Indian Journal of Chemistry
Vol. 63, January 2024, pp. 40-48
DOI: 10.56042/ijc.v63i1.2312

# Carbon nanotubes immobilized copper(salen) nanocomposite for electrochemical oxygen evolution reaction

Mandakini Gupta[a#], Narvadeshwar[b#], Angesh Kumar Maurya[b], Vikas Jangra[b], Anamika Pandey[b], Piyush Kumar Sonkar*[b] & Upendra Kumar[c]

[a] Department of Chemistry, Sunbeam College, Varuna, Varanasi 221 002, India
[b] Department of Chemistry, MMV, Banaras Hindu University, Varanasi 221 005, India
[c] Advanced Functional Materials Laboratory, Department of Applied Sciences, IIIT Allahabad, Prayagraj 211 015, India

E-mail: piyush.sonkar37@gmail.com, piyushchem.mmv@bhu.ac.in

*Received 03 June 2023; accepted(revised) 14 December 2023*

Efficient oxygen evolution reaction (OER) electrocatalysts are widely required in the realm of water electrolysis and rechargeable metal-air batteries. This work describes an easy and simple method for the synthesis of copper salen (Cu(Salen))-functionalized multiwalled carbon nanotubes (MWCNTs) nanocomposite materials (Cu(Salen)/MWCNTs). It has been used for OER in the basic medium (0.1 M KOH). The resulting nanocomposite, Cu(Salen)/MWCNTs, has been studied using spectroscopic and microscopic techniques such as Fourier transform infrared (FT-IR), UV-visible spectroscopy, powder X-ray diffraction (p-XRD), scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDAX). The electrochemical characterization of prepared Cu(Salen)/MWCNTs nanocomposite based modified glassy carbon (GC) electrodes (GC/Cu(Salen)/MWCNTs) and their application towards OER have been performed using an electrochemical method. The Tafel slope of nanocomposite material is 159.6 mV/dec in 0.1 M KOH solution, indicating that GC/Cu(Salen)/MWCNTs could be a promising and cost-effective electrode material for the OER. This study demonstrates a novel way for creating an active nanocomposite catalyst for OER in alkaline media.

**Keywords**: Copper (salen), MWCNTs, Oxygen evolution reaction, Electrochemical, Nanocomposite, Modified electrode

As the world's population and industrialization grow, so does the need for a lot of energy. At the moment, most of the energy we use comes from carbon-based resources like oil, coal, natural gas, *etc.* Since carbon emissions have emerged as a serious environmental issue as it is one of the main causes of global warming and further results in the greenhouse effect, now is the alarming time for us to shift our energy demand to not only renewable and sustainable resources of energy but also resources that cause no harm to the environment. Accordingly, replacements for fossil fuels are being widely researched by scientists to achieve a better alternative to fossil fuels that can contribute to sustainable energy resources for fulfilling our energy demands [1,2].

Hydrogen production is one of the cost effective methods that utilizes electrolytic splitting of water molecules with the evolution of oxygen as a byproduct.The water electrolysis basically involves the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), which occur simultaneously on both half cells as represented by the following equations:

At Cathode: $4H^+(aq) + 4\ e^- \rightarrow 2\ H_2(g) E_R = 0.00$ V

At Anode: $2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+ + 4e^-\ E_L = 1.23$ V

Overall Reaction involves : $2H_2O(l) \rightarrow + O_2\ (g) + H_2\ (g)\ E_{Cell} = 1.23$ V

For the reaction to continue, a voltage of 1.23 V is needed [3]. However, an overpotential is also required due to the potential loss arising on account of multi-step reactions with single-electron transfer at each step during electrochemical reactions and so causing kinetic limitations that further result in the OER being much more sluggish than the HER. Hence, it is obvious to search for a suitable electrocatalyst that can lower the overpotential required for OER. For example, precious metal-based electrocatalysts were widely investigated for OER. In addition, electrocatalysts based on Ru, Ir, and their oxides exhibited superior OER activity under both acidic and alkaline conditions, but the high cost of these metals limits their application in large-scale production of

# Both the authors contributed equally to the article.

$H_2$. By reducing adsorption energies [4-6] or improving the electrical conductivity of the catalysts, combinations of multimetal systems now show significant electrocatalytic activity and high efficiency towards OER.

Recently, salen(N,N-bis(Salicylidene)ethylenediamine ligand (Molecular formula: $C_{16}H_{16}N_2O_2$) based metal complexes have received enormous attention from scientists across the globe due to their applications in many fields such as in the treatment of cancer [7], in food industry,as antiviral agents[8], fungicide agents [9], antibacterial agents [10-11], and in different biological activities *e.g*. antitumor activity of salen complexes arises because of its DNA binding properties[12]. Salen refers to a tetradentate $C_2$-symmetric chelating ligand, conformationally flexible and hence, can adopt a variety of geometries. Considerable attention has been done previously for the preparation and characterization of various transition metal complexes ofCo, Ni, Fe, Cu, *etc*. with salen-type ligands due to their grandeur catalytic property [13-15].On the other hand, copper is reported to be the best thermal conductor as reported earlier (401 W $m^{-1}$ $K^{-1}$ at 27°C) [16]. Apart from this, copper is strong, ductile, has a high current-carrying capacity [17-18], and is resistant to corrosion [19]. Hence, Cu(Salen) was chosen for the development of the electrocatalyst.

