REVIEW OF RESEARCH
ISSN: 2249-894X
IMPACT FACTOR : 5.7631(UIF)
VOLUME - 14 | ISSUE - 10 | JULY - 2025

ELECTROCHEMICAL ENERGY STORAGE APPLICATION OF SOL-GEL DEPOSITED BINARY (CO: CU) METAL OXIDE

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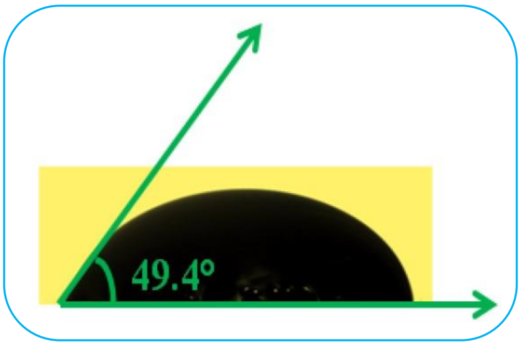
ABSTRACT:

Here, we report about synthesis of binary Cobalt copper metal oxide electrode material by Sol-gel spin coating method. The samples were analyzed for their composition, functional group, structure/morphology, surface area and electrochemical property using X-ray diffraction (XRD),Fourier transform infrared (FT-IR) spectroscopy, Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET) and Cyclic Voltametry (CV), Galvanostatic charge-discharge (GCD), Electrostatic Impedance Spectroscopy (EIS) respectively. CoCuO exhibits cubic crystal structure and porous, rough surface morphology. The binary Cobalt Copper metal oxide electrode shows maximum specific capacitance of 471 F/g measured in KOH electrolyte at a scan rate of 5mVs-1. From discharging curve a maximum specific capacitance of 305 F/g is obtained at current density of 1 mA/cm2. Additionally, the CoCuO electrode has a power density of 213.22 KW/kg and energy density of 32 Wh/kg at 1mA/cm2 with 60% efficiency. The electrode's high surface area and electronic conductivity are credited with significant improvement in electrochemical behavior.



KEYWORDS: *(Co: Cu) oxide, Sol-gel, Aqueous electrolyte electrode, specific capacitance.*

1. INTRODUCTION

Electrochemical capacitors are designed to meet the need for high power in short time. In electrochemical capacitors, electrochemical energy is stored in the electric field at the interface between the electrode and electrolyte [1-4]. The key component of the electrochemical capacitor electrode is its electrode material since all storage mechanisms depend on its type, structure, morphology, and amount in the electrode [5]. Electrical double-layer capacitor (EDLC), Pseudocapacitor (PSC) and battery like electrochemical capacitor are three types of electrochemical capacitors, which are categorized based on the charge-storage mechanism of the electrode material[6-7]. Transition metal oxides (TMOs) have attracted a wide range of concerns as an electrode material to fabricate pseudocapacitors (PCs) and battery like electrochemical capacitors [8].

Especially, binary transition metal oxides have also gained widespread research interest as an electrochemical capacitor electrode materials because of their greater stability and superb electronic conductivity [9]. Cobalt copper oxide [10, 11], nickel cobalt oxide [12], and copper manganese oxide [13] are the best material candidates to offer awesome electrochemical performance against corresponding single metal oxide.

Among these electrode materials examples, binary cobalt-copper metal oxide has enhanced interests due to several fascinating advantages. More precisely, copper oxide based electrochemical capacitors have gained considerable attention because they are inexpensive, ecologically benign and shows superior electrochemical performance [14].

In the current work we analyzed about electrochemical performance of binary Cobalt copper metal oxide electrode using 0.1 M KOH electrolyte solution. The binary Cobalt copper metal oxide electrode is prepared by simple Sol-gel spin coating method that is suitable to get porous structured electrodes. The electrochemical behavior of the electrochemical capacitor is examined by cyclic Voltametry (CV), Galvanostatic charge-discharge and Electrochemical Impedance Spectroscopy (EIS) techniques. The electrode shows a maximum specific capacitance of 471 F/g measured in KOH electrolyte at a scan rate of 5 $mVs^{-1}$with 213 KW/Kg and energy density of 32 Wh/kg at $1mA/cm^2$.The surface area of the as deposited binary (Co: Cu) metal oxide is obtained to be 1710.7 $m^2 g^{-1}$ from BET plot.

