Elevated performance of binder-free $\text{Co}_3\text{O}_4$ electrode for the supercapacitor applications

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Abstract

In the present work, we have designed a symmetric supercapacitor (SS) device by synthesizing a pseudocapacitive binder-free cobalt oxide ($\text{Co}_3\text{O}_4$) thin film based electrode using reactive DC magnetron sputtering technique. The thin film electrodes were characterized by x-ray diffraction, Raman spectroscopy and x-ray photoelectron spectroscopy to reveal the crystallographic details, stoichiometry, and electronic configuration, respectively. Furthermore, $\text{Co}_3\text{O}_4$ thin film electrode is used for pseudocapacitor and electrochemically tested in 1M aqueous KOH electrolyte solution, in addition, a symmetric supercapacitor (SS) device was fabricated. It was found that the SS device exhibits tremendous electrochemical stability in terms of high capacitance and good cycling stability. The value of specific capacitance for $\text{Co}_3\text{O}_4$ thin film electrodes and the SS device was calculated to be 392 F g$^{-1}$ and 95 F g$^{-1}$, respectively, at a scan rate of 2 mA cm$^{-2}$. The SS device exhibits high specific energy (29 W h kg$^{-1}$) along with comparable good specific power (4745 W kg$^{-1}$). In this work, the fabricated SS device demonstrates 91.40% cyclic and capacitance retention at 8 mA cm$^{-2}$ beyond 10 000 cycles. The excellent electrochemical stability and capacitive performance of the SS device suggest that it would be an ideal and potential candidate for energy storage applications in the future.

1. Introduction

In recent years, enormous research has been done to design and develop energy storage devices which include supercapacitor, batteries and fuel cell, etc to fulfil the requirement of energy for current and next-generation [1–3]. Among all these energy storage devices, the electrochemical supercapacitor is taken into account as an intermediate between batteries and conventional capacitor due to its long life span, high power density and good charging/discharging characteristics which can fulfil the energy and power gap between batteries and conventional capacitor [4–9]. The supercapacitors are of two types i.e. first one is known as electric double-layer capacitors (EDLC) that store the charge by faradic and non-faradic mechanism whereas the second one is pseudo-capacitors which store the charge by adsorbing electrons onto the electrolyte-electrode double layer [2, 10–13]. Based on transition metal oxide, the pseudo-capitance mechanism has the advantage due to its high capacitance, which accesses a higher amount of energy density in comparison to EDLC. This is the reason that all transition metal oxide electrodes can be investigated as pseudo-capacitor [14, 15]. Ruthenium oxide ($\text{RuO}_2$) was reported as one of the ideal electrode material due to its advantages in terms of high specific capacitance and good electrochemical stability. On the other hand, $\text{RuO}_2$ has been constrained to use as an electrode material due to its high cost, toxicity, and scarcity [16–19]. Although, many transition metal oxide have been studied for pseudocapacitive properties especially oxides of Manganese, Molybdenum, Iron, Nickel ($\text{MnO}_2$, $\text{MoO}_3$, $\text{Fe}_2\text{O}_3$, $\text{NiO}$), etc from all these, $\text{MoO}_3$ used as a negative electrode but due to its low specific capacitance, it is rarely used [20]. However, cobalt-based oxides considered as an ideal candidate and can be used for a pseudocapacitive electrode as its theoretical calculated specific capacitance is very high (3560 F g$^{-1}$) due to...
multiple oxidation states so that the maximum number of the electron can be trapped during redox process, large surface area, cost-effectiveness, eco-friendly, electrochemical stability and rich redox reaction [4, 12, 17, 21–25]. Cobalt oxide has a spinel structure, which is based upon cubic close packing (CPP) array of oxide ions, and Co$^{2+}$ and Co$^{3+}$ ions occupy tetrahedral 8a and octahedral 16d site, respectively [26]. Cobalt oxide is a p-type semiconductor which makes it a potential candidate for electrochemical device fabrication. Co$_3$O$_4$ has also considered as a battery material in bulk form and there is an effective transportation of electron, fast ion diffusion, good cycling life, and excellent rate capability which makes Co$_3$O$_4$ an ideal material to be considered and used as an electrochemical supercapacitor [27]. There are three well-known forms of cobalt oxide which are polymorphs i.e. CoO known as cobaltous oxide, Co$_2$O$_3$ as cobaltic oxide, and Co$_3$O$_4$ as cobaltosic oxide or cobalt cobaltite [28–30]. The Co$_3$O$_4$ thin film can be deposited by using various synthesis methods such as chemical vapor deposition (CVD) [31], electrochemical deposition [32], sol-gel [33], spray pyrolysis [34, 35], and magnetron sputtering [36–38]. The physical method is much preferred to use, as chemical methods include several drawbacks such as long-time treatment, toxic and nitrogen sources, which are not environmentally friendly. The magnetron sputtering synthesis technique is considered as one of the versatile method to deposit thin film for binder-free electrodes due to its high deposition rate, excellent uniformity and good adhesion between the film and the deposited surface i.e. the current collector [39, 40]. In addition to that, the binder free sputtering method provides the clean and ecofriendly approach to grow nanostructured thin film electrode and due to absence of binder, electrode shows good electronic conductivity without distorting the innate electrode material properties. Additionally, the electrochemical stability of a thin film based electrode depends on its particle size, surface area, crystal structure, and morphology. In this regard, Co$_3$O$_4$ thin films exhibit small charging current leakage and high discharging voltage, which make these thin films a potential candidate to be considered as an active electrode for the supercapacitor devices.