Carbon nanotubes (CNTs) were discovered in 1991 and are novel nanocarrier systems that possess a wide range of applications in science, engineering, and the environment.They have high tensile strength, and high thermal and electrical conductivity [20-25]. It has negligible surface fouling when used as a modified electrode [26]. It makes MWCNTs one of the suitable materials for various applications. Basically, the major issue that needs to be considered while working with MWCNTs is their strong tendency to agglomerate, as they are typically present as bundles of nanotubes. Although several methods have been reported to resolve this issue, such as ultrasonication, plasma treatment, ball-milling, chemical functionalization, which comprises either covalent or non-covalent functionalization of nanotubes, and polymer wrapping around MWCNTs [27]. Out of all mentioned methods, non-covalent functionalization is of great importance since this method not only supports proper dispersion of MWCNTs in an aqueous medium but also prevents the destruction of π bonds present on the surface of MWCNTs. In addition, few reports are available to utilize the unique properties of copper metals and MWCNTs together, where MWCNTs are dispersed in the metal matrix for preparing nanocomposite[17]. Further, the addition of MWCNTs to Cu matrix has been reported to improve mechanical, electrical, and thermal properties compared to individual components [17]. A still more popular powder-processing method is used for preparing nanocomposite of Cu by adding MWCNTs as reinforcing agents, but to our knowledge, no reports are available in the literature for the application of Cu(Salen)/MWCNT material in electrochemical catalysis of OER. Since it is well known that the high surface area of MWCNTs combined with metal nanoparticles or metal oxides can improve the performance of the prepared nanocomposite materials [28-31]. However, little attention has been paid to systems in which MWCNTs are functionalized with a copper salen complex where salen is utilized for both purposes, *i.e*. acting as a ligand for attaching Cu metal to MWCNTs and enhancing its electrocatalytic efficiency. Considering the high electrocatalytic demand for OER, we have decided to select an electrocatalyst that could act as a better version of their individual contribution as an electrocatalyst. Therefore, we have prepared a nanocomposite that can have combined effect ofCu metal, salen ligand, and MWCNTs, which can enhance the electrocatalytic effect as compared to the individual components from which they are made. Therefore, in this paper, we are proposing the preparation of a novel copper (salen) complex Schiff base functionalized multiwalled carbon nanotubes (Cu(Salen)/MWCNTs) nanocomposite modified GC electrode (GC/Cu(Salen)/ MWCNTs), which further has been utilized for oxygen evolution reactions (OER).

## Experimental Section

### Reagents and materials

Multiwalled carbon nanotubes (MWCNTs) were purchased from Sigma Aldrich, India. Salicylaldehyde pure was purchased from SRL, India. Ethylenediamine for the synthesis of salen ligand was purchased from Merck, India. Whatman™Filter paper (41 ash less diameter 125 mm) was used for the filtration process. Triple distilled water was used for all the synthesis and electrochemical experiments. All the other chemicals were of analytical grade as received.

## Instrumentation

The UV-vis spectroscopic measurement of an aqueous solution was recorded with a UV-vis scanning

spectrophotometer (UV-1700 Pharma spec). Fourier transform infrared (FT-IR) spectra were recorded from a PerkinElmer spectrophotometer using KBr pellets over the range of 400-4000 $cm^{-1}$. X-ray diffraction (XRD) spectra were recorded from a RigakuMiniflex 600 desktop x-ray diffraction system. SEM spectra and EDAX measurements of MWCNTs and Cu(Salen)MWCNTs nanocomposite were recorded with an EVO-Scanning Electron Microscope MA15/18. Electrochemical studies were performed with the CHI-760 electrochemical workstation (CH Instruments, USA). Glassy carbon (GC) electrode with a diameter of 3 mm was used as a working electrode. Ag/AgCl electrodes and Pt-wire were used as counter and reference electrodes, respectively. Electrochemical Impedance Spectroscopy was measured between the frequency range of100 kHz to 1 Hz using a 5 mV amplitude with an applied potential of 0.2 V. The experimentally observed potential against the Ag/AgCl reference electrode is converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation:[32-34].

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + E^{\circ}_{Ag/AgCl}$$

where$E_{Ag/AgCl}$is the experimentally measured potential against Ag/AgCl reference electrode $E^{\circ}_{Ag/AgCl}$is 0.966V at 25°C.

## Preparation of Cu(Salen)

Cu(Salen) complex can be synthesized from salicylaldehyde (sal) and ethylenediamine (en). The molecular structure can be represented by two Salicylimine groups connected by an ethylene bridge [35]. The ligand salen was prepared according to the previous literature with slight modification[36]. In a round bottom flask, salicylaldehyde (50 ml) was mixed with ethylene diaminein a 1:3 ratio. Further, distilled ethanol (30 ml) and ethylene diamine (100 ml) were mixed together and added to the above reaction mixture. The colour of the solution changes to yellow, and the reflux process has been continued for another half hour. The ligand has been dried at laboratory temperature under the desiccators. Typically, the ligand salen was dissolved in ethanol, stirred, and heated till the solution became transparent. Further, Cu-nitrate was dissolved in hot water and added dropwise to salen solution with constant stirring. The reaction mixture was refluxed for 15 minutes, cooled the reaction content, was filtered, washed, and dried in a vacuum.

## Preparation of composites material

The 1.0 mM solution of Cu(Salen) in 15 mL of DMF was mixed, and the solution was stirred and heated till it became transparent. Further, 0.01g of MWCNTs was dissolved in 15 ml of DMF and was added dropwise to the Cu(Salen) solution. The reaction content was allowed to stir for 24 hours. The reaction mixture was filtered and washed. The solid product was dried in a vacuum at room temperature; it is abbreviated as Cu(Salen)/MWCNTs. For the preparation of composite materials, 10mg of MWCNTs were added to a 1.0 mM, 5.0 mM, and 0.5 mM solution of Cu(Salen) (in 10 mL DMF) for the preparation of Cu(Salen)/MWCNTs Grade-1, Cu(Salen)/MWCNTs Grade-2, and Cu(Salen)/ MWCNTs Grade-3, respectively. The above reaction mixture was stirred for 24 hours, filtered, washed with DMF, and dried.