2. EXPERIMENTAL

2.1 Materials

Reagents like Cobalt Chloride ($CoCl_2$ $6H_2O$), Cupric chloride ($CuCl_2$ $2H_2O$) and Ethanol (AR grade) were brought from Thomas Baker without including any chemical treatment.

2.2 Preparation of binary (Co: Cu) metal oxide thin film

Binary (Co: Cu) metal oxide thin films were deposited on Stainless steel (SS) substrate via Sol-gel method followed by annealing. First of all solution was prepared by taking 0.0125 M Nickel chloride ($CoCl_2$ $6H_2O$) and 0.2 M Cupric chloride ($CuCl_2$ $2H_2O$) precursors. Initially stainless steel substrate were polished with the help of zero grade polish paper then the substrates were cleaned using detergent, washed thoroughly with double distilled water, then rinsed with acetone and dried completely. The solution was prepared with percentage of Cu as 50%. Ethanol was then added to the solution for the gel formation and stirred for 6 hours on magnetic stirrer at temperature of 60^0C. For the sake of formation of gel the solution was kept aside for 24 hours. A clear and viscous solution was formed after aging. Obtained solution was purple in color. Then this solution was used for deposition on the stainless steel substrate via spin coating deposition technique. Then obtained thin films were annealed at 300^0C.

2.3 Characterizations

The structural analysis was carried out using X-ray Diffractometry with Cu-Kα radiation (λ = 1.54 A^0). JEOL JSM-IT200 Scanning Electron Microscope instrument is used for surface morphological analysis as well as for compositional analysis. Bruker Alpha spectrophotometer (375 to 7500 cm^{-1}) is used for the FT-IR. The electrochemical analysis of the as deposited binary (Co: Cu) metal oxide thin film electrode was carried out using EIS technique by Zive MP1 Multichannel instrument. Synthesized NiCuO electrode is utilized as a working electrode, Platinum as a counter electrode and Hg/HgO (Mercury/Mercury Oxide Electrode) as a reference electrode.BET analysis was carried out using BET surface area analyzer instrument.

3. RESULT AND DISCUSSION

3.1 XRD Analysis

X-ray Diffractometry is used to study structural properties of as deposited Cobalt copper film. The XRD result of binary (Cobalt: Copper) metal oxide thin films annealed at 300^0C is shown in Fig.1. The samples are crystalline in nature. XRD patterns were obtained with source CuKα (λ = 1.54 A^0), 2θ angle is varied from 10^0 to 90^0. The XRD pattern implies that as deposited films are crystalline in nature with cubic structure. XRD pattern indicated the several sharp peaks of Cobalt Copper oxide. The different Cobalt Copper oxide peaks with corresponding *hkl* planes are as shown in the following fig. 1[15].