2. Experimental details

2.1. Synthesis of cobalt oxide thin film based electrode

Co$_3$O$_4$ thin film was synthesized by DC magnetron sputtering on stainless steel 304 substrate (work as the current collector). The stainless steel substrate was thoroughly cleaned by an ultrasonic bath in acetone for 15 min [41, 42]. A pure metallic Co target of 50.8 mm diameter and 2 mm thickness with 99.9% purity was used for the sputtering. The crystallinity of as-deposited thin film was optimized by varying substrate temperatures from RT to 500 °C and sputtering pressure from 5 to 20 mTorr at constant sputtering DC power of 50 Watt. The base pressure of the sputtering chamber was ≤ 5 × 10$^{-6}$ mTorr and the film has been deposited for 20 min. The deposition was carried out with a constant flow of O$_2$: Ar gas mixture with a 1:8 gas ratio by using the mass flow controller. In table S1 is available online at stacks.iop.org/NANOX/2/010002/mmmedia, optimized parameters for DC magnetron sputtering are depicted and figure 1 shows the schematic diagram of the electrode preparation process.

2.2. Fabrication of symmetric supercapacitor (SS) device

The SS device was also designed by using two-electrode configuration in which Co$_3$O$_4$ electrode was used as working electrode for both positive and negative electrode taken face to face and were separated by Whatman filter paper soaked in 1 M KOH electrolyte solution. Negative electrode, separator, and positive thin film electrode are stacked in sandwich like structure. The electrochemical performance and stability of SS were tested with the electrochemical workstation (Autolab PGSTAT302N).

2.3. Material characterizations

The crystal phase and structure of Co$_3$O$_4$ thin film electrode was observed by using XRD (Bruker AXS, D8 Advance), with Cu Kα radiation with wavelength (λ = 0.154 18 nm). The surface morphology of the sample was investigated by using FE-SEM (Carl Zeiss FE-SEM ultra plus). Raman Spectroscopy was used for the study of the chemical structure of the film and the formation of chemical bonds. An electronic structure and composition of elements present in the film were demonstrated by XPS (PHI Versa probe III) and EDS was used to know about the elemental composition of the thin film by using the Oxford instrument. The analysis of surface roughness and topography of the film was done by AFM (NTMDTNTegra) in tapping mode.

2.4. Electrochemical studies

The electrochemical study of an electrode was carried out by using a three-electrode electrochemical system (Autolab PGSTAT302N potentiostat/galvanostat). Electrochemical tests were performed in 1M aqueous KOH electrolyte solution in which Ag/AgCl was taken as a reference electrode whereas platinum (Pt) electrode was taken as a counter electrode The related data of Electrochemical Impedance Spectroscopy (EIS) was measured at
frequency varied from 0.1 MHz to 1 Hz after obtaining Open Circuit Potential (OCP) and all the electrochemical measurements were performed at room temperature.

