicated that  $\text{CuO@Fe}_2\text{O}_3$  composite containing 10 wt% of  $\text{CuO}$  ( $\text{CuFe-10}$ ) reaches optimal OER activity with high current density ( $J$ ,  $38.8\text{ mAcm}^{-2}$ ), high active surface area ( $A$ ,  $0.87\text{ cm}^{-2}$ ), slight Tafel slope ( $TS$ ,  $143\text{ mVdec}^{-1}$ ), low charge transfer resistance ( $R_{ct}$ ,  $22.4\ \Omega$ ), highest diffusion co-efficient ( $D^\circ$ ,  $3.5 \times 10^{-8}\text{ cm}^2\text{s}^{-1}$ ), mass transport co-efficient ( $m_t$ ,  $3.6 \times 10^{-4}\text{ cms}^{-1}$ ), heterogenous rate constant ( $k^\circ$ ,  $4.3 \times 10^{-4}\text{ cms}^{-1}$ ). In addition, all the composite electrocatalysts showed high stability, selectivity, and applicability for electrochemical water oxidation. In conclusion, the synergistic effects between  $\text{CuO}$  and  $\text{Fe}_2\text{O}_3$  increase the number of active catalytic sites and help rapid charge transfer at the electrode/electrolyte interface, and hence, promote the electrocatalytic OER activity.

### Keywords

$\text{CuO}$ -coated  $\text{Fe}_2\text{O}_3$ ; precipitation-impregnation method; cyclic voltammetry; oxygen evolution reaction; high OER performance

## 1. Introduction

In developing countries, the pursuit of economic sustainability, population growth, and better living standards has resulted in a rise in ecological disparities and environmental problems due to industrialization and the usage of fossil fuels [1]. Hydrogen gas is a viable alternative due to its higher energy density, accessibility, availability, and reactivity [2]. In this regard, electrochemical water splitting reactions have become essential processes to produce green hydrogen from renewable sources [3]. The electrochemical splitting of water consists of two half-reactions: oxygen evolution reaction (OER) occurs at the anode ( $2\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{O}_2 + 4\text{e}^-$ ), and hydrogen evolution reaction (HER) occurs at the cathode ( $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ ) [4, 5]. Anodic OER hinders the large-scale synthesis of green hydrogen due to its sluggish kinetics. To address this, electrode materials or electrocatalysts are utilized to attain lower overpotential. Although materials based on Ir and Ru are selective and practical, their limited availability prevents them from being widely used in the commercial sector for the affordable manufacture of hydrogen. Since transition metal-based materials, particularly transition metal oxides, are abundant and non-precious, they are being investigated as alternative electrocatalysts [6-10].

According to conventional research, heterostructures—which combine two or more metals to produce exceptional catalytic capabilities—often exhibit outstanding catalytic properties, while simple metal oxides frequently perform inadequately. Oxides of transition metals like iron, copper, cobalt, zinc, and manganese have become promising electrocatalysts for OER in alkaline media due to their high performance and good stability [11-20]. Among them, the iron oxide and copper oxide heterostructure is an efficient catalyst for OER due to its high surface-to-volume ratio, porous structure, and high stability. The semi-conducting properties of hematite are often beneficial in the conversion of solar energy, as a photocatalyst, and water splitting [21-27]. Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) is an intriguing n-type semiconductor metal oxide due to its favorable optical band gap (about 2.1 eV),

chemical stability, natural abundance, nontoxicity, and inexpensive cost. In contrast, cupric oxide (CuO), a p-type semiconductor with a low band gap of  $\sim 1.2$  eV, offer promise performance in solar cells, batteries, supercapacitors, catalysis, and sensors [28-31].

Anza Farooq and co-workers synthesized  $\text{CoFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$  and C- $\text{CoFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$  (carbon-doped) electrocatalysts through a facile calcination method for electrochemical water oxidation. The synthesized composite materials showed an overpotential of 260 mV and a Tafel slope of 183 mV  $\text{dec}^{-1}$  [32]. P. Mohana et al. synthesized a non-noble  $\text{CuO}/\text{NiO}/\text{rGO}$  nanocomposite through a co-precipitation approach and applied it for the electrochemical OER process in alkaline media. As-synthesized nanocomposite maintained an overpotential of 200 mV at 10  $\text{mAcm}^{-2}$  Tafel and a Tafel slope of 165 mV $\text{dec}^{-1}$  [33]. Ye et al. tested various iron-copper oxides with different Cu/Fe ratios for OER in 1 M KOH. The oxide that demonstrated the best performance was  $6\text{CuO}_2\text{-Fe}_2\text{O}_3$ , with an overpotential of 510 mV at 10  $\text{mAcm}^{-2}$ . All the samples were stable in the reaction conditions. The performance was attributed to the coexistence of the metal oxides, but the overpotentials are still high, which shows that further improvements can be made [34].

In this contribution, we follow a rapid and cost-effective synthesis route for the fabrication of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{CuO}@ \text{Fe}_2\text{O}_3$  (5-15% CuO). As-synthesized nano-composite materials confirmed the synergistic effect between CuO and  $\text{Fe}_2\text{O}_3$  with enhanced oxygen evolution activity. The crystalline structure, morphological and textural properties were studied through different characterization techniques including XRD, FTIR, and SEM. Electrochemical activity of as-synthesized nanocomposites for OER was investigated through CV, LSV, EIS, and chronoamperometry.  $\text{CuO}@ \text{Fe}_2\text{O}_3$  (10% CuO) nanocomposite demonstrated outstanding OER activity with a low overpotential of 170 mV vs. NHE at 10  $\text{mAcm}^{-2}$  in alkaline media. Moreover, the composite electrocatalysts exhibited excellent electrocatalytic parameters such as slight Tafel slope (143 mV $\text{dec}^{-1}$ ), low charge transfer resistance ( $R_{\text{ct}}$ , 22.4  $\Omega$ ), highest diffusion co-efficient ( $D^\circ$ ,  $3.5 \times 10^{-8} \text{ cm}^2\text{s}^{-1}$ ), mass transport co-efficient ( $m_t$ ,  $3.6 \times 10^{-4} \text{ cms}^{-1}$ ), heterogenous rate constant ( $k^\circ$ ,  $4.3 \times 10^{-4} \text{ cms}^{-1}$ ) were observed for  $\text{CuO}@ \text{Fe}_2\text{O}_3$  with 10% of CuO contents [35]. This work could provide valuable insights into the design of coupled metal oxide advanced catalysts for OER and beyond.

## 2. Materials & Methods

### 2.1 Chemicals

Iron nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) (99.99%), Potassium hydroxide (KOH) (99%), Copper nitrate hexahydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) (98%), Acetone ( $\text{CH}_3\text{OCH}_3$ ) (98%), Potassium ferrocyanide trihydrate ( $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ ) (98%), Potassium hydroxide (KOH), Potassium chloride (KCl) (98%), Aluminum oxide ( $\text{Al}_2\text{O}_3$ ) (97%), Methanol (MeOH) (96%), Nafion (5 wt./V% solution) ( $\text{C}_7\text{HF}_{13}\text{O}_5\text{C}_2\text{F}_4$ ), and Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) (97%) were acquired from Sigma Aldrich and used in synthesis and experimental process without further treatment.

### 2.2 Synthesis of $\alpha\text{-Fe}_2\text{O}_3$ Nanoparticles

The precipitation method was employed for the synthesis of single-phase iron oxide ( $\alpha\text{-Fe}_2\text{O}_3$ ) nanoparticles by mixing 4.052 g of iron (III) nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) in 100 ml of deionized water, and a 2 M aqueous solution of KOH base in 50 ml of deionized water was used to maintain the pH at 11 [36]. The solution was heated at 80°C under magnetic stirring at 400 rpm for

3 h until the rusty brown precipitates of  $\text{Fe}(\text{OH})_3$  began to form, which were then subjected to centrifugation at 6000 rpm and then dried at  $80^\circ\text{C}$  for 2 h. After that, the powdered hydroxide precursor was calcined for 4 h at  $500^\circ\text{C}$ . The powdered material was ground in the acetone and media, and then ball milling was performed for 2 h to get homogeneous nanoparticles.