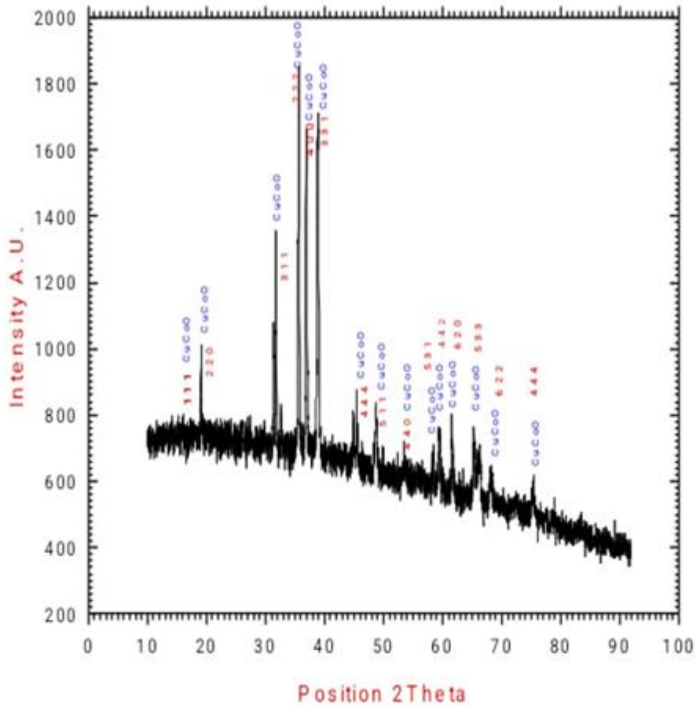


Fig.1: X-ray Diffraction pattern of binary metal (Co: Cu) oxide thin film.

3.2 SEM Analysis

The SEM micrographs exhibited the formation of thin film and it is well adherent to the substrate. These images of binary metal (Co: Cu) oxide with different magnifications are as shown in the Fig.2. SEM micrographs contain several small uniform sized, aggregated porous particles with rough surface morphology. The porosity results in possibility of better electrochemical supercapacitor behavior of binary (Co: Cu) metal oxide thin film [16].

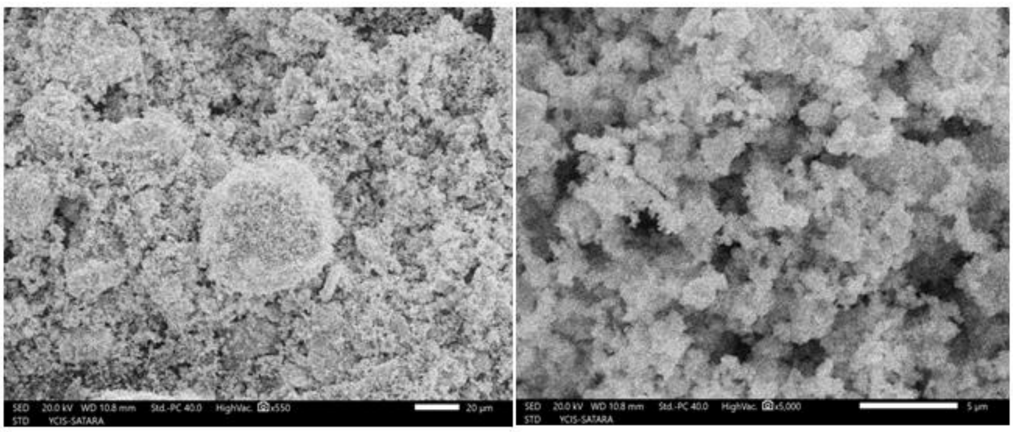
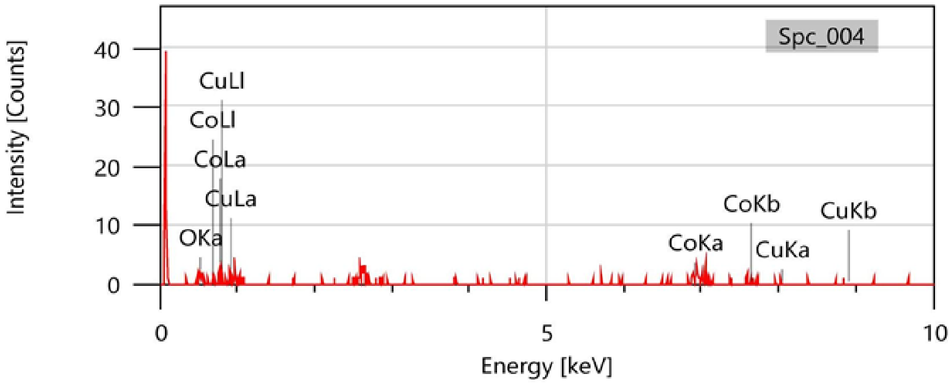


Fig. 2: Scanning Electron Microscope images of binary metal (Co: Cu) oxide thin film at (a) X550 magnification (b) X5000 magnification.

3.3 EDAX Analysis

EDAX spectrum was shown in the Fig.3 to explore elemental composition of the as prepared material surface. It shows the formation of binary (Co: Cu) metal oxide on the substrate. In the EDAX measured result, Cobalt, Copper and Oxygen were observed which gave evidence for the formation of binary Cobalt Copper metal oxide on the substrate.