3. Results and discussion

3.1. Structural and morphological analysis
X-Ray diffraction pattern of Co$_3$O$_4$ thin film is shown in figure 2(a) and it exhibits diffraction peaks at 36.8°, 42.8°, and 44.8° which corresponds to (311), (200) and (400) planes, respectively, with a = 8.08 Å, b = 8.08 Å, and c = 8.08 Å are as lattice parameters. Thus, these results of the Co$_3$O$_4$ film relate to the spinel cubic structure as per JCDPS reference no. 01-073-1701. Furthermore, the XRD pattern of the same sample was also recorded after 10 000 charging-discharging cycles of the SS device. It was observed that there was no change in the corresponding XRD peaks, only the intensities of observed peaks were slightly changed which confirms the excellent cyclic stability of the constructed SS device (figure S1). In the XRD pattern, additional peaks of bare stainless steel 304 at 43.5°, 50.7°, and 74.6° were also observed due to the use of stainless steel 304 as a current
The crystallite size was calculated for (311) plane by using the Scherer’s formula:

$$\beta(2\theta) = \frac{0.9 \lambda}{D \cos \theta}$$

Where, $\beta$ is the (FWHM) Full Width Half Maximum with Bragg’s angle $\theta$, $\lambda = 1.56$ Å as the wavelength of the copper target and D is the crystallite size which obtained as 40.5 nm.

As the Co$_3$O$_4$ has a spinel structure with Co$^{2+}$ placed at the tetrahedral site whereas Co$^{3+}$ placed at the octahedral site so the reduction of Co$^{3+}$ into Co$^{2+}$ represents these vibrational modes in the raman spectra of Co$_3$O$_4$ thin film (figure 2(b)). The peaks were observed at 482, 522, 620, and 690 cm$^{-1}$ wave numbers which correspond to $E_g$, $F_{2g}$, $F_{3g}$, and $A_{1g}$ modes, respectively. All the four modes i.e. $E_g$, $A_{1g}$, $F_{2g}$, and $F_{3g}$ were identified and observed as Raman active modes that approve the arrangement of crystalline Co$_3$O$_4$ [44, 45].

The FE-SEM image revealed the formation of smooth and spherical shape grains as shown in figure 3(a). The elemental mapping by EDS depicts that the elements such as Co and O are having good stoichiometry as shown in figures 3(b), (c). The supplementary figure S2(b) shows the FE-SEM image of the SS device after 10 000 charging-discharging cycles, which confirms that the electrodes illustrate prolonged nanostructure. The elemental mapping of the electrodes also displays the presence of Co and O along with potassium (K) which might be due to the insertion of electrolyte ions during the charging and discharging of the SS device.

AFM 3D micrograph and grain size distribution are shown in figures 4(a) and (b), respectively. The root mean square ($\delta_{rms}$) surface roughness was calculated further and it found to be around 6.5 nm as shown in figure 4(a). The roughness of Co$_3$O$_4$ thin film electrode depends on the shape and orientation of the collector. The crystallite size was calculated for (311) plane by using the Scherer’s formula [43]

$$\beta(2\theta) = \frac{0.9 \lambda}{D \cos \theta}$$

Figure 3. (a) FE-SEM image of Co$_3$O$_4$ thin film, (b) Mixing of grains of Co K and O K, and (c) EDS spectrum of Co$_3$O$_4$ thin film showing Co and O elements.

Figure 4. (a) 3D micrograph of Co$_3$O$_4$ thin film by AFM, (b) Grain size distribution Co$_3$O$_4$ thin film, (a’) Surface roughness histogram of Co$_3$O$_4$ thin film and (b’) Grain size distribution of Co$_3$O$_4$ thin film by using the histogram.
grains. The surface roughness affects the capacitive behavior of the device and as the surface roughness increases, the device capacitance also increases [47]. The grain size distribution histogram is shown in figure 4(b') and it exhibits that the maximum grains are of nanometer range in square area. In the present work, the particles are downsized up to a nanoscale which possesses the space charge layer is comparable to the grain dimension. Therefore, the electrical conduction is predominantly grain controlled which leads to an increment in electronic conduction and thus, the overall capacitance [48].