### **2.3 Synthesis of $\text{CuO@Fe}_2\text{O}_3$ Nanoparticles**

Five different wt% compositions (5, 7, 10, 12, and 15) of CuO supported on  $\alpha\text{-Fe}_2\text{O}_3$  were synthesized by using the wet impregnation method. For this purpose, a calculated amount of pre-dried support i.e.,  $\alpha\text{-Fe}_2\text{O}_3$  was soaked in the measured volume of 1 M copper nitrate hexahydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) solution for all the five compositions and left overnight. Subsequently, the materials were dried for 1 h in an oven, and then grinding and calcination took place at  $500^\circ\text{C}$  for 2 h. After that, acetone media was used to grind the final powder, dried, and then ball milling was performed for 2 h to get homogeneous nanoparticles.

### **2.4 Physical Characterizations**

To study the crystallinity of nanoparticles powders XRD PANalytical X'PERT high score diffractometer was used, equipped with Cu-K $\alpha$  radiations of 0.154 nm in the scan rate of 0.625 s at a scan range of  $20\text{--}80^\circ$  [37]. By using the Nicolet 5PC instrument, where all the samples were mixed with KBr powder, FTIR spectra were acquired for all the synthesized nanoparticles in the wavelength range of  $400\text{--}4000\text{ cm}^{-1}$ . Morphology of all synthesized compositions was examined through scanning electron microscopy (SEM) by TESCAN, acquired from Germany.

### **2.5 Electrochemical Characterizations and Electrode Modification**

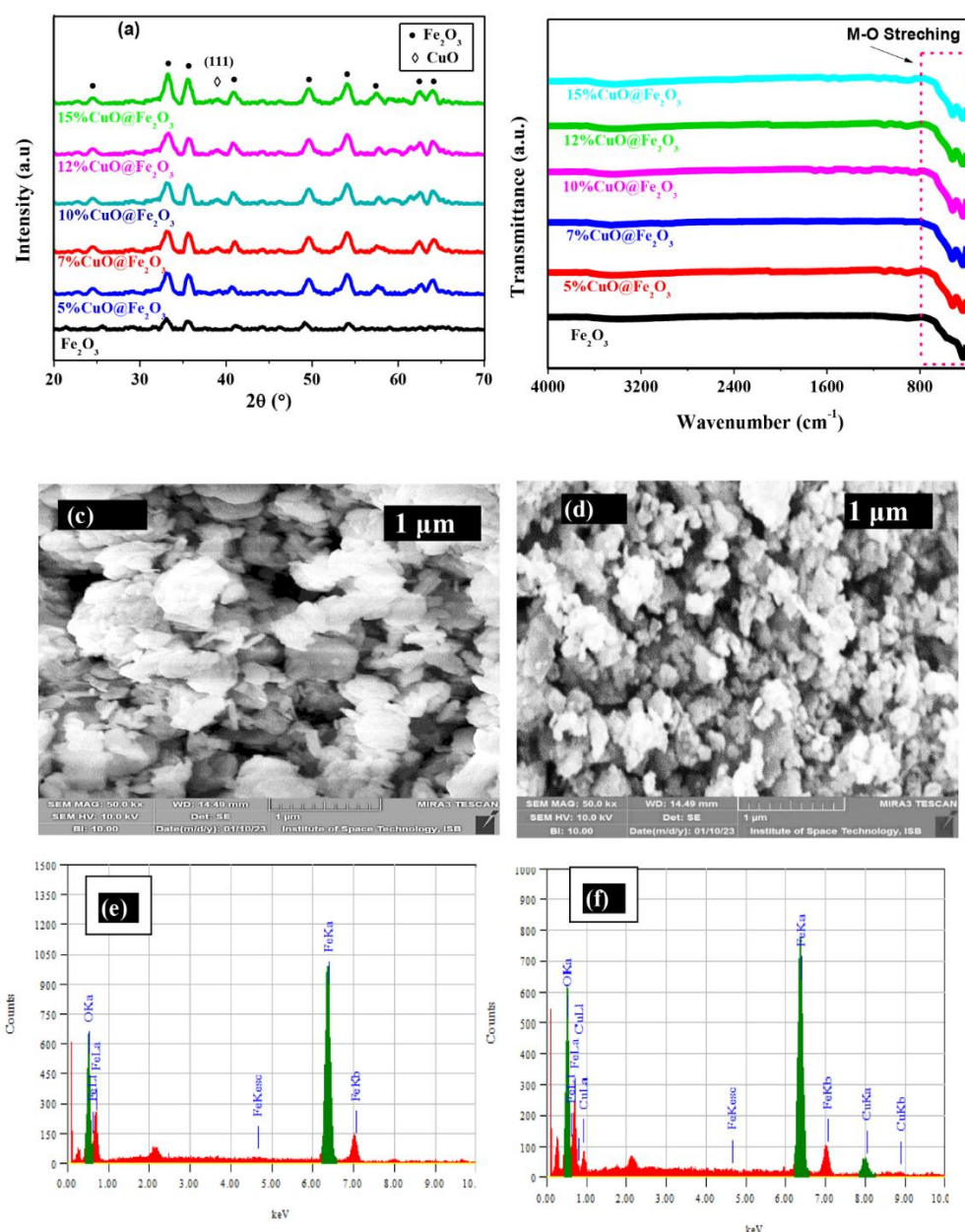
The drop cast method was used for the modification of the working electrode [38], in which a cleaned GC electrode's surface was dampened with 2  $\mu\text{l}$  of pure ethanol, and 0.1 mg of purely ground powder of electrocatalyst was drop cast on it by using 2  $\mu\text{l}$  of 0.5% Nafion. The electrode was dried at  $45^\circ\text{C}$  in an oven for 30 min [16, 17, 39].

The electrochemical measurements were conducted using the Gamry-potentiostat interface 1000. Electrochemical characterization of metal oxides was done to study the conductive behavior of synthesized materials using three electrode systems: a glassy carbon electrode functions as the working electrode, a platinum wire acts as the counter electrode, and Ag/AgCl (3 M KCl) is used as the reference electrode. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed in alkaline medium, and the potential recorded against Ag/AgCl was converted to RHE using the equation ( $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.0591 * \text{pH}$ ), and electrocatalytic parameters were calculated. Conductive nature and electron transfer behavior of all prepared electrocatalysts were studied by performing electrochemical impedance spectroscopy (EIS) in both AC and DC voltage. Double-layer capacitance ( $C_{\text{dl}}$ ) was calculated by performing CV in the non-Faradic region. Chronoamperometric analysis was carried out for the stability test of modified electrodes.

### 3. Results & Discussion

#### 3.1 Physical Characterizations

X-ray diffraction analysis was carried out to examine the crystallinity and phase purity of the prepared samples. The XRD pattern of the pure  $\text{Fe}_2\text{O}_3$  is well matched with the reference pattern of the rhombohedral structure of hematite (JCPDS No. 00-024-0072). The XRD pattern for all doped compositions is shown in Figure 1(a), in which a peak at  $38.5^\circ$  confirms the successful incorporation of CuO nanoparticles on  $\text{Fe}_2\text{O}_3$  support. It is evident that the peak intensity kept on increasing with the incorporation of different concentrations of CuO. The peaks indexed to CuO and  $\alpha\text{-Fe}_2\text{O}_3$  are sharp, which reveals crystallized behavior of the prepared samples.