## Preparation of the modified electrodes

The modified electrodes were prepared by drop casting a 1% solution/suspension (in DMF) of MWCNTs (5.0µL) on a GC electrode. The GC coated electrode was dried for 4 hours at room temperature and abbreviated as GC/MWCNTs. A similar procedure was followed for the preparation of GC/Cu(Salen) and GC/Cu(Salen)/MWCNTs. The modified electrodes GC/MWCNTs, GC/Cu(Salen), and GC/MWCNTs/Cu(Salen) were used for the electrochemical oxygen evolution reaction [37].

## Results and Discussion

### IR and UV-vis interpretation

FT-IR was used to analyse the structural properties of Cu-salen, MWCNTs, Cu(Salen)/MWCNTs/Grade-1, Cu(Salen)/MWCNTs/Grade-2, Cu(Salen)/MWCNTs/ Grade-3. The FT-IR spectrum of Cu-salen, as shown in Fig. 1A (a), represents the stretching frequencies of -OH at 3390 $cm^{-1}$, -NH at 2782 $cm^{-1}$, and -C-H at 1188 $cm^{-1}$. These stretching bands shifted to a lower wave number due to the coordination of Cu ions and salen ligands[38-39].The FT-IR spectra of MWCNTs are shown in Fig. 1A (b). There are three major peaks located at 1562 $cm^{-1}$, 1720 $cm^{-1}$, and 3428 $cm^{-1}$ for MWCNTs. The O-H stretch from carboxyl groups (O=C-OH and C-OH) is responsible for the peak at 3428 $cm^{-1}$. The peak at 1725 $cm^{-1}$ is due to carboxylate anion. However, the peak at 1562 $cm^{-1}$ is associated with -C=O stretching of the carboxyl group[40]. In the FT-IR spectra of the Cu(Salen)/

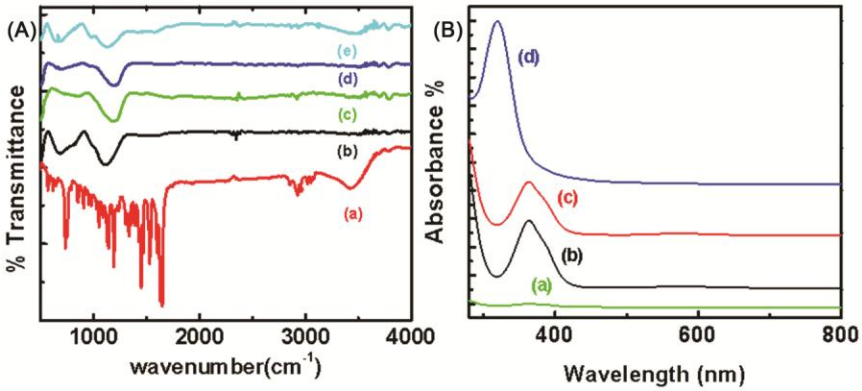


Fig. 1 — (A) FT-IR spectra (a) Cu(Salen), (b) CNT, (c) Cu(Salen)/MWCNTsGrade-1, (d) Cu(Salen)/MWCNTsGrade-2, (e) Cu(Salen)/MWCNTs/Grade-3 and (B) UV-Visible spectra of (a) CNT, (b) Cu(Salen), (c) Cu(Salen)/MWCNTs/Grade-2and (d) Salen

MWCNTs/Grade-1(c),Cu(Salen)/MWCNTs/Grade-2(d), and Cu(Salen)/MWCNTs/Grade-3(e), the –NH and –CH groups are represented, indicating the successful formation of composite materials. Other peaks are much less intense due to the small quantity of Cu(Salen) loaded on the MWCNTs.

The UV-vis spectra of the compounds and composite materials (solution/suspension in DMF) were recorded. In the wavelength region of 280nm to 800nm, the UV-vis absorption spectra of MWCNTs reveal no appreciable absorbance bands [40]. The UV-vis spectra of salen ligand have a peak at 319 nm. This peak shift to 362 nm in Cu(Salen), indicating the formation of the Cu(Salen) complex. The Cu(Salen)/MWCNTs Grade-2 represents the peak at 364 nm. This small variation in the absorption peak may arise due to interaction between MWCNTs and Cu(Salen). It is clear from the FT-IR and UV-vis studies, the Cu(Salen) was successfully immobilized on the MWCNTs.

**X-ray diffraction characterization**

The X-ray diffraction patterns of Cu(Salen), MWCNTs, Cu(Salen)/MWCNTs Grade-1, Cu(Salen)/MWCNTs Grade-2, and Cu(Salen)/MWCNTs Grade-3 are shown in Fig. 2. From Fig. 2, it can be seen clearly that the diffracted peaks of Cu(Salen) and Cu(Salen)/MWCNTs are sharp enough, which indicates their good crystallinity[42-45]. The characteristics 2Θ peak of MWCNTs (d) were observed at 25.8° and 42.8°, which correspond to the (002) and (101) planes, respectively. The XRD 2Θ peak of Cu(Salen) indicates peaks at 19.9°, 20.7°, 24.0°, and 32.5°, respectively. These peaks were very low in all three grades of the composite materials. It occurs possibly due to the reorientation or loss of crystalline behaviour of Cu(Salen) in the composite