XPS was further employed to investigate the elements and chemical bonding state of the Co₃O₄ film surface as depicted in figure 5. The full scan (figure 5(a)) revealed the existence of Co, O, and C elements in Co₃O₄ thin film without any impurities [49]. The main component peaks are present in survey spectra corresponds to two electronic levels i.e. 2p₃/₂ and 2p₁/₂ along with shake-up satellite peaks [50]. These satellite peaks come in existence due to the electrons transition from 3d orbit to 4s orbitals which is empty during the ejection of core 2p photoelectron. Figure 5(b) describes the high-resolution spectrum of Co 2p of two prominent doublet peaks, having binding energies 779.9 eV and 795.0 eV. These peaks correspond to the splitting of Co 2p spectra into another two spectra i.e. Co2p₃/₂ and Co2p₁/₂, respectively. Two ‘shake up’ satellite peaks having binding energies at 789.2 eV and 803.6 eV confirms the co-existence of Co³⁺ and Co²⁺ [51]. It is also verified that there is no other oxidation peaks present which confirms the presence of pure Co₃O₄ thin film. High-resolution O 1s spectra are shown in figure 5(c) and according to the Dupin et al deconvoluted peaks of O 1s, where, O²⁻ assigned lower binding energy while the middle peak assigned to O¹⁻ with the binding energy of 529.5 eV, and higher binding energy peak to Ochem which absorbed oxygen chemically from the surface [52]. The prominent peaks related to O 1s with binding energies of 528.3 eV and 530.1 eV are also observed [53]. Furthermore, the XPS analysis has also been done for SS device after 10 000 charging-discharging cycle (figure S3) and all the peaks of desired elements were observed in the survey spectrum along with an additional peak of potassium (K) at the binding energy of 292.4 eV. This confirms that even after the 10 000 cycles, the electrodes show a good configuration of Co₃O₄ and can be used repeatedly for a high number of cycles.

Figure 5. (a) XPS of full survey scan, (b) Co 2p XPS spectrum, and (c) O 1s XPS spectrum.
3.2. Preparation of Co$_3$O$_4$ thin film active electrode for electrochemical stability

The electrochemical stability of the Co$_3$O$_4$ thin film electrode has been explored by using the three-electrode system. In order to check the electrochemical stability, different tests such as GCD (galvanic charging-discharging), EIS (electrochemical impedance spectroscopy), and CV (cyclic voltammetry) were performed. Figure 6(a) shows the CV curves of the thin film electrode at the scan rate varied from 10 mVs$^{-1}$ to 100 mVs$^{-1}$ with a potential window of $-0.3$ to $+0.5$ V. The mechanism for charge storage in Co$_3$O$_4$ thin film electrode is given below, where, OH$^-$ ions from KOH solution enters in the electrode and takes part in the reaction [54].

$$
\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \underset{\text{charging}}{\overset{\text{discharging}}{\leftrightarrow}} 3\text{CoOOH} + e^-
$$

It was observed that the CV curves do not have perfect quasi-rectangular shape which indicates that the Co$_3$O$_4$ thin film electrode shows pseudo-capacitive behavior [28]. The peak current increased, with an increase in the scan rate from 10 mVs$^{-1}$ to 100 mVs$^{-1}$, which reflects good reversibility against the fast charging-discharging response. Areal and specific capacitance of electrode from the cyclic voltammetry curve can be calculated by using the equations (2) and (3).

\begin{equation}
\text{Areal Capacitance of Electrode, } C_{\text{electrode}} = \frac{\text{Area under the curve}}{\text{Scan Rate} \times \text{Window} \times \text{Electrode area}}
\end{equation}

\begin{equation}
\text{Specific Capacitance of Electrode, } C_{\text{electrode}} = \frac{\text{Area under the curve}}{\text{Mass of electrode} \times \text{Scan rate} \times \text{Volage}}
\end{equation}

The value of areal and specific capacitance obtained from the CV curve were 190 mFcm$^{-2}$ and 414 Fg$^{-1}$, respectively at a scan rate of 10 mVs$^{-1}$, which are matching well with the previously reported data. Kandalkar et al [55] adopted the chemical route to prepare the thin film and obtained the maximum value of specific capacitance around 165 Fg$^{-1}$ at 10 mVs$^{-1}$ in 1.0 M KOH electrolyte solution. The comparison of related capacitance values with other reported data on Co$_3$O$_4$ electrodes synthesis using various methods, presented in table 1.