Element	Line	Mass%	Atom%
O	K	20.33±7.30	48.99±17.59
Co	K	56.31±19.57	36.84±12.80
Cu	K	23.36±16.37	14.17±9.93
Total		100.00	100.00
Spc_004			Fitting ratio 0.9384

Fig. 3: Energy-dispersive X-ray analysis of binary metal (Co: Cu) oxide thin film

3.4 FT-IR Analysis

FT-IR spectroscopy is an important technique for studying the vibrational modes of molecules and identifying functional groups within the material including metal oxides. Fig.4. shows FT-IR spectrum of binary Cobalt Copper metal oxide in the wave number region in between 400 to 4000 cm^{-1}. The sharp peak positioned at 422 cm^{-1} relates current absorption bond. Followed by this, two more strong peaks positioned at 573cm-1, 664 cm-1 which belongs to stretching vibration mode of Co^{3+}- O^{2-} and Cu^{2+}- O^{2-} in the tetrahedral and in octahedral sites respectively. The peak observed at 1088, 1636 cm^{-1} corresponds to –COO carboxylic acid, C⍰O stretching While the peak at 1438 cm-1 were assigned to vibrational band of CO ions. The peak at 2321.87 cm-1 with small intensity was obtained, confirming C–C bond. The broad band around 3436.53 cm-1 is belongs to O–H stretching vibrations reveals hydrous in nature [17].

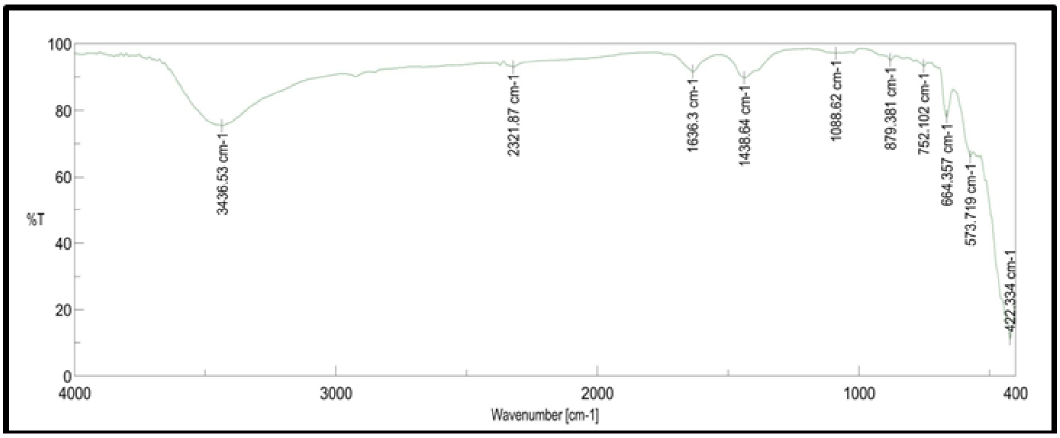


Fig. 4: Fourier Transform Infrared Spectroscopy graph of binary metal (Co: Cu) oxide thin film.

3.5 Angle of Contact Analysis

Surface Wettability test was performed to know the interaction between the liquid and CoCuO thin film. High wettability leads to small contact angle (θ) and surface is hydrophilic. On the contrary, Low wettability leads to large contact angle (θ) and surface is hydrophobic. A contact angle of 0^0 corresponds to complete wetting and a contact angle of 180^0 gives rise to complete non-wetting. Superhydrophillic surfaces are dominant for superpacitor application. The contact angle of CoCuO electrode with water is as shown in the fig.5. Contact angle is observed to be 49.4^0 which are hydrophilic in nature [18].