**Figure 1** (a) XRD patterns and (b) FTIR spectra of pure and doped compositions, (c & d) SEM micrographs of  $\text{Fe}_2\text{O}_3$  and 10%  $\text{CuO}@Fe_2O_3$  at 1  $\mu\text{m}$  magnification scale, respectively, (e & f) EDS spectra of  $\text{Fe}_2\text{O}_3$  and 10%  $\text{CuO}@Fe_2O_3$ , respectively.

Average crystallite size of synthesized materials was estimated by using Debye Scherer formula [40]:

$$D_{av} \text{ (nm)} = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Where,  $D_{av}$  is the average crystallite size,  $k$  is the shape factor, and  $\beta$  is the diffraction peak width (radians). The calculated crystallite size of the synthesized samples was 10-28 nm and is shown in Table 1.

**Table 1** Crystallite size of all compositions.

| Sample                                 | $D_{av}$ (nm) |
|----------------------------------------|---------------|
| $\text{Fe}_2\text{O}_3$                | 10            |
| 5% $\text{CuO}@\text{Fe}_2\text{O}_3$  | 21            |
| 7% $\text{CuO}@\text{Fe}_2\text{O}_3$  | 28            |
| 10% $\text{CuO}@\text{Fe}_2\text{O}_3$ | 13            |
| 12% $\text{CuO}@\text{Fe}_2\text{O}_3$ | 28            |
| 15% $\text{CuO}@\text{Fe}_2\text{O}_3$ | 19            |

FTIR was performed in the range of 400-4000  $\text{cm}^{-1}$  in order to examine the phase purity and successful fabrication of nanocomposites. Sharp bands are observed at wavenumber below 800  $\text{cm}^{-1}$  that correspond to characteristics CuO vibrational modes [41], confirming that CuO has been successfully incorporated into the  $\text{Fe}_2\text{O}_3$  matrix. FTIR spectra of all loaded compositions are shown in Figure 1(b). SEM and EDS analysis were carried out to examine the surface morphology and phase purity of all samples. The SEM micrographs of  $\text{Fe}_2\text{O}_3$  and 10%  $\text{CuO}@\text{Fe}_2\text{O}_3$  at 1  $\mu\text{m}$  revealed an agglomerated structure, as shown in Figure 1(c & d), respectively. EDS analysis results of wt% and atomic% are in good agreement with the stoichiometric amount taken for the synthesis of the nanocomposite material. Figure 1(e & f) represents the EDS spectra of  $\text{Fe}_2\text{O}_3$  and 10%  $\text{CuO}@\text{Fe}_2\text{O}_3$ , respectively.

### 3.2 OER Response of Pure and Composite Nanomaterials ( $x\text{CuO}@\text{Fe}_2\text{O}_3$ )

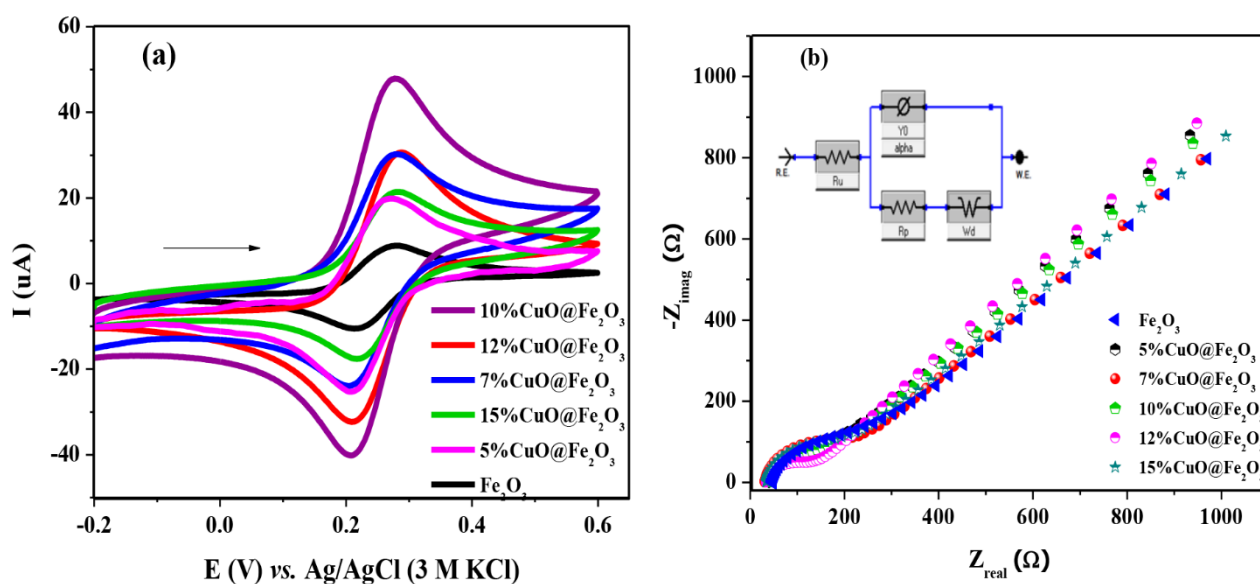
#### 3.2.1 CV and EIS Analysis in Potassium Ferricyanide Solution

Cyclic voltammetry was performed in a 5 mM solution of potassium ferricyanide with 3 M KCl electrolyte. The active surface was calculated from the current responses of the working electrode for the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple, which showed the single-electron transfer process. Figure 2(a) represents the CV profile of all the catalyst-modified electrodes, which demonstrates the change in current responses as the compositions of CuO varied. Randles-Sevick equation was used to calculate the active surface area of modified electrodes [16, 42]:

$$I_p = 2.69 \times 10^5 n^{3/2} A C D^{1/2} \nu^{1/2} \quad (2)$$

Where  $I_p$  represents the redox peak current of the analyte,  $\nu$  denotes the scan rate in  $\text{Vs}^{-1}$ ,  $C$  is the concentration in  $\text{mol cm}^{-3}$ ,  $D$  denotes the diffusion coefficient ( $0.76 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ ),  $A$  is the surface

area in  $\text{cm}^2$ , and  $n$  is the number of electrons transferred. The maximum current response was observed for the 10%  $\text{CuO}@Fe_2O_3$ , thus offering the highest active surface area of  $0.041 \text{ cm}^2$ , indicative of the enhanced redox potential of 10% copper-doped iron oxide.



**Figure 2** (a) CV response of  $x\text{CuO}@Fe_2O_3$  modified GC electrode in 5 mM  $K_3[Fe(CN)_6]$  + 3 M KCl at  $0.1 \text{ V s}^{-1}$  in potential window range of -0.2 to 0.6 V, (b) Simulated EIS spectra of all compositions performed in 5 mM  $K_3[Fe(CN)_6]$ :3 M KCl, with its equivalent circuit model in the inset.

EIS was also performed for all the compositions in 5 mM  $K_3[Fe(CN)_6]$  and 3 M KCl to study the charge transfer parameters, and a Nyquist plot was obtained from the acquired data. At the high frequency domain, a Nyquist plot shows a distinct semicircle which is analogous to the electron transfer resistance ( $R_{ct}$ ) and at lowest frequency an inclined part which is analogous to the diffusion process that defines Warburg resistance ( $R_w$ ). The faster transfer of electrons at the electrode surface is shown by a small  $R_{ct}$  value, because of high conductivity. To calculate the apparent electron transfer rate constant, the following equation is used [43].

$$k_{app} = RT/F^2 R_{ct} C \quad (3)$$

In this equation,  $R$  represents the gas constant ( $8.314 \text{ J mol}^{-2} \text{ K}^{-1}$ ),  $T$  denotes the absolute temperature,  $F$  is the Faraday constant, and  $C$  is the analyte's concentration ( $\text{mol cm}^{-3}$ ). Figure 2(b) shows the EIS profiles along with model-fitted spectra of all compositions in 5 mM  $K_3[Fe(CN)_6]$  and 3 M KCl. Various EC parameters were acquired from EIS data by the model fitting of the observed spectra of all the compositions are shown in Table 2. 10% copper-doped iron oxide shows the highest  $k_{app}$  and the lowest  $R_{ct}$  values, which marks it for the fast electron transfer process as compared to other catalysts [44]. A small value of  $R_{ct}$  represents a fast electron transfer process at the electrode-electrolyte interface, rendered by the coherence between a smaller particle size and better conductivity.