Subsequently, the electrochemical study was accomplished by GCD and the related curves at different current densities from 2–8 mAcm$^{-2}$ are shown in figure 6(b). The calculated specific capacitance from the GCD curve found to be 392 Fg$^{-1}$, 283 Fg$^{-1}$, 182 Fg$^{-1}$, and 135 Fg$^{-1}$ at different current densities of 2, 4, 6 and 8 mAcm$^{-2}$, respectively. Whereas areal capacitance obtained from the GCD curve found to be 180 mFcm$^{-2}$ to 62 mFcm$^{-2}$ at the same current densities from 2 to 8 mAcm$^{-2}$, respectively. Interfacial capacitance and specific capacitance are plotted in figure 6(c) as a function of current density. The specific capacitance values achieved at higher current density are superior to the previously reported literature on the Co$_3$O$_4$ electrode. Zhu et al [57] reported Co$_3$O$_4$ as a needle-like electrode that can deliver the value of specific capacitance around 111 Fg$^{-1}$ at the current density of 1 Ag$^{-1}$. The calculated value of specific capacitance from GCD can be given by the
Table 1. Comparison of electrochemical performance of as-prepared Co₃O₄ electrode with previously reported data on different synthesis methods by using standard three-electrode Cell.

| Methods                        | Electrolyte | Electrode materials          | Cₘ   | Scan rate | Voltage window | References |
|--------------------------------|-------------|------------------------------|------|-----------|----------------|------------|
| Spray pyrolysis                | 2 M KOH     | Co₃O₄ thin film              | 74 Fg⁻¹ | 5 mVs⁻¹   | 0.6 V          | [50]       |
| Potentiodynamic Electrodeposition | 1 M KOH     | Co₃O₄ thin film              | 365 Fg⁻¹ | 5 mVs⁻¹   | 0.8 V          | [44]       |
| Chemical Route                 | 1 M KOH     | Co₃O₄ thin film              | 165 Fg⁻¹ | 10 mVs⁻¹  | 0.8 V          | [55]       |
| Multi-step hard template route | 4 M KOH     | Co₃O₄ microsphere            | 102 Fg⁻¹ | 3 mVs⁻¹   | 0.7 V          | [56]       |
| Facial Approach                | 2 M KOH     | Porous Co₃O₄                | 111 Fg⁻¹ | 1 Ag⁻¹    | 0.7 V          | [57]       |
| Solid state Thermolysis        | 2 M KOH     | Porous Co₃O₄                | 150 Fg⁻¹ | 1 Ag⁻¹    | 0.5 V          | [58]       |
| Facile binary-solution route   | 3 M KOH     | Co₃O₄ Nano sheet            | 92 Fg⁻¹  | 5 mACm⁻²  | 0.6 V          | [59]       |
| DC Sputtering                  | 1 M KOH     | Co₃O₄ thin film             | 392 Fg⁻¹ | 2 mACm⁻²  | 0.8 V          | Present Work |

equation [60]:

\[
C_m = \frac{I \times \Delta t}{m \times \Delta V}
\]  

Where, \(C_m\) is the specific capacitance (Fg⁻¹), \(I\) is the current density (mAcm⁻²), \(\Delta t\) is the discharging time, \(\Delta V\) voltage window (V), and \(m\) represents the electrode mass. The maximum specific capacitance of electrode from the GCD curve was calculated at 2 mACm⁻² and it found to be 392 Fg⁻¹. This specific capacitance value is also comparable to the results obtained by Xiong et al [59] attained a specific capacitance value of 92 Fg⁻¹ at a current density of 5 mACm⁻² by using 3 M KOH solution.