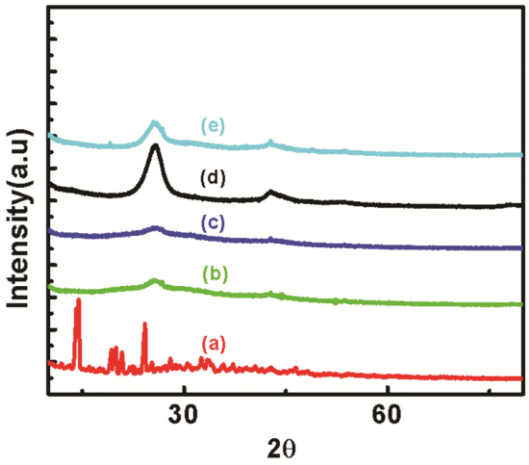


Fig. 2 — Powder XRD of (a) Cu(Salen), (b) Cu(Salen)/MWCNTs Grade-1, (c) Cu(Salen)/MWCNTsGrade-2, (d) MWCNTs, (e) Cu(Salen)/MWCNTsGrade-3

material [46]. The characteristics peak at 2Θ= 25.8 and 42.8° observed for MWCNTs are more intense in Cu(Salen)/MWCNTs Grade-3 compared to MWCNTs, Cu(Salen)/MWCNTs Grade-1 and Cu(Salen)/MWCNTs Grade-2. It possibly occurs due to low amount of Cu(Salen) in the Cu(Salen)/MWCNTs Grade-3 composition that dominates the MWCNT. However the peak position represents very slight or negligible variation in the peak position, indicating conservation of the structural conformation of Cu(Salen) and MWCNT in the composite materials.The current analysis *via* powder XRD also corroborates the outcomes derived from the FT-IR and UV-Vis investigations.

**Scanning electron microscopy (SEM) and EDAX**

SEM has been used to investigate the morphology of Cu(Salen), MWCNTs, and Cu(Salen)/MWCNTs composite materials. The surface of pure MWCNTs

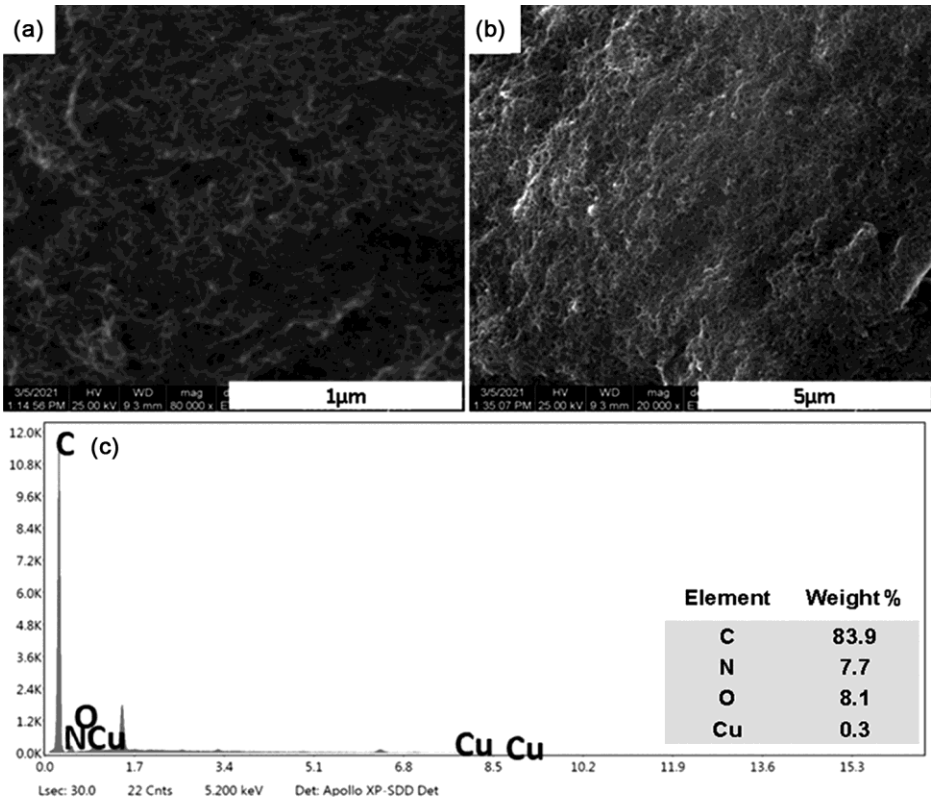


Fig. 3 — SEM image (A-B) and EDAX (C) of Cu(Salen)/MWCNTsGrade-2 composite material

has a net-like, fibrous nature [40–41,47]. The numerous fine thread-like structures representing tubes of MWCNTs appear to be dispersed over the surfaces; all these visuals help to construct a stable 3D nanostructure. Even though SEM analysis gives valuable information on the morphological and structural characterization of MWCNTs, it is not sufficient to establish the ultimate nature of carbon nanotubes. However, the highest resolution SEM can reveal the fine details of nanotubes structure, even the number of carbon layers in their walls, and characterize surface coatings and functionalizations of the tubes[48–50]. Fig. 3(A-B) displays the SEM image of Cu(Salen)/MWCNTsGrade-2 which show thread like structure with some globular appearance. It might appear due to the presence of Cu(salen) on the surface of MWCNT in the composite material. Further, to support the above claim, EDAX Fig. 3(C) analysis has also been performed, and the EDAX data represents a definite weight ratio between copper and carbon, supporting the functionalization of MWCNTs by Cu(Salen). The nanotube reinforces copper grains and retains its tubular and multi-walled features with the copper matrix [51, 52].