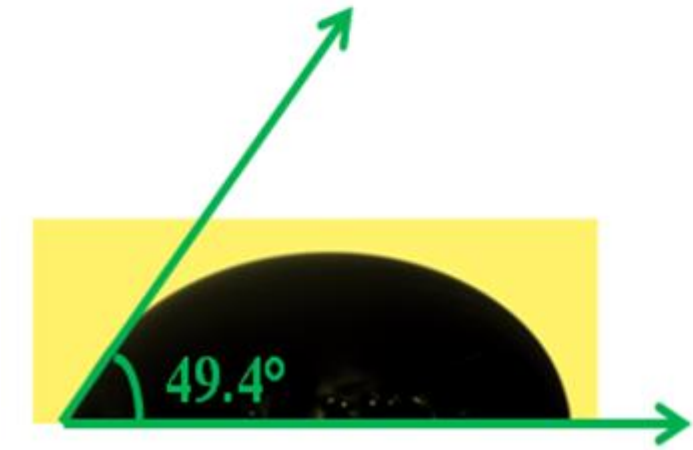


Fig. 5: Surface Wettability test of binary metal (Co: Cu) oxide thin film.

3.6 Electrochemical Analysis by Cyclic Voltametry

The CV is an important technique in electrochemistry which provides the qualitative information about the electrochemical process, whether the process is Faradic or non-Faradic, that takes place in the material. The electrochemical analysis of binary metal (Co: Cu) oxide thin film was done with cyclic Voltametry (CV) measurements was subjected at various scan rates from 5 mV/s to 100 mV/ s in 0.1M KOH electrolyte with potential window of 0V to 0.5 V. During the different scan rate, it was observed that the current under the curve gradually increased with scan rate. From this we can conclude that Voltammetric current is directly proportional to the scan rates of CV and is a good sign of supercapacitive behavior [19].

To calculate the specific capacitance (SC) of the electrode from the CV curves following formula was used.

$$SC = \frac{c}{m} = \frac{\int_{v1}^{v2} I\,dV}{m(V)\frac{dV}{dt}} \qquad (1)$$

Where m is mass of active material, V1 and V2 are the potential limits, $\frac{dV}{dt}$ is the scan rate potential.

Fig. 6 shows cyclic Voltammograms with potential window of 0 V to 0.5 V at various scan rates 5, 20, 50, 80 and 100 mV s^{-1}. From CV analysis, the electrode exhibited maximum specific capacitance of 471 F/g at 5mVs^{-1} scan rate. The obtained results of CoCuO electrode with various scan rates are given in the table 1. As current under curve slowly increased with scan rate, we conclude that the Voltammetric current is directly proportional to scan rate and this is a good indication of supercapacitive behavior.

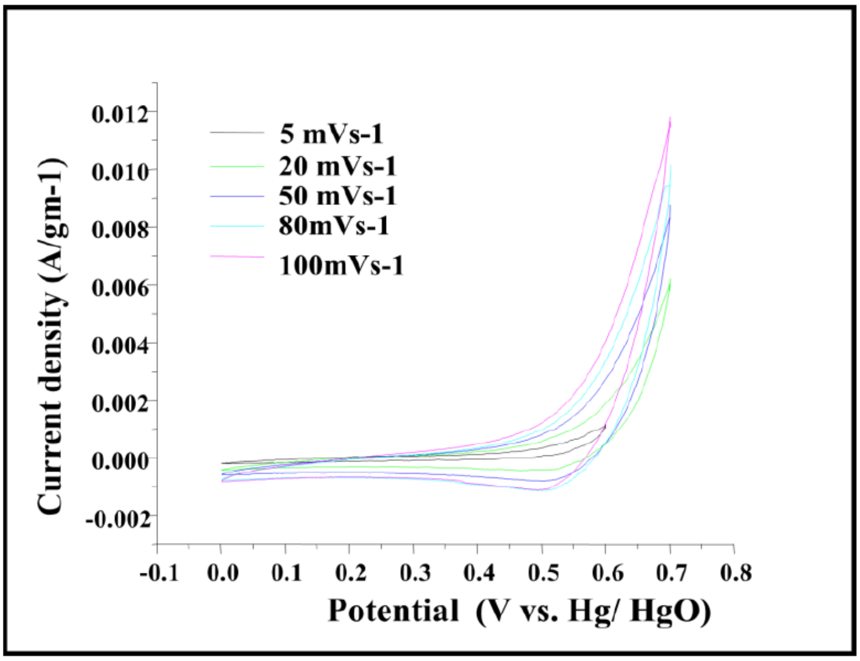


Fig. 6: Cyclic Voltammograms curves of CoCuO thin film electrode in 0.1 M KOH electrolyte