**Table 2** EIS parameters values for all the compositions.

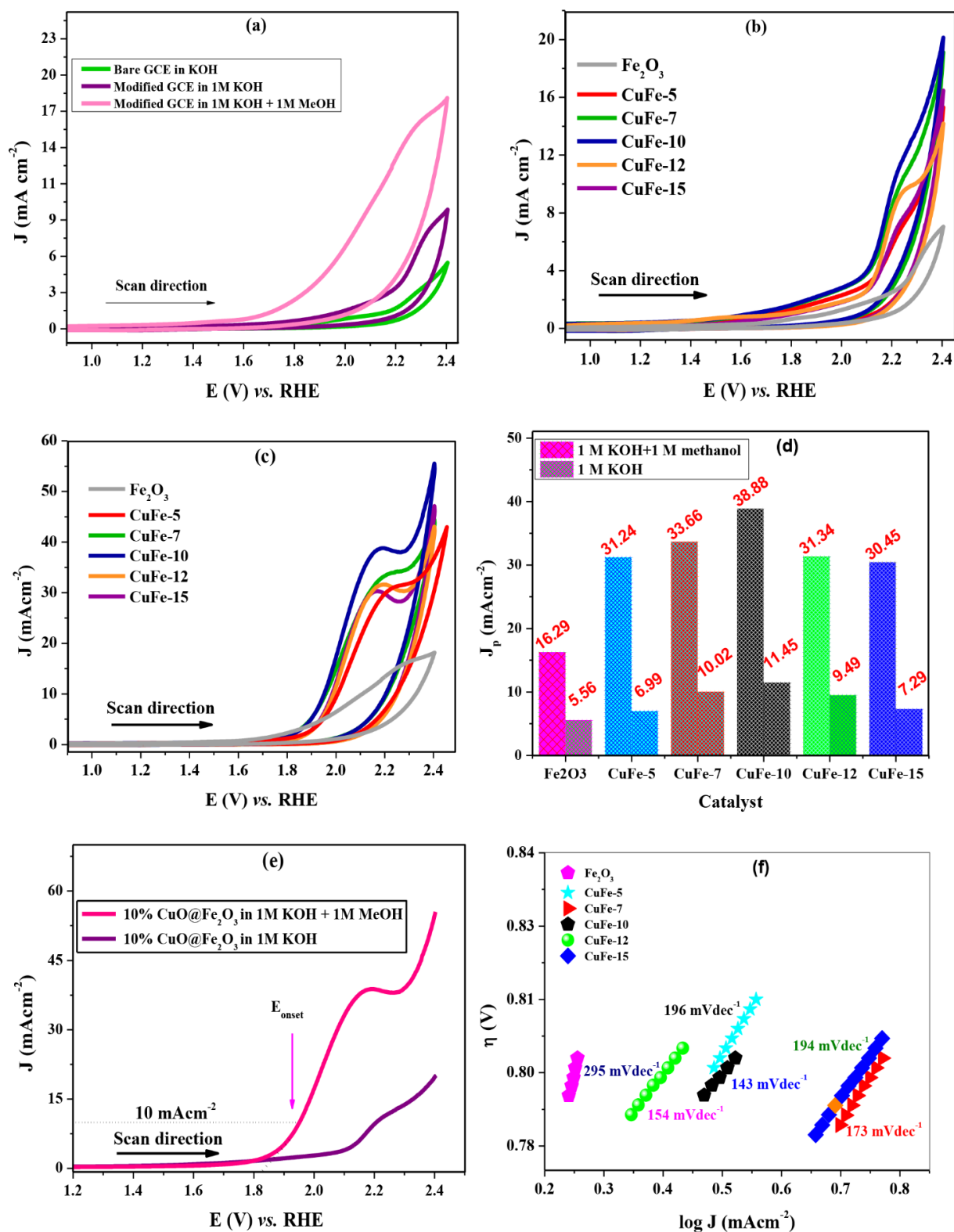
| Catalyst                               | Active Surface Area (cm <sup>2</sup> ) | R <sub>s</sub> (Ω) | R <sub>ct</sub> (Ω) | α     | CPE (μF) | R <sub>w</sub> (μΩ) | k <sub>app</sub> × 10 <sup>-4</sup> (cm s <sup>-1</sup> ) |
|----------------------------------------|----------------------------------------|--------------------|---------------------|-------|----------|---------------------|-----------------------------------------------------------|
| Fe <sub>2</sub> O <sub>3</sub>         | 0.007                                  | 46                 | 170                 | 0.911 | 4.21     | 317                 | 3.1                                                       |
| 5% CuO@Fe <sub>2</sub> O <sub>3</sub>  | 0.016                                  | 40                 | 100                 | 0.980 | 2.54     | 370                 | 5.3                                                       |
| 7% CuO@Fe <sub>2</sub> O <sub>3</sub>  | 0.024                                  | 31                 | 90                  | 0.954 | 3.15     | 403                 | 6.0                                                       |
| 10% CuO@Fe <sub>2</sub> O <sub>3</sub> | 0.041                                  | 21                 | 65                  | 0.952 | 3.30     | 285                 | 8.1                                                       |
| 12% CuO@Fe <sub>2</sub> O <sub>3</sub> | 0.026                                  | 30                 | 78                  | 0.93  | 2.88     | 697                 | 6.8                                                       |
| 15% CuO@Fe <sub>2</sub> O <sub>3</sub> | 0.018                                  | 34                 | 145                 | 0.999 | 3.87     | 799                 | 3.7                                                       |

R<sub>s</sub> = solution resistance, R<sub>ct</sub> = charge transfer resistance, α = roughness factor, CPE = constant phase element, R<sub>w</sub> = Warburg resistance.

### 3.2.2 Determination of Electrocatalytic Parameters (j, E<sub>on</sub>, η, TS, R<sub>s</sub>, and R<sub>ct</sub>)

Current density is one of the most essential OER criteria for assessing any catalyst's performance. The catalyst becomes more active as its current density increases. To distinguish the response of bare glassy carbon electrode (GCE) and modified iron oxide in both 1 M KOH and 1 M MeOH systems at 0.1 V s<sup>-1</sup>, a comparison of cyclic voltammograms recorded in the potential range of 0 to 1.5 V is shown in Figure 3(a). Methanol was used as a facilitator, and from the CV profile, it can be inferred that the current density was enhanced from 8 mA cm<sup>-2</sup> to 16 mA cm<sup>-2</sup> for iron oxide by the addition of methanol. Peak current densities were observed to be higher for the doped iron oxide as compared to pure iron oxide. CV responses of all compositions in 1 M KOH and 1 M KOH + 1 M methanol are shown in Figure 3(b & c), respectively. All doped iron oxide nanomaterials were responsive to water electrocatalysis and exhibited good OER performances. However, 10% CuO@Fe<sub>2</sub>O<sub>3</sub> composition shows the highest current density, thus exhibiting better electrocatalytic composition than others. Current densities were estimated from the peak heights in the voltammograms collected in 1 M KOH and 1 M KOH/1 M methanol system, and it is also represented in graphical form in Figure 3(d). Due to the increase in oxidation rate of OH<sup>-</sup> ions to produce the oxygen in the OER process, there was a 3 to 4 order increment in the peak current densities in KOH+ methanol as compared to that in KOH only. This may have occurred because of salt-like species, MeO<sup>-</sup>K<sup>+</sup>, produced due to OH<sup>-</sup> and methanol, which facilitates the migration of OH<sup>-</sup> ions towards the electrode surface (KOH + MeOH → MeO<sup>-</sup>K<sup>+</sup> + H<sup>+</sup> + OH<sup>-</sup>). More OH<sup>-</sup> ions move toward the electrode's surface, to get oxidized, and more oxygen is produced. The enhanced charge transfer kinetics of the OER process at the electrode surface render an increase in the current density.