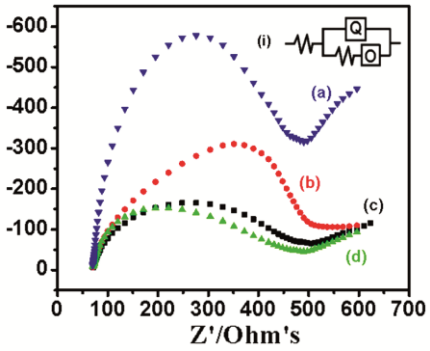


Fig. 4 — Nyquist plot for (a) GC, (b) Cu(Salen)/MWCNTs Grade-2, (c) Cu(Salen)/MWCNTs Grade-1, and (d) Cu(Salen)/MWCNTs Grade-3 in 0.1M $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$(1:1molar ratio) containing 0.1M KCl. Inset (i) shows the most compatible equivalent circuit for the Nyquist plots

## Electrochemical Impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is used to study how electrochemical sensing platforms behave at their interfaces [57]. Fig. 4 shows the Nyquist plot for GC, GC/G-2, GC/G-1, and GC/G-3 in 0.1M $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$ (1:1 molar ratio) as a redox probe containing 0.1M KCl. The inset of Fig. 4 (i) represents the well-matched comparable circuit for

the respective Nyquist plot. $R_s$ and $R_{ct}$ in this circuit represent solution resistance and charge transfer resistance, respectively. The solution resistances ($R_s$) of the prepared materials, GC, Cu(Salen)/MWCNTsGrade-1, Cu(Salen)/MWCNTsGrade-2, and Cu(Salen)/MWCNTsGrade-3 are almost similar at 70.0 Ω. However, the capacitive resistances ($R_{ct}$) of GC, Cu(Salen)/MWCNTsGrade-1, Cu(Salen)/MWCNTs Grade-2, and Cu(Salen)/MWCNTsGrade-3 are 426 Ω, 432 Ω, 434 Ω, and 418 Ω, respectively. The lower $R_{ct}$ values of the composite materials indicate their high electrochemical conductivity. The constant phase element is connected with the parameter O, which corresponds to the Warburg impedance due to mass diffusion and capacitance of the double layer (interface between the polarised electrode and the electrolytic solution) [58,59].

## Electrochemical Characterization

With the help of cyclic voltammetry (CV) and linear square wave voltammetry (LSV), the electrodes' electrochemical performance was measured (Fig. 5). The redox behaviour of Cu(II) in copper solder was examined in 0.1M KOH by a LSVon GC electrode at room temperature [56–57]. The LSV scan of the GC/Cu(Salen)/MWCNTs does not represent any characteristic redox signal in a 0.1 M KOH solution. An increase in oxygen evolution reaction (OER) current was observed from an onset potential of 1.67 V at GC/Cu(Salen)/MWCNTs/Grade-2. However, OER onset potential is higher in GC/MWCNTs (1.8 V), GC/Cu(Salen)/MWCNTs/Grade 1 (1.69 V), and GC/Cu(Salen)/MWCNTs/Grade-3 (1.7 V) as compared to GC/Cu(Salen)/MWCNTs/Grade-2 [52]. The OER current for GC/Cu(Salen)/MWCNTs/Grade-2 reaches 10 $mAcm^{-2}$ at 1.94 V. However, GC/MWCNTs, GC/Cu(Salen)/MWCNTs/Grade-1, and GC/Cu(Salen)/MWCNTs/Grade-3 do not reach 10 mA $cm^{-2}$ current. It is suggested that the modified electrode, GC/Cu (Salen)/MWCNTs/Grade-2, has better OER activity compared to other electrodes. The high concentration of Cu(Salen) in Cu(Salen)/MWCNTs/Grade-2 provides the more synergistic effect for electro-chemical oxygen evolution reaction. Hence, the OER activity of GC/Cu(Salen)/MWCNTs/Grade-2 is higher compared to other two grades. It is indicating that GC/Cu (Salen)/MWCNTs/Grade-2 could be a promising material for the development of efficient, and reliable electrocatalysts for OER.

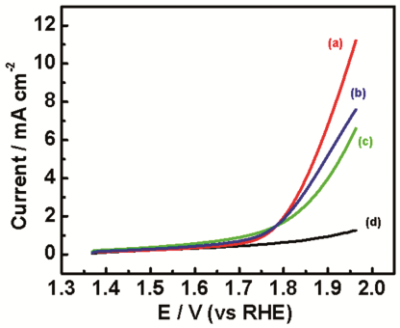


Fig. 5 — Linear sweep voltammetry of (a) GC/Cu(Salen)/MWCNTs/Grade-2, (b) GC/Cu(Salen)/MWCNTs/Grade-1, (c) GC/Cu(Salen)/MWCNTs/Grade-3, (d)MWCNTs, with 0.1M KOH at a scan rate of 5 $mVs^{-1}$.

## Stability

The stability of the modified electrode, GC/Cu(Salen)/MWCNTs/Grade-2, was tested using the cyclic voltammetry (CV) technique. The operational stability of GC/Cu(Salen)/MWCNTs/Grade-2 was tested in 0.1M KOH using 1000 CV cycles. The first and 1001st CV scans of GC/Cu (Salen)/MWCNTs/Grade-2 is shown in Fig. 6. The CV scan suggests that GC/Cu(Salen)/MWCNTs/Grade-2 retain more than 80% of their OER current even after 1000 CV cycles with no variation in the onset potential. The stability study suggests that the GC/Cu(Salen)/MWCNTs/Grade-2 has good operation stability in the basic medium, 0.1 M KOH.