Table No.1 Specific capacitance at various scan rates of CoCuO thin film electrode in 0.1 M KOH electrolyte

Scan Rate mV/s	Specific Capacitance F/g
5	471.1
20	120.9
50	78.2
80	55.8
100	52.4

3.7Galvanostatic Charge-discharge

Galvanostatic charge-discharge curves at various current densities of binary metal (Co: Cu) oxide is as shown in the Fig. 7. The specific capacitance, can also calculated from charging/discharging curves according to the equation

$$Cs = \frac{I \, . \, t}{m \, . \, \Delta V} \qquad (2)$$

Where 'I' is the applied charging/discharging current, t is the discharge time, m indicates the mass of active electrode material and ΔV is the potential range of scanning segment [20]. The specific capacitance is calculated according to discharging curve using above formula. A specific capacitance of 305 F/g is obtained at current density of 1 mA/cm^2.

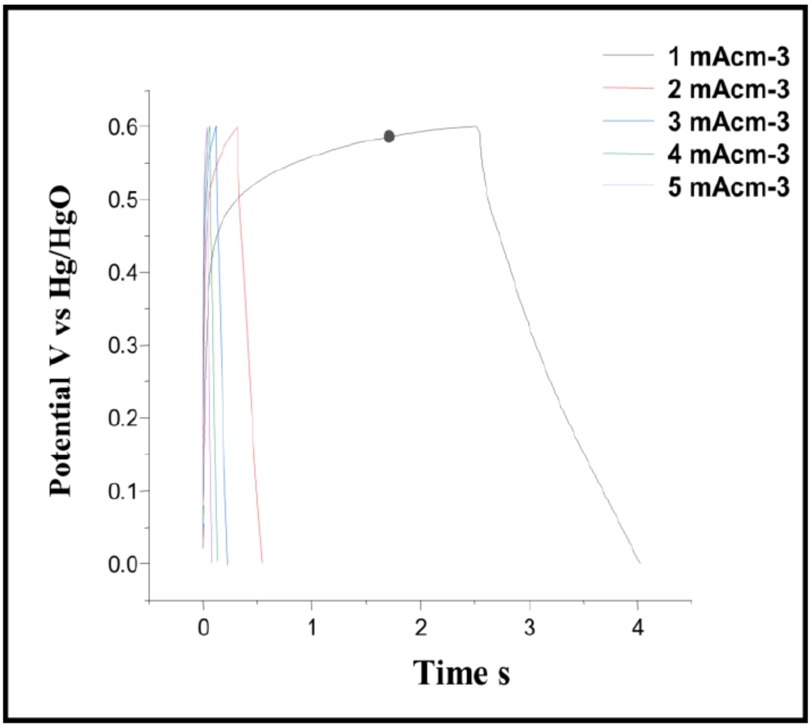


Fig. 7: Charge Discharge curves of as CoCuO electrode in 0.1 M electrolyte.

The electrical parameters like specific power (SP) and specific energy (SE) were calculated using the following relations [21].