EIS analysis was further performed to examine the electrochemical stability and performance of the Co₃O₄ thin film based electrode and the Nyquist plot with circuit fitting is shown in figure 6(d). This comprises the supercapacitor’s resistive nature which consists of an electrode, electrolyte solution, and current collector [28]. The straight line is the characteristics of semi-finite diffusion \(W_1\) which is known as Warburg impedance. The effect of finite length was observed at a lower frequency with a transition from the 45° line towards the vertical line (open Warburg impedance, \(W_2\)), which demonstrates the good capacitive behavior of an electrode. In this case, the straight line is shown in the lower frequencies due to the fact that during charging-discharging, there would be the presence of ionic diffusion [44]. A simplified equivalent circuit which consists of electrode’s bulk resistance (R), pseudo-capacitance (C), Warburg resistance (\(W_1\)) and open Warburg element (\(W_2\)) is shown in figure 6(d). The initial line represents the contact of an electrolytic resistance (R) with the current collector (C) and an electrode. The fitting results also indicate that the Co₃O₄ electrode is more beneficial for a rapid redox reaction. The values of R and C are 6.93 Ω and 76.0 μF, respectively, and the value of \(W_1\) and \(W_2\) are 49.4 μMho * s⁻¹/2 and 2.47 mMho * s⁻¹/2, respectively, obtained by the circuit. The CV curve up to 5000 cycles at 100 mVs⁻¹ is shown in figure 6(e) which depicts that there is no significant change in the CV curve from the starting i.e. from first cycle to the last cycle i.e. 5000 cycle at 100 mVs⁻¹. This implies a good capacitance retention up to 95% as shown in figure 6(f). These results prove that the Co₃O₄ electrode would be an ideal and potential candidate for the SS device.

### 3.3. Electrochemical study of symmetric supercapacitor (SS) device

The SS device was prepared by employing the Co₃O₄ electrode as both cathode and anode, and the schematic diagram is shown in figure 7. The electrochemical measurements of the SS device was performed by two cell setup by using 1 M aqueous KOH electrolyte solution soaked filter paper as a separator. CV curves at the scan rate varied from 10 to 100 mVs⁻¹ and potential window (1.6 V) range from 0 to +1.6 V, are depicted in figure 8(a). For the enhancement of an electrochemical performance and stability of a device, one can optimize the length and mass loading of electrode [61]. The shape of the CV curve remains the same without redox peaks, when the scan rate increases, this indicates the performance of the device is excellent. During the fabrication of the SS device, the area of the electrode is the main component to get desirable areal capacitance, and in the present work, the area for SS device was taken as 1 cm². At a scan rate of 10 mVs⁻¹, the maximum value of areal capacitance for the SS device was found to be 93 mFcm⁻². Whereas, at the same scan rate, the value of specific capacitance was obtained around 102 Fg⁻¹ which is maximum. In order to calculate the areal and specific capacitance of the cell from the CV curve, the following formulae are used [62].

\[
\text{Areal capacitance, } C_{Cell} = \frac{\text{Area under the curve}}{\text{Scan Rate} \times \text{Voltage Window} \times \text{Area of deposited electrode}}
\]  

References
Furthermore, the SS device was electrochemically investigated by GCD curves taken at varied current densities (mA cm\(^{-2}\)) as shown in figure 8(b). The specific capacitance from GCD curve of SS device can be calculated by the following equation:

\[
C_m = \frac{4 \times I \times \Delta t}{m \times \Delta V}
\]  

(7)

Where, \(C_m\) is the specific capacitance (F g\(^{-1}\)), \(I\) is the current density (mA cm\(^{-2}\)), \(\Delta t\) is the discharging time, \(\Delta V\) is voltage window (V) and \(m\) represents the total active electrode mass in the cell. From equation (7), the specific capacitance value for SS device was measured to be 95, 77, 61, and 55 F g\(^{-1}\) at different current densities of 2, 4, 6,
Table 2. Comparison of specific energy and specific power of the SS device with previously reported data.

| Specific energy (W-hkg$^{-1}$) | Specific power (Wkg$^{-1}$) | References |
|--------------------------------|-----------------------------|-------------|
| 24.18                          | 8.50                        | [68]        |
| 12                             | 432                         | [69]        |
| 5.8                            | 128                         | [70]        |
| 29                             | 4745                        | Present Work |

and 8 mAcm$^{-2}$, respectively. The areal capacitance was also obtained from the GCD curve at the same current densities and found to be 87, 70, 56, and 50 mFcm$^{-2}$. The areal and specific capacitance versus current density of the SS device is depicted in figure 8(c).