**Figure 3** (a) Comparison of voltammograms of bare GCE and modified GCE at  $0.1 \text{ V s}^{-1}$  in  $1 \text{ M KOH}$  and  $1 \text{ M KOH} + 1 \text{ M MeOH}$  systems, (b & c) Comparison of voltammograms of all composition modified electrodes at  $0.1 \text{ V s}^{-1}$  in  $1 \text{ M KOH}$  and  $1 \text{ M KOH} + 1 \text{ M MeOH}$ , respectively, (d) graphical representation of current densities of all the compositions in  $1 \text{ M KOH}$  and  $1 \text{ M KOH} + 1 \text{ M MeOH}$ , (e) comparison of LSV plot of  $10\% \text{ CuO@Fe}_2\text{O}_3$  at  $0.1 \text{ V s}^{-1}$ , and (f) Tafel slopes of all compositions.

The performance of a catalyst can also be examined by its peak current and onset potential. To determine the catalytic behavior of a material, the onset potential is a vital parameter [45]. The catalyst with the highest peak current and lowest onset potential value is the optimal one. Figure 3(e) shows peak current and onset potential of 10% CuO@Fe<sub>2</sub>O<sub>3</sub> in both systems at 100 mV s<sup>-1</sup>. Among all the electrocatalysts, 10% CuO@Fe<sub>2</sub>O<sub>3</sub> showed low onset and overpotential values, which confirms that it is a powerful catalyst for the OER process.

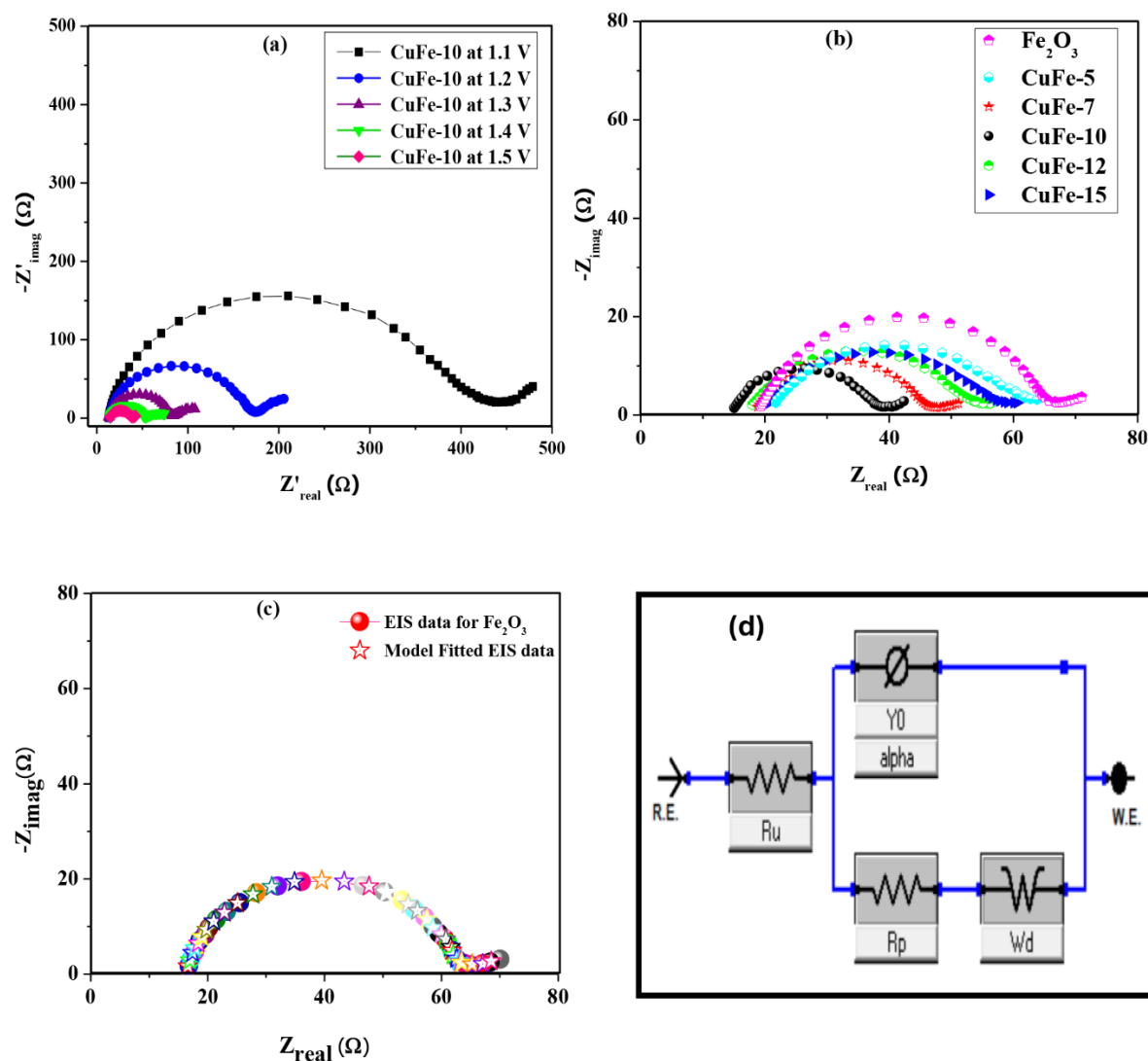
To examine the mechanism and kinetics of the redox process, Tafel analysis was carried out, which is also an applicable criterion for the comparison of the catalytic activity of various catalysts [46]. The Tafel equation ( $\eta = a + b \log(j/J_0)$ ) was used to calculate the Tafel slopes for all the modified electrodes. Figure 3(f) represents the comparison of Tafel slopes of all the catalysts in 1 M KOH: 1 M MeOH. The lowest Tafel slope is observed for 10% CuO@Fe<sub>2</sub>O<sub>3</sub>, which indicates that current density increases with a smaller overpotential value, suggesting a faster reaction rate. All the above electrochemical parameters obtained for all compositions are summarized in Table 3.