## Kinetics studies for OER activity

Tafel slope mainly suggests the overpotential increment required to raise the current density by ten times. A small tafel slope corresponds to a step rise in the electrocatalytic current density. Also, to derive kinetic information, including exchange current density and tafel slope, we can experimentally perform the tafel analysis of the electrode polarization

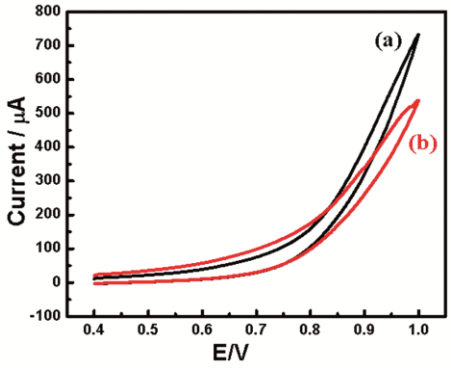


Fig. 6 — CV response of GC/Cu(Salen)/MWCNTs/Grade-2 in 0.1M KOH before and after 1000 CV cycles at scan rate of 20 $mVs^{-1}$.

Table 1 — Comparison table of reported OER electrocatalysts with Cu(Salen)/MWCNTs composites

| Catalyst | Electrolyte | Overpotential (mV) at current density 10 mA.cm$^{-2}$ | Tafel slope (mV/dec) | References |
|---|---|---|---|---|
| Oxygen doped cobalt sulfide | 1.0 M KOH | 370 | 59.5 | 61 |
| $Co_3O_4$@$Co_3S_4$ | 0.5 M KOH | 417 (20 mA.cm$^{-2}$ ) | 80 | 62 |
| Ni-Fe LDH | 1.0 M KOH | – | 62.7 | 63 |
| $IrO_2$@Ir | 1.0 M KOH | 255 | 45 | 64 |
| MWCNTs-CoDMTPP | 0.1 M KOH | 540 | 130 | 65 |
| MWCNTs-CoDHTPP | 0.1 M KOH | 510 | 73 | 65 |
| Fe-Ni@NC-CNTs | 1.0 M KOH | 274 | – | 66 |
| $NiPS_3$ | 1.0 M KOH | 437 | 73 | 67 |
| $CoFe_2O_4$ NPs-on-CFP | 1.0 M NaOH | 378 | 73 | 68 |
| Ag@$Co_xP$ | 1.0 M KOH | 310 | 76.4 | 69 |
| GC/Cu(Salen)/MWCNTs/Grade-1 | 0.1 M KOH | – | 188.2 | This work |
| GC/Cu(Salen)/MWCNTs/Grade-2 | 0.1 M KOH | 671 | 159.6 | This work |
| GC/Cu(Salen)/MWCNTs/Grade-3 | 0.1 M KOH | – | 170.3 | This work |

$CoFe_2O_4$ NPs-on-CFP:$CoFe_2O_4$ nanoparticle on carbon fiber, Ag@$Co_xP$: Ag core surrounded by $Co_xP$ Shell, Fe-Ni@NC-CNTs: Iron/nickel-based bimetallic metal-organic framework/dicyandiamide composite, Ni-Fe LDH: NiFe layered double hydroxide, MWCNTs-CoDMTPP: 5,10,15,20-tetrakis(3',5'-dimethoxyphenyl)porphyrinato cobalt(II) immobilized multi-walled carbon nanotubes, MWCNTs-CoDHTPP: 5,10,15,20- tetrakis(3',5'-dihydroxyphenyl)porphyrinato cobalt(II) immobilized multi-walled carbon nanotubes, $IrO_2$@Ir: Ir spheres around the $IrO_2$.

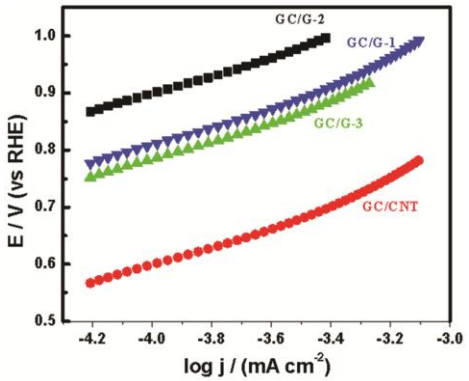


Fig. 7 — Tafel plot of all tested electrodesGC/MWCNTs, GC/Cu(Salen)/MWCNTs/Grade-1, GC/Cu(Salen)/MWCNTs/Grade-2, GC/Cu(Salen)/MWCNTs/Grade-3

curve. Low tafel slopes, large exchange current densities, and a small overpotential are the characteristics of ideal catalysts. However, these parameters are not entirely independent of each other. In Fig. 7, GC/Cu(Salen)/MWCNTs/Grade-2 have the lowest Tofel slope of 159.6 mV/dec compared to GC/Cu(Salen)/MWCNTs/Grade-3 (170.3 mV/dec), GC/Cu(Salen)/MWCNTs/Grade-1 (188.2 mV/dec), and GC/MWCNTs (188.2 mV/dec). Thisindicates the high OER activity on GC/Cu(Salen)/MWCNTs/Grade-2. Out of GC/Cu(Salen)/MWCNTs/Grade-3 and GC/ Cu(Salen)/MWCNTs/Grade-1, the tafel slope for GC/Cu(Salen)/MWCNTs/Grade-3 is lower compared to GC/Cu(Salen)/MWCNTs/Grade-1[60]. It is clear from this study that the modified electrode GC/Cu(Salen)/MWCNTs/Grade-2 has better OER activity compared to other electrodes.

