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Research Article

Comparative studies of $NiMnCo_3O_4$ thin film electrodes for supercapacitors applications

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Abstract

Present work is devoted to preparing ternary $NiMnCo_3O_4$ electrodes by electrodeposition method on copper and porous copper substrate. The structural, morphological and electrochemical characterizations of the prepared samples studied and confirmed by using XRD, SEM, EDAX, FTIR and electrochemical measurements. Structural analysis confirms that $NiMnCo_3O_4$ film has face-centered cubic with polycrystalline nature. Electrochemical measurements prove that $NiMnCo_3O_4$ electrode deposited on a porous copper substrate has an improved super capacitive behavior, compared with $NiMnCo_3O_4$ electrode deposited on a copper substrate. The high specific capacity of 947 F/g at 10 mV/s was observed. Electrochemical performances were investigated at different scan rate range. And it reveals the prepared electrode has excellent capacitance behavior as well as reversibility. Moreover, stable cycle capability 90.2%inthe capacitance retention was achieved after 3000 cycles. These outstanding electrochemical properties indicate that the obtained $NiMnCo_3O_4$ electrode materials are fairly ideal for supercapacitors.

Keywords: Thin films, Electrodeposition, Nickel Manganese cobalt ternary oxide, supercapacitor.

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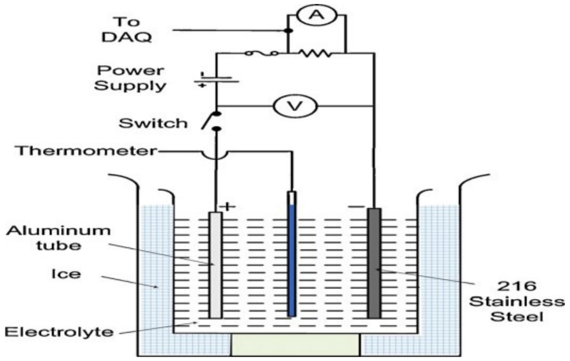
1. Introduction

Since last few years, the trouble for clean, efficient, and renewable energy sources is remarkable and thereby driving intense scientific concern in the production, storage and management of this precious energy [1-2]. Among the variety of electrical energy storage devices, supercapacitors (SCs), also known as electrochemical capacitors, grabs an enormous research and industrial attention because of their high power density and very long cycle stability as compared to their counterparts such as batteries, fuel cells, and conventional capacitors, etc. [3,4]. In general, SCs are classified into two types according to the energy storage mechanism: Electric double layer capacitors (EDLCs) and pseudocapacitors (PCs). The EDLCs store energy based on the electrostatic accumulation of charges in the electric double-layer near the electrode/electrolyte interfaces and the PCs is governed by fast surface faradaic reactions using redox-active materials [5-7]. Unlike the Electric double layer capacitance and Pseudocapacitance usually, deliver much higher specific capacitance and higher energy density than the conventional EDLCs due to their fast and reversible redox reaction. The MnO_2, NiO_2, and RuO_2 have been considered as PCs materials and these materials have an I–V curve whose its shape is close to that of the EDLC and they showed EDLC like behaviors [8]. In addition to the MnO_2 and RuO_2, B.E. Conway briefly indicated that the others metal oxides such as Co_3O_4 and Mn_3O_4, and WO_3 and also conductive polymers could have pseudocapacitive properties[9], and generally indicated that the metal oxides with the following properties could be good for use as pseudocapacitive materials in the electrochemical SCs:(1) The oxide should be electronically conductive,(2) the metal can exist in two or more oxidation states that exist over a continuous range with no phase changes involving irreversible modification so far 3-dimensional structure, and (3) the protons can freely intercalate into the oxide lattice on reduction (and out of the lattice on oxidation), allowing facile interconversion of $O^{-2} \leftrightarrow OH^{-1}$. Truly, for some cases, it is difficult to determine a boundary between pseudocapacitors and batteries behaviors and their behavior depending on various parameters such as type of electrolyte, morphology, and thickness of the electro-active materials, range of applied potential and current densities, output energy and power densities [10-11]. To date, considerable effort is being widely focused on further improving the performance of PCs [12-13]. Some monolithic transition metal oxides and hydroxides compounds have been widely explored for producing PCs which each of them presented advantages and limitations in their specific capacitance, energy density, cost, toxicity, and flexibility in structures and morphology [14-15]. Thus, it is necessary to overcome the gap performance between these materials. Construction of hierarchical structures of binary metal oxides such as $NiCo_2O_4$ and $MnCo_2O_4$ is of great significance and has shown better capacity and cycling stability compared with monolithic systems such as Co_3O_4, MnO_2, and NiO [16-22]. Mixed metal oxide compounds have been synthesized by various methods including solgel, electrodeposition, hydrothermal. Facile control of crystal size, morphology, and structures can be obtained by the hydrothermal method. Although numerous previous studies related to binary transition metal oxides have been reported, only a few reports are related to ternary oxides [23-25] that are prepared on the surface of hard nickel foams. Mesoporous ternary nanostructures exhibit excellent electrochemical performance due to their large surface area that promotes contact between electrode and electrolyte; mesoporous enable facile electrolyte penetration and diffusion. For example, Tu *et al* have synthesized manganese-nickel cobalt ternary oxide ($MnNiCo_3O_4$) electrode materials which have better capacitance, energy density, safety performance, and lower cost compared to pure Co_3O_4 electrode materials [26]. Also, C. Wu *et al* Have prepared Nickel foam supported hierarchical mesoporous ZnNiCo ternary oxide (ZNCO) nanowire arrays which possess excellent electrochemical performances [27]. The obtained results by these authors indicated that the incorporation of three metal ions and the porous feature soft these nanowires increase the number of electroactive sites and facilitate the electrolyte penetration as well as electron transfer kinetics, but the flexibility is still debatable based on the survey above, this paper presents an alternative approach by preparing novel ternary metal oxide $NiMnCo_3O_4$, demonstrating high specific capacitance, high cycling stability, and outstanding rate capability. In addition, the supercapacitor performance of the ternary oxides is studied and compared with the corresponding binary and monolithic compounds. In present work, we have deposited, Nickel manganese cobalt oxide $NiMnCo_3O_4$ thin films from an alkaline solution of cobalt chloride, Nickel chloride and Manganese chloride using the electrodeposition method. These films are characterized by X-ray diffraction (XRD), and Field Emission scanning electron microscopy (FSEM) and Energy Dispersive x-ray Analysis (EDAX) and Fourier transform infrared spectroscopy (FT-IR), Electrochemical studies of cyclic voltammetric (CV), Galvanostatic charge-discharge study (GCD) and stability studies.