**Table 3** EC parameters of all the composition determined from CV, LSV and EIS.

| Electrocatalysts→<br>(1 M KOH + 1 M MeOH) |                         | 5%<br>Fe <sub>2</sub> O <sub>3</sub> | 7%<br>CuO@<br>Fe <sub>2</sub> O <sub>3</sub> | 10%<br>CuO@<br>Fe <sub>2</sub> O <sub>3</sub> | 12%<br>CuO@<br>Fe <sub>2</sub> O <sub>3</sub> | 15%<br>CuO@<br>Fe <sub>2</sub> O <sub>3</sub> |
|-------------------------------------------|-------------------------|--------------------------------------|----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| EC parameters↓                            |                         | Fe <sub>2</sub> O <sub>3</sub>       | Fe <sub>2</sub> O <sub>3</sub>               | Fe <sub>2</sub> O <sub>3</sub>                | Fe <sub>2</sub> O <sub>3</sub>                | Fe <sub>2</sub> O <sub>3</sub>                |
| E <sub>on</sub> (v) vs. Ag/AgCl           |                         | 0.92                                 | 0.91                                         | 0.88                                          | 0.86                                          | 0.92                                          |
| E <sub>on</sub> (v) vs. NHE               |                         | 1.12                                 | 1.107                                        | 1.077                                         | 1.057                                         | 1.117                                         |
| η <sub>10</sub> (V) vs. Ag/AgCl           |                         | 1.16                                 | 1.10                                         | 1.05                                          | 1.04                                          | 1.09                                          |
| η <sub>10</sub> (V) vs. NHE               |                         | 1.357                                | 1.297                                        | 1.247                                         | 1.237                                         | 1.277                                         |
| Tafel slope (mVdec <sup>-1</sup> )        |                         | 295                                  | 196                                          | 173                                           | 143                                           | 154                                           |
| 1 M KOH                                   | j (mAcm <sup>-2</sup> ) | 5.56                                 | 6.99                                         | 10.02                                         | 11.45                                         | 9.49                                          |
|                                           | R <sub>s</sub> (Ω)      | 16.24                                | 19.17                                        | 17.87                                         | 17.41                                         | 16.51                                         |
|                                           | R <sub>ct</sub> (Ω)     | 167.4                                | 112.2                                        | 74.6                                          | 67.5                                          | 105.3                                         |
|                                           | j (mAcm <sup>-2</sup> ) | 16.29                                | 31.24                                        | 33.66                                         | 38.88                                         | 31.34                                         |
| 1 M KOH + 1 M MeOH                        | R <sub>s</sub> (Ω)      | 19.34                                | 21.77                                        | 18.87                                         | 15.06                                         | 17.95                                         |
|                                           | R <sub>ct</sub> (Ω)     | 47.2                                 | 40.2                                         | 28.5                                          | 22.4                                          | 33.5                                          |

Electrochemical impedance spectroscopy was carried out in 1 M KOH and 1 M KOH + 1 M MeOH, to study the charge transfer kinetics of OER process. Figure 4(a) shows the EIS spectra of 10% CuO@Fe<sub>2</sub>O<sub>3</sub> at different voltage ranges (1.1-1.5 V), and the lowest charge transfer resistance was observed at 1.5 V. Figure 4(b) represents the comparison of EIS data of all compositions in 1 M KOH + 1 M MeOH. At a high frequency region (1 MHz), a complete semicircle is obtained, which demonstrates the charge transfer process. In contrast, at a low frequency region (0.1 Hz), an inclined part confirms the diffusion process. Table 3 shows the charge transfer resistance values of all the compositions, and 10% CuO@Fe<sub>2</sub>O<sub>3</sub> showed the fastest electron transfer reaction with the minimum charge transfer resistance of 22.4 Ω in 1 M KOH: 1 M MeOH. Figure 4(c) represents the model-fitted Nyquist plot obtained for Fe<sub>2</sub>O<sub>3</sub> in 1 M KOH + 1 M MeOH. At high frequency domain, Nyquist plot shows a distinct semicircle which is analogous to the electron transfer resistance (R<sub>ct</sub>) and at lowest frequency an inclined part which is analogous to the diffusion process that defines

Warburg resistance ( $R_w$ ) [44]. The faster transfer of electrons at the electrode surface is shown by a small  $R_{ct}$  value, because of high conductivity.



**Figure 4** (a) EIS spectra of 10% CuO@Fe<sub>2</sub>O<sub>3</sub> at 1.1-1.5 V in 1 M KOH + 1 M MeOH, (b) comparison of EIS plots for all the compositions at 1.5 V in 1 M KOH + 1 M MeOH, (c) Model fitted EIS spectra of Fe<sub>2</sub>O<sub>3</sub> in 1 M KOH + 1 M MeOH, and (d) Equivalent circuit model of data acquisition.

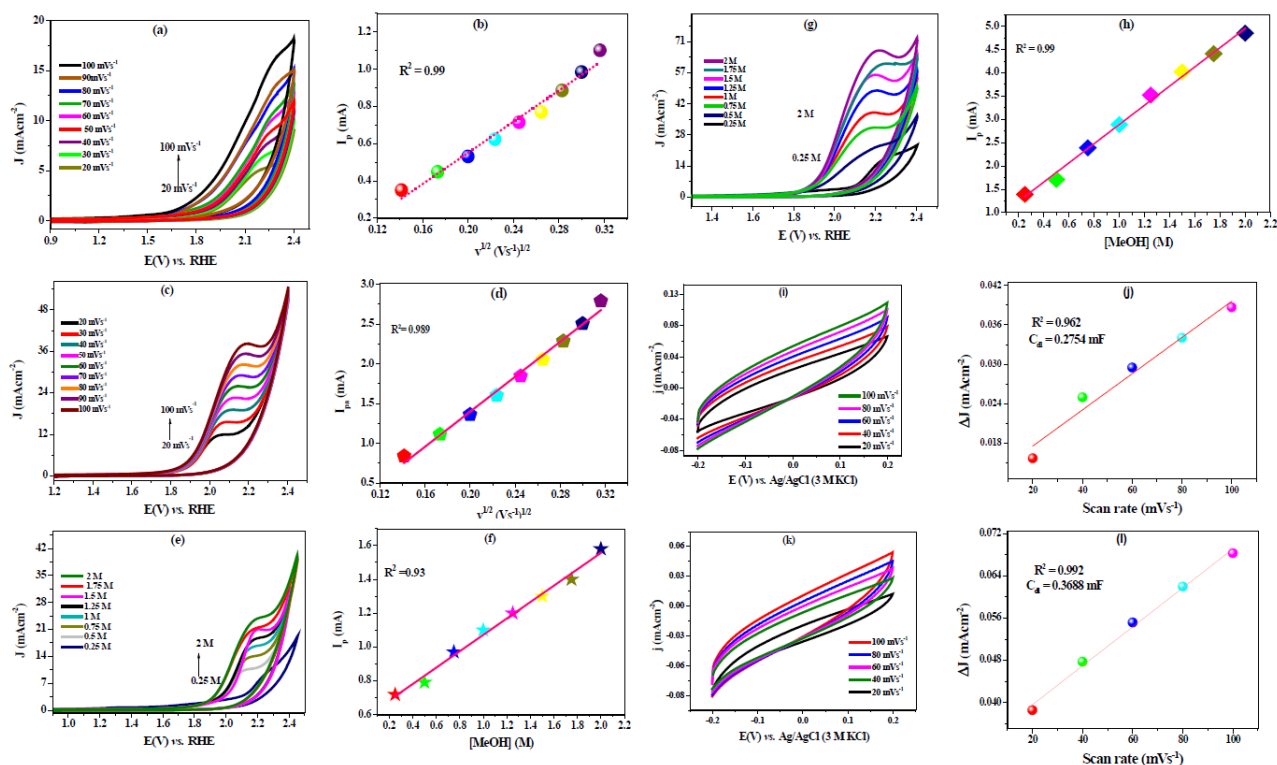
For the quantification of EIS data, equivalent circuit models are fitted for simulation of the EIS data as shown in Figure 4(d). Any modification on the electrode surface has no effect on solution resistance ( $R_s$ ) and Warburg resistance ( $R_w$ ), which show the properties of electrolyte solution and electrocatalyst-dependent diffusion in the solution, respectively.