The OER parameters of the modified electrode GC/Cu(Salen)/MWCNTs were compared with those of other reported OER electrocatalysts (Table 1) [61–69]. Oxygen doped cobalt sulphide represents the overpotential at 370 mV[61]. On the other hand, $IrO_2$@Ir represents the overpotential at 255 mV[64]. Where, GC/Cu(Salen)/MWCNTs/Grade-2 shows the overpotential at 671 mV, which is comparable toMWCNTs-CoDMTPP (540 mV) and MWCNTs-CoDHTPP (510 mV). The tafel slope for the $IrO_2$@Ir is 45 mV/dec, which represents the high OER activity. MWCNTs-CoDMTPP show the Tafel slope at 130 mV/dec, which is comparable to GC/Cu (Salen)/MWCNTs/Grade-2 (159 mV/dec). The OER activity of the proposed electrocatalyst is a little weaker than that of other reported materials [61–69]. However, the activity can be improved with the other transducers, such as graphene, SWCNTs, and conducting polymers. So, it could be a cost effective, eco-friendly electrocatalyst for the replacement of the OER catalyst in the fuel cells.

## Conclusions

In the present work, a nanocomposite has been prepared by functionalizing multiwalled carbon nanotubes (MWCNTs) with Cu (Salen). MWCNTs, Cu(Salen), and Cu(Salen)/MWCNTs/Grade-1, Cu (Salen)/MWCNTs/Grade-2, and Cu(Salen)/ MWCNTs/ Grade-3 were characterized with UV-Vis, FT-IR, powder XRD, and electro-chemical techniques. UV-Vis and FT-IR studies confirm the composite formation. SEM studies with EDAX spectra show the

clear appearance of the MWCNT fibres. However, the elemental composition of the EDAX measurements confirms the immobilization of Cu(Salen) on the MWCNTs. The modified electrodes, Cu(Salen)/ MWCNTs/Grade-1,Cu(Salen)/MWCNTs/Grade-2, and Cu(Salen)/MWCNTs/Grade-3, have been utilized for the OER activity in a basic medium, and their activity towards OER has also been compared. Out of the four electrodes, Cu(Salen)/MWCNTs/Grade-2 have superior OER activity in the basic medium. Hence, the proposed modified electrodes could be used as a promising material for the development of a catalyst in the fuel cells.

**Acknowledgments**

University Grant Commission (UGC, No. F.30-431/2018 (BSR)), New Delhi, and the Institute of Eminence at Banaras Hindu University (for the Seed Grant and Trans-Disciplinary Project, Scheme No.-6031), India, are gratefully acknowledged for their financial support.

**References**

1 Suen T N, Hung F S, Quan Q, Zhang N, Xu J Y & Chen M H,*ChemSoc Rev*, 46 (2017) 337.
2 Eriksson L E & Gray M E, *Appl Energy*, 202 (2017) 348.
3 Jacobson Z M, Colella G W & Golden M D, *Science*, 308 (2005) 901.
4 Hu S, Cui Y & Liu N, *Nat Mater*,16 (2017) 16.
5 Kim J S, Kim B, Kim H & Kang K, *Adv Energy Mater*,8 (2018) 1702774.
6 Morales O D, Yanez I L, Koper T M & Vallejo C F, *ACS Catal*, 5 (2015) 5380.
7 She W Z, Kibsgaard J, Dickens F C, Chorkendorff B I, Nørskov J K & Jaramillo T F, *Science*, 355 (2017) 4998.
8 Ng J W, Melchor M G, Bajdich M, Chakthranont P, Kirk C, Vojvodic& Jaramillo T F, *Nat Energy*, 1 (2016) 1.
9 Wang M, Wang L F , Li Y Z, Li Q X, Xu Z D &Qu D M, *Transit Met Chem*, 26 (2001) 307.
10 Tarasconi P, Capacchi S, Pelosi G, Cornia M , Albertini R, Bonati A, Dall'Aglio P P, Lunghi P &Pinelli S, *Bioorg Med Chem*, 8 (2000) 157.
11 Charo J, Lindencrona J A, Carlson L M, Hinkula J & Kiessling R, *Virol J*, 78 (2004) 11321.
12 Musa M A, Khan M O F, Aspedon A &Cooperwood J S, *Lett Drug Des Discov*, 7 (2010) 165.
13 Nair M S, Kumari S S&Neelakantan M A, *J CoordChem*, 60 (2007) 1291.
14 Canali L, Cowan E, Deleuze H, Gibson C L & Sherrington D C, *J ChemSoc Perkin Trans*, 1 (2000) 2055.
15 Reger T S & Janda, *J Am ChemSoc*, 122 (2000) 6929.
16 Zhao Z P, Li M S, Zhang J Y, Li H N, Zhu P P& Liu W F, *IndEngChem Res*,51(2012) 9531.
17 Baleizão C, Gigante B, Garcia H & Corma A, *J Catal*, 221 (2004) 77.
18 Sundaram R M, Sekiguchi A, Sekiya M, Yamada T & Hata K, *R Soc Open Sci*, 5 (2018) 180814.
19 Subramaniam C, Yamada T, Kobashi K, Sekiguchi A, Futaba D N, Yumura M &Hata K, *Nat Commun*, 4 (2013) 2202.
20 Mohammadikish M, *CrystEngComm*, 16 (2014) 8020.
21 Ebbesen T W &Ajayan P M, *Nature*, 358 (1992) 220.
22 Iijima S, *Nature*, 354 (1991) 56.
23 Raphey V R, Henna T K, Nivitha K P, Mufeedha P, Sabu C & Prmod K, *Mater SciEng C*, 100 (2019) 616.
24 Usui Y, Haniu H, Tsuruoka S & Saito N, *Med Chem*, 2 (2012) 1.
25 Zhang Y, Bai Y & Yan B, *Drug Discov Today*, 15 (2010) 428.
26 Kateb B, Yamamoto V, Alizadeh D, Zhang L, Manohara M, Bronikowski&Badie B, *JITC*, (2010) 307.
27 Rosen Y & Elman N M, *Expert Opin Drug Deliv*, 6 (2009) 517.
28 Liu Z, Sun X, Nakayama-Ratchford N & Dai H, *ACS Nano*, 1(2007) 50.
29 Díez-PascualA M, *Macromol* 1 (2021) 64.
30 Bekyarova E, Ni Y, Malarkey E B, Montana V, McWilliams J L, Haddon R C &Parpura V, *J NanosciNanotechnol*, 1 (2005) 3.
31 Zhang W & Zhang Y, *Nanoscale Res Lett*, 6 (2011) 1.
32 Ferrero G, Preuss K, Fuertes A, Servilla&Titirici M M, *J Mater Chem A*, 4 (2016) 2581.
33 Bard A J, Faulkner L R, Leddy J &Zoksi C G, *Wiley New York*, (1980).
34 Chung D Y, Jun S W, Yoon G, Kwon S G, Shin D Y, Chung Y H & Kim H, *J Am ChemSoc*, 137 (2015) 15478.
35 Silvestre N, *Int J Compos Mater*, 3 (2013) 28.
36 Mohammadikish M, *CrystEngComm*, 16 (2014) 8020.
37 Tonle I K, Ngamani E, Tchieno M M&Walcarious A, *J Solid State Electrochem*, 19 (2015) 1949.
38 Zid T B, Khedher I &Ghorbel A, *React Kinet Mech Catal*, 100 (2010) 131.
39 Inba P J K, Annaraj B, Thalamuthu S & Neelakantan M A, *Bioinorg Chem*, 2013 (2013) 1.
40 Sonkar P K, Ganesan V, Yadav D K & Gupta R, *Chemistr Select*, 1 (2016) 6726.
41 Sengupta J, Jana A, Singh P N, Mitra C & Jacob C, *Nanotechnology*, 21(2010) 415605.
42 Wang W, Serp P, Kalck P, Silva C G &Faria J L, *Mater Res Bull*, 43(2008) 958.
43 Tessonnier P J, Rosenthal D, Hansen W T, Hess C, Schuster E M, Blume R, Girgsdies F, Pfander N, Timpe O, Su S D & Schlogl R, *Carbon*, 47(2009) 1779.
44 Reznik D, Olk H C, Neumann D A & Copley J R, *Physical Review B* 52 (1995) 116.
45 Belin T &Epron F, *Mater SciEng B*, 119 (2005) 105.
46 Ma W, Yang Y, Zhao F,Xu, Zhang J, Zhang M, & Feng Z, *RSC Adv*, 10 (2020) 1769.
47 Shabaan Ola A, Jahin H S &Mahamed G G, *Arab J Chem*, 13 (2020), 4797.
48 Ghani N T Abdel, Chaghaby G A El &Helal F S, J *Adv Re*, 6 (2015) 405.
49 Takassi M A &Zadehnazari A, *Fuller Nanotub Carbon Nanostructures*, 24 (2016) 128.
50 Saito Y, Yoshikawa T, Bandow S, Tomita M & Hayashi T, *Phy Rev B*, 48 (1993) 1907.
51 Sengupta J, Jana A, Singh N D P, Mitra C & Jacob C, *Nanotechnology*, 21(2010) 1.
52 KNikoofar, F Mehrikaran, M Lashanizadegan & AAghaei, *Polycycl Aromat Comp*, 41(2019) 663.