$$SP = \frac{I \times V}{m} \qquad (3)$$

$$SE = \frac{I \times t \times V}{m} \qquad (4)$$

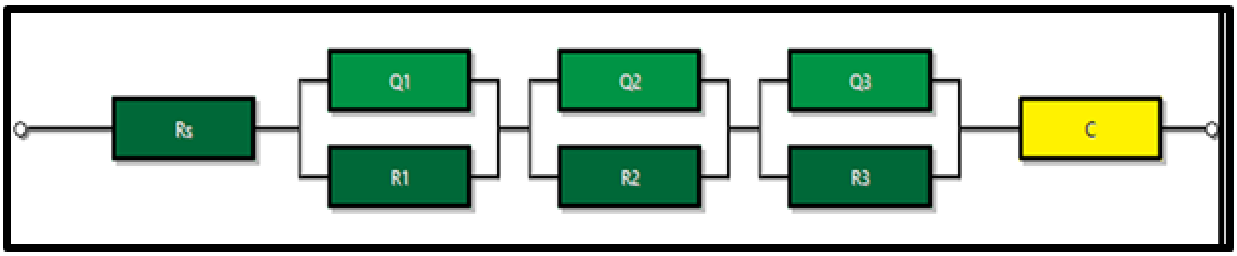
Where, SP specific power is in KW/Kg and SE is specific energy is in Wh/kg. The above expressions indicates discharge current (I) in amperes, voltage range (V) in volts, mass of electroactive material (m) in kilograms and discharge time in seconds. We obtained power density of 213 KW/kg and energy density of 32 Wh/kg at 1mA/cm^2 respectively. The columbic efficiency is calculated using the following relation [22].

$$\eta = \frac{tD}{tC} \times 100 \qquad (5)$$

Where t_C and t_D denotes the time of charging and discharging respectively. The calculated columbic efficiency is 60%.

3.8 Electrochemical Impedance Spectra Analysis

The charge transfer study of binary (Co: Cu) metal oxide thin film electrode was carried out in the frequency range 0.01 Hz to 100 kHz. The equivalent circuit we chosen to fit the measured EIS data is as shown in the Fig. 8(a) the fitted result (red dots) shows a quite good match with the measured result (black dots). In this circuit, R_s represents equivalent series resistance, R_1 represents electrolyte resistance, R_2 represents charge transfer resistance and W is the Warburg diffusion resistance [23]. The Figure 8(b) obviously represents three variation ranges including a partial semi-circle part, a slope with 45^0 and a slope with angle more than 70^0. It is well known that a larger semicircle means a larger charge transfer resistance; the slope with 45^0 indicates the Warburg resistance caused by electrolytic ions diffusion and steeper slope signifies a lower ion-diffusion rate [24]



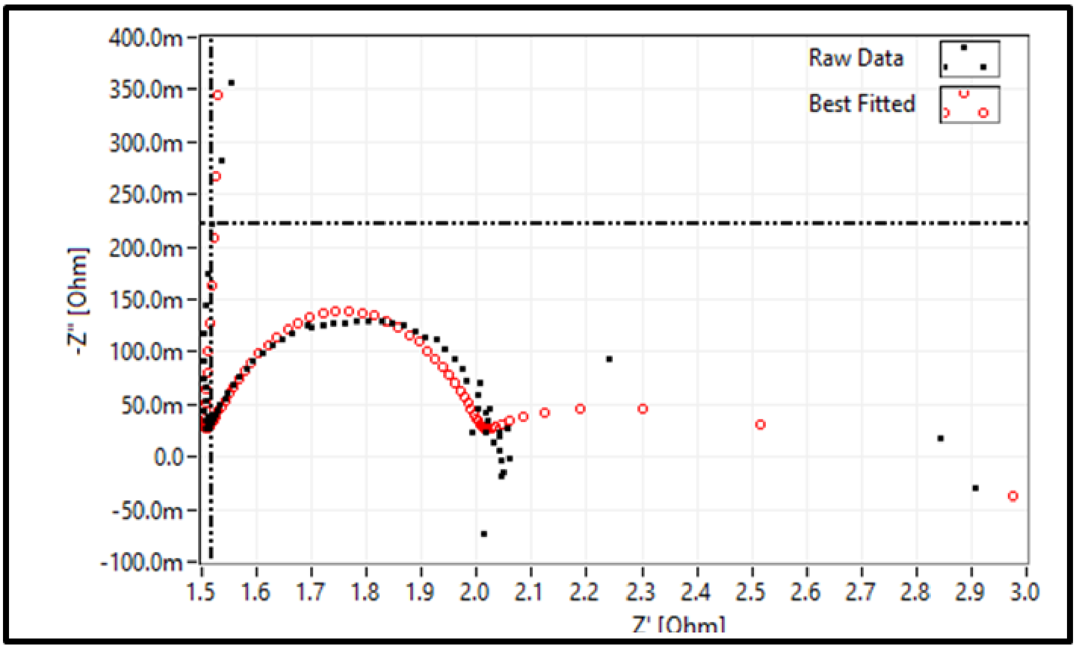


Fig. 8: Electrochemical Impedance Spectra of CoCuO electrode in 0.1 M electrolyte (a) Equivalent circuit (b) Nyquist plots at frequencies between 100 kHz and 0.01 Hz.