### 3.2.3 Determination of $D^\circ$ , $m_T$ , $k^\circ$ , $C_{dl}$ , and ECSA

Cyclic voltammetry was performed for all compositions and Figure 5(a & c) represent the CV response of Fe<sub>2</sub>O<sub>3</sub> and 10% CuO@Fe<sub>2</sub>O<sub>3</sub>, respectively at different scan rates in 1 M KOH + 1 M MeOH where the current density increases by increasing the scan rate. This study explores the impact of

scan rate on diffusion kinetics. The water oxidation process being irreversible, the relevant Randles-Sevcik equation was employed to estimate the diffusion coefficient values [42].

$$I_p = 2.99 \times 10^5 n^{3/2} \alpha^{1/2} A C D^{1/2} \nu^{1/2} \quad (4)$$



**Figure 5** Cyclic voltammograms of (a)  $\text{Fe}_2\text{O}_3$  and (c) 10%  $\text{CuO}@\text{Fe}_2\text{O}_3$  modified electrode in 1 M KOH + 1 M methanol recorded at 20-100  $\text{mVs}^{-1}$  scan rates, (b & d) Linear functional plots of  $I_p$  vs.  $\nu^{1/2}$  of  $\text{Fe}_2\text{O}_3$  and 10%  $\text{CuO}@\text{Fe}_2\text{O}_3$  respectively, (e & g) CV response for OER recorded in 0.25-2 M methanol and (f & h) their resultant linear plots of  $I_p$  vs.  $[\text{MeOH}]$  for  $\text{Fe}_2\text{O}_3$  and 10%  $\text{CuO}@\text{Fe}_2\text{O}_3$  respectively, (i & k) cyclic voltammetric responses recorded in non-faradic region and (j & l) the resultant linear plots of  $\text{Fe}_2\text{O}_3$  and 10%  $\text{CuO}@\text{Fe}_2\text{O}_3$ , respectively for the determination of  $C_{dl}$ .

The linear functional plot of peak current versus square root of scan rate was used for the estimation of diffusion coefficient value and are given in Figure 5(b & d) for  $\text{Fe}_2\text{O}_3$  and 10%  $\text{CuO}@\text{Fe}_2\text{O}_3$ . The oxidation process at the electrode-electrolyte interface was facilitated by all electrodes, which showed a similar trend of rising currents with the scan rate. The linear trends of Randles-Sevcik plots confirmed that the water oxidation is a diffusion-controlled reaction. The mass transport coefficient was also calculated by using the following equation [47].

$$m_T = [D^0 / (RT/F\nu)]^{1/2} \quad (5)$$

The reversibility of any chemical reaction can be identified by comparison of its diffusion coefficient values with the  $k^0$  values. Slow and fast electrode kinetics are related to mass transport and for an irreversible system;  $k^0 \leq 10^{-5}$  is followed.

The effect of methanol concentration was studied by performing cyclic voltammetric measurements for all the modified electrodes. By changing the methanol concentration from 0.25 M to 2 M in a 1 M KOH solution at room temperature, the OER peak current was enhanced in all systems. Methanol concentration effects on OER responses of Fe<sub>2</sub>O<sub>3</sub> and 10% CuO@Fe<sub>2</sub>O<sub>3</sub> are represented in Figure 5(e & g), respectively.

The heterogeneous rate constant is a crucial factor for the estimation of the activity of synthesized materials, and it demonstrates how quickly the electrochemical reaction occurs. It also reflects the reversibility and irreversibility of response. The value of the heterogeneous rate constant was estimated by using the Reinmuth equation:

$$I_p = 0.227 n F A C k^\circ \quad (6)$$

Where F represents the Faraday's constant, n denotes the number of electrons,  $I_p$  represents the anodic peak current, A is the area of the electrode, C is the methanol concentration, and  $k^\circ$  is the heterogeneous rate constant. A Reinmuth graph is plotted between  $I_p$  and methanol concentration, and from the slope value, k is estimated. Figure 5(f & h) show the plots of  $I_p$  vs. methanol concentration for Fe<sub>2</sub>O<sub>3</sub> and 10% CuO@Fe<sub>2</sub>O<sub>3</sub>, respectively.  $D^\circ$ ,  $m_T$  and  $k^\circ$  for all compositions are summarized in Table 4 where the highest values are obtained for 10% CuO@Fe<sub>2</sub>O<sub>3</sub>, which is an indication of the good potency of catalyzing the water oxidation process.

**Table 4** Estimated kinetic parameters for water oxidation on CuO@Fe<sub>2</sub>O<sub>3</sub> materials.

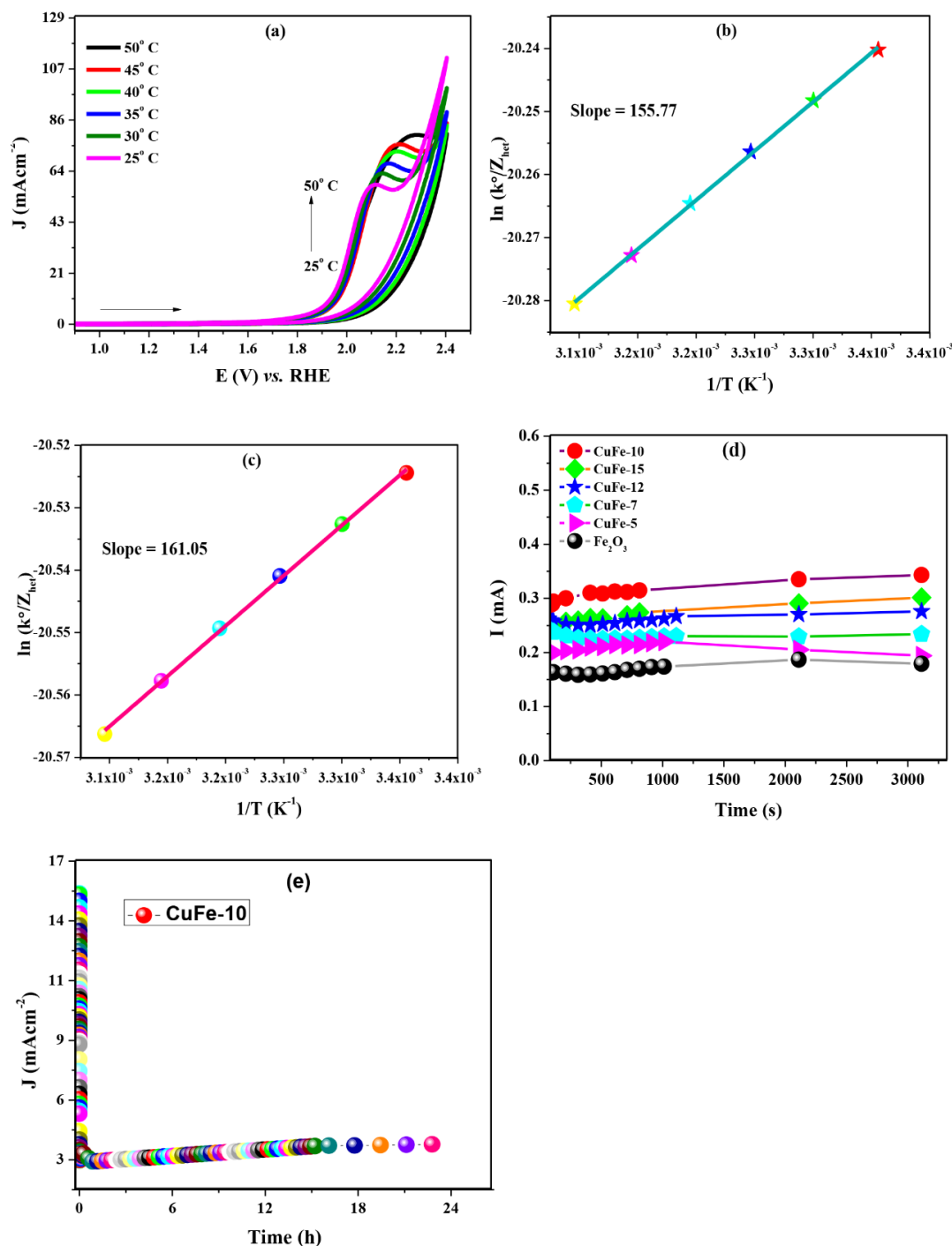
| Electrocatalysts               | $D^\circ \times 10^{-8}$<br>(cm <sup>2</sup> s <sup>-1</sup> ) | $m_T \times 10^{-4}$<br>(cms <sup>-1</sup> ) | $k^\circ \times 10^{-4}$<br>(cms <sup>-1</sup> ) | $C_{dl}$ (mF) | ECSA (cm <sup>2</sup> ) | $R_F$  |
|--------------------------------|----------------------------------------------------------------|----------------------------------------------|--------------------------------------------------|---------------|-------------------------|--------|
| Fe <sub>2</sub> O <sub>3</sub> | 0.6                                                            | 1.5                                          | 1.4                                              | 0.27          | 6.88                    | 97.31  |
| CuFe-5                         | 2.1                                                            | 3.0                                          | 3.1                                              | 0.30          | 7.53                    | 106.50 |
| CuFe-7                         | 2.7                                                            | 3.2                                          | 3.6                                              | 0.33          | 8.46                    | 119.64 |
| CuFe-10                        | 3.5                                                            | 3.6                                          | 4.3                                              | 0.36          | 9.22                    | 130.39 |
| CuFe-12                        | 1.5                                                            | 2.4                                          | 3.2                                              | 0.34          | 8.56                    | 121.05 |
| CuFe-15                        | 1.3                                                            | 2.2                                          | 3.3                                              | 0.31          | 7.91                    | 111.86 |