The specific energy and power are other major parameters for knowing about the supercapacitor performance. Further, the specific energy and power calculation of Co$_3$O$_4$ SS device from GCD curve is given by the following relation [63–66]

$$E = \frac{C_m \times \Delta V^2}{2 \times 3.6}$$  \hspace{1cm} (8)

$$P = \frac{E \times 3600}{\Delta t}$$  \hspace{1cm} (9)

Where $C_m$ is the specific capacitance (Fg$^{-1}$) measured from the two-electrode system, $\Delta t$ is the discharging time, $V$ is the voltage window (V), $E$ is the specific energy (W-hkg$^{-1}$) and $P$ is the specific power (Wkg$^{-1}$).

Figure 8(d) shows the Ragone plot which indicates the specific energy and power of the symmetric supercapacitor device fabricated from the Co$_3$O$_4$ electrode. The SS device exhibits good specific energy of 29 W-h K$^{-1}$ g$^{-1}$ and specific power of 4745 W K$^{-1}$ g$^{-1}$ at a current density of 2 mAcm$^{-2}$, which are comparable with the previously reported data shown in table 2. The EIS plot of the SS device with circuit fitted data is shown in figure 8(e). The line inclined in the low-frequency range is approximately straight and this inclined line is also parallel to an imaginary axis which confirms an ideal capacitive behavior of SS device. At high-frequency region, the real part intercept and determine the equivalent series resistance and its value is ($R_{ESR}$ = 1.01 $\Omega$) which indicates that there is a combination of resistances such as electronic resistance of electrode material, electrolytic ionic resistance and contact resistance at different interfaces. $C_1 = 106 \mu$F is known as electric double-layer capacitance which is due to the interaction of an electrode and electrolyte at the surface. In a low-frequency region, the value of Warburg resistance is $W_1 = 390 \mu$Mho $s^{-1/2}$ is known as Warburg resistance and this is due to the transportation of ions in an electrode from the electrolyte. In a low-frequency region, the value of Warburg resistance is $W_2 = 8.68 $nMho $s^{-1/2}$ [67]. The cyclic stability of the device is another important factor for supercapacitor practical application. In this work, the cyclic stability of the Co$_3$O$_4$ thin film based SS device is tested for 10,000 cycles in 1 M KOH electrolyte solution and excellent cyclic retention is maintained. Figure 8(f) illustrates the cyclic stability of the SS device which having a voltage range varied from (0 to $+1.6$ V) in 1 M KOH electrolyte solution. In this study, the cyclic retention of the SS device was also found to be 91.40% at a current density of 8 mAcm$^{-2}$ for 10,000 cycles. The developed SS device shows an excellent cyclic life span.

4. Conclusions

In this work, the synthesis of the Co$_3$O$_4$ thin film (as current collector) based binder-free electrode was successfully done by- using the DC magnetron sputtering technique on a stainless steel 304 substrate. Due to its unique surface structure, the Co$_3$O$_4$ thin film based symmetric supercapacitor (SS) device is found imperative for fabrication. The electrochemical stability of both Co$_3$O$_4$ thin film based electrode and SS device was tested at 1 M aqueous KOH electrolyte solution which shows high capacitance of 392 Fg$^{-1}$ and 95 Fg$^{-1}$ at 2 mAcm$^{-2}$, respectively. The SS device was showing high specific energy of 29 W-hKg$^{-1}$ and specific power of 4745 Wkg$^{-1}$ with a wide operating voltage of 1.6 V. It was observed that the cyclic stability and capacitance retention of SS device at 8 mAcm$^{-2}$ current density was 91.40% which confirms the excellent cyclic stability of SS device. These superior results of constructed SS device recommend it to be worthwhile in energy storage applications.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

There are no conflicts to declare.

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