53 Azarniya A, Safavi M S, Sovizi S, Azarniya A, Chen B, Hosseini H R M & Ramakrishna S, *Metals*, 7 (2017) 384.

54 Choi D, Blomgren G E &Kumta P N, *Adv Mater*, 18 (2006)1178.

55 Xia X, Zhu C, Luo J, Zeng Z, Guan C, Ng C F, Zhang H & Fan H J, *Small*, 10 (2014) 766.

56 Zhu K, Zhu X & Yang W, *Angew ChemInt Ed*, 58 (2019) 1252.

57 Bonanni A, Pumera M, Miyahara Y, *Phy Chem Chem Phy*, 13 (2011) 4980.

58 KesavanS ,Revin S B & John S A, *J MaterChem*, 22 (2012) 17560.

59 Matemadombo F &Nyokong T, *ElectrochimActa*, 52 (2007) 6856.

60 Rajagopal V, Manivannan M, Kathiresan M, Suryanarayanan V & Jones L A, *MaterChemPhys*, 285 (2022) 126104.

61 Sultana U K, He T, Du A &Mullane A P O, *RSC Adv*, 7 (2017) 54995.

62 Mahala C, Sharma M D &Basu M, *New J Chem*, 43 (2019) 15768.

63 Yadav D K, Ganesan V, Sonkar P K & Gupta R, *Chem Electrochem*, 4 (2017) 3134.

64 Zhong W, Lin Z, Feng S, Wang D, Shen S, Zhang Q, Gu L, Wang Z & Fang B, *Nanoscale*, 10 (2019) 4407.

65 Yadav M, Sonkar P K, Prakash K, Ganesan V, Sankar M, Yadav D K & Gupta R, *Int J Hydrog Energy*, 45 (2020) 9710.

66 Zhao X, Pachfule P, Li S, Simke J R J, Schmidt J & Thomas A, *Angew ChemInt Ed*, 57 (2018) 8921.

67 Song B, Li K, Yin Y, Wu T, Dang L, Acevedo M C, Han J, Gao T, Wang X, Zhang Z, Schmidt J R, Xu P & Jin S, *ACS Catal*, 7(2017) 8549.

68 Kargar A, Yavuz S, Kim T K, Li C-H, Kuru C, Rustomji C S, Jin S & Bandaru P R, *ACSAppl Mater Interfaces*, 7 (2015) 17851.

69 Hou Y, Liu Y, Gao R, Li Q, Guo H, Goswami A, Zboril R, Gawande M. B &Zou X, *ACS Ctal*, 7 (2017) 7038.