2. Experimental details

2.1Anodization of the copper substrate

Anodization is an electrolytic process for protection or decoration of metal surfaces. In the present study, Copper substrates were anodized before the deposition of $NiMnCo_3O_4$. The Copper substrate with the thickness of 0.1mm and surface area of 5x1.5 cm^2 was ultrasonically cleaned. This cleaned copper substrate was used as anode and Nickel rod was chosen as cathode during the experiment. Based on previous literature, the cleaned copper substrate was anodized under different electrolyte condition in order to obtain a copper porous on substrates. [28].



2.2 Preparation of Nickel manganese cobalt oxide thin films

The $NiMnCo_3O_4$ films are deposited on both copper and porous copper substrate by electrodeposition (Galvanostatic mode) method. The electrodeposition has been carried out from respective chlorides of Cobalt, Nickel, and Manganese. Along with that Boric acid was used as a complexing agent. This chloride composed solution was complexed with ammonium hydroxide (NH_3OH), and a $_pH$ of the electrolyte solution was maintained at 10. At first, the copper substrate (5.0 x1.5 cm^2) was carried for the cleaning process by mechanically and electrochemically. The $NiMnCo_3O_4$ films were deposited on copper and porous copper substrate with the optimized current of density 7 mA/cm^2 under the deposition times of 20-50 minutes. After the deposition, deposited electrodes were annealed at 300°C for 2 hours, and used for further characterization.

2.3 Thickness measurement

The thickness of the film was optimized by depositing these films on 20, 30, 40 and50 minutes of deposition time and annealing at 300°C for 2 hours. Mass balance method was employed for the measurement of film thickness. Figure 1, shows the variation of a thickness (mg cm^{-2}) with deposition time. It is obvious that as the number of deposition time increased, the film thickness also increased, and finally, a maximum thickness of 0.34 mg cm^{-2} was achieved after 50 minutes of deposition times. The film deposited above 55 minutes peeled off due to the development of internal stress which tends to cause delamination when the film becomes thick. The maximum thickness obtained for the $NiMnCo_3O_4$ film was 0.34 mg cm^{-2} and used for further characterization.