3.9 BET Analysis

In order to confirm the specific area and pore size of the CoCuO samples, the product was tested by BET nitrogen adsorption-desorption measurements. The specific area of the as-deposited samples was estimated using the Brunauer-Emmett-Teller (BET) equation based on the nitrogen adsorption isotherm [25]. The BET plot of as deposited binary (Co: Cu) metal oxide thin film is as shown in the Fig. 9. The Brunauer-Emmett-Teller (BET) surface area of the sample is calculated to be 1710.7 $m^2 g^{-1}$. The mean pore diameter of 1.7084 nm is obtained.

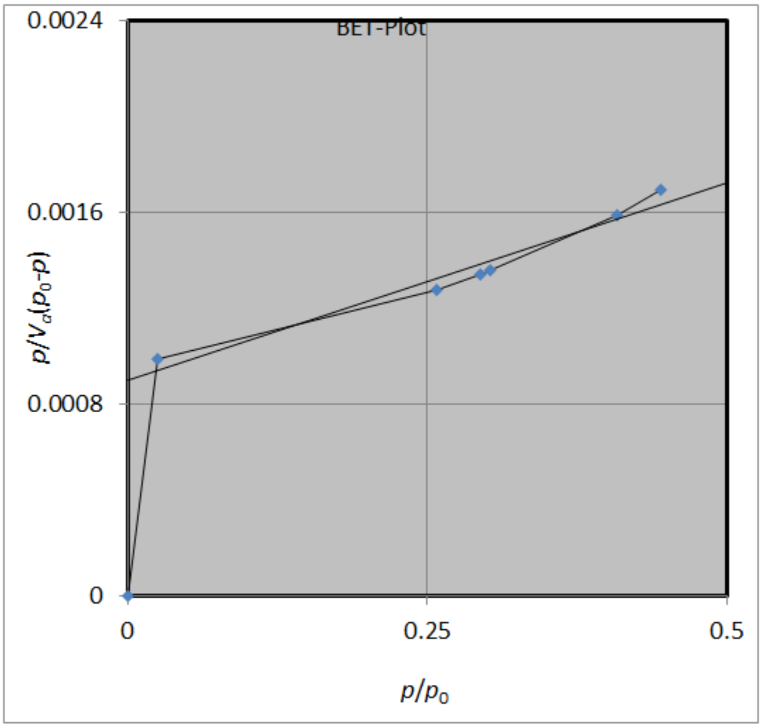


Fig. 9: Brunauer-Emmett-Teller plot of binary (Co: Cu) oxide thin film

CONCLUSION

It is concluded that binary (Co: Cu) metal oxide thin film has been successfully deposited on SS substrate and employed as a supercapacitor. The presence of characteristic bonds of nickel copper oxide was verified by FT-IR studies. A rough surface having porous morphology offers more active sites for electrochemical reaction. Cobalt copper oxide electrode exhibits maximum specific capacitance obtained is 471 F/g at 5mV^{-1} scan rate. From GCD a high specific capacitance of 305 F/g is obtained at current density of 1 mA/cm^2.The power density(P) and energy density (E) were 213 KW/kg, 32 Wh/kg at 1mA/cm2 and efficiency is 60%. From BET analysis the surface area of the sample is calculated to be 1710.7 m^2 g$^-$1.This studies corroborates that cobalt copper oxide is a promising material as an electrochemical capacitor electrode.

ACKNOWLEDGMENTS

The author Savita C. Gavandi thanks SAIF-CFC-DST centre, Shivaji University, Kolhapur for providing material characterization facility. Additionally, author would like to thank Research And Development, Y. C. Institute of Science, Satara for providing material characterization facility.

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