$D^\circ$  = diffusion coefficient,  $m_T$  = mass transport coefficient,  $k^\circ$  = heterogeneous rate constant,  $C_{dl}$  = double layer capacitance.

Double layer capacitance  $C_{dl}$ , was calculated by performing the cyclic voltammetry in non-faradic region at various scan rates (20-100 mV s<sup>-1</sup>) in 1 M KOH + 1 M MeOH for Fe<sub>2</sub>O<sub>3</sub> and 10% CuO@Fe<sub>2</sub>O<sub>3</sub> are shown in Figure 5(i & k), while their linear plots are presented in Figure 5(j & k), respectively [48]. Double-layer capacitance was calculated from the slope of linear plots and ECSA was calculated by using the equation ( $ECSA = C_{dl}/C_{sp}$ ) where  $C_{sp}$  denotes the general specific capacitance for metal oxide electrodes in alkaline solution (0.040 mF cm<sup>-2</sup>) [49]. For catalytic activity, another parameter is used, which is called the roughness factor ( $R_F$ ). It is calculated by dividing the ECSA by the geometric surface area of the glassy carbon electrode (0.0707 cm<sup>2</sup>). Electrochemical parameters obtained for all compositions are shown in Table 4.

## 3.2.4 Effect of Temperature on OER Response and Stability Test

Cyclic voltammograms were recorded in the temperature range of 298 to 323 K with a 5°C interval to study the temperature effect on the OER kinetics. The peak current was observed to increase slightly with temperature. As the temperature rises, more molecules become mobile, which in turn increases the oxidation process, thereby enhancing the OER kinetics. Figure 6(a) represents the cyclic voltammograms for the temperature effect of OER on CuFe-10.



**Figure 6** (a) CV responses of CuFe-10 at different temperature range in 1 M KOH + 1 M MeOH, (b) and (c) Functional plots of CuFe-10 for determination of  $\Delta H$  and  $\Delta S$  values in 1 M KOH and 1 M KOH + 1 M MeOH respectively, (d) Chronoamperometry stability test

performed for all compositions for 3100 s, and (e) Stability test performed for CuFe-10 for 24 hours.

Electrocatalytic stability of catalysts can be studied by using an effective technique called chronoamperometry [50]. Figure 6(d) represents the current-time response for all prepared samples in 1 M KOH + 1 M methanol for 3100 s. The scan shows no significant change in current; however, a slight fluctuation in the scan could be due to oxygen bubble formation on the electrode surface. This conforms to good stability and long-term application of the synthesized compositions.

To calculate the thermodynamic parameters, Marcus equation was used:

$$k^{\circ} = Z_{\text{het}} \exp[-\Delta G/RT] \quad (7)$$

Where,  $Z_{\text{het}}$  is the collision frequency, and its value can be calculated at different temperature with the help of following relation:

$$Z_{\text{het}} = (RT/2\pi M)^{1/2} \quad (8)$$

Where,  $M$  stands for the analyte's molar mass.

Marcus equation can be written in the more simplified form in the following way:

$$\ln(k^{\circ}/Z_{\text{het}}) = -\Delta H^{\circ}/RT + \Delta S^{\circ}/R \quad (9)$$

Figure 6(b & c) shows the linear functional plots of  $\ln(k^{\circ}/Z_{\text{het}})$  vs.  $1/T$  in 1 M KOH and 1 M KOH + 1 M methanol, respectively and  $\Delta S$  and  $\Delta H$  values were calculated from the intercept and slope of linear plots.  $\Delta H$  and  $\Delta S$ , calculated from the above plots, are tabulated in Table 5.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (10)$$

**Table 5** Thermodynamic parameters for OER on CuFe-10 modified GC electrode.

| Thermodynamic parameters                          | CuFe-10 |                    |
|---------------------------------------------------|---------|--------------------|
|                                                   | 1 M KOH | 1 M KOH + 1 M MeOH |
| $\Delta H$ (kJ mol <sup>-1</sup> )                | -1.29   | -1.33              |
| $\Delta S$ (J K <sup>-1</sup> mol <sup>-1</sup> ) | -172.61 | -175.12            |
| $\Delta G$ (kJ mol <sup>-1</sup> )                | 50.14   | 50.85              |

The positive value of  $\Delta G$  indicates the reaction is non-spontaneous and energy-driven at low temperatures in the 298 to 323 K range. The thermodynamic parameters are the indicators of the compatibility between the material surface properties and the interface. These parameters are nearly the same in KOH only and KOH plus MeOH, thus corresponding to their catalytic suitability in both the alkaline medium and methanol fuel cell applications.

#### 4. Conclusions

Pure iron oxide and different compositions of CuO@Fe<sub>2</sub>O<sub>3</sub> were successfully synthesized via facile precipitation and impregnation methods, respectively. XRD patterns confirmed the rhombohedral crystal structure of hematite, and FT-IR confirmed metal oxygen bond formation.

SEM and EDX showed agglomerated shapes and the purity of the synthesized materials, respectively. EIS and CV were conducted to study the redox properties of the synthesized materials, which revealed that 10% CuO@Fe<sub>2</sub>O<sub>3</sub> is the best candidate among all the catalysts. 10% CuO@Fe<sub>2</sub>O<sub>3</sub> showed better catalytic behavior with the highest peak current and low onset and overpotential values. Water oxidation was observed to be diffusion-controlled using all the modified electrodes with the highest diffusion co-efficient ( $3.5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ), mass transport co-efficient ( $3.6 \times 10^{-4} \text{ cm s}^{-1}$ ) for 10% CuO@Fe<sub>2</sub>O<sub>3</sub>. From the electrochemical responses, the OER performance order can be visualized as: 5% CuO@Fe<sub>2</sub>O<sub>3</sub> < 7% CuO@Fe<sub>2</sub>O<sub>3</sub> < 10% CuO@Fe<sub>2</sub>O<sub>3</sub> > 12% CuO@Fe<sub>2</sub>O<sub>3</sub> > 15% CuO@Fe<sub>2</sub>O<sub>3</sub>. The interesting application of these simple materials as potential catalysts for electrochemical water oxidation is being reported for the first time, and the catalytic potency is found at par with the reported catalytic materials.

### Author Contributions

Hira Khalid, Muhammad Asim, Akbar Hussain, Tehmeena Maryem Butt, and Sadia Kanwal: Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing, Visualization. Naveed Kausar Janjua: Principal Supervisor. All authors have read and agreed to the published version of the manuscript.

### Competing Interests

The authors have declared that no competing interests exist.

### Data Availability Statement

The data that support the plots in this paper and other findings of this study are available from the corresponding author upon reasonable request.

### AI-Assisted Technologies Statement

AI tool, ChatGPT, was used for language editing purposes only, and the author takes full responsibility for the content of the manuscript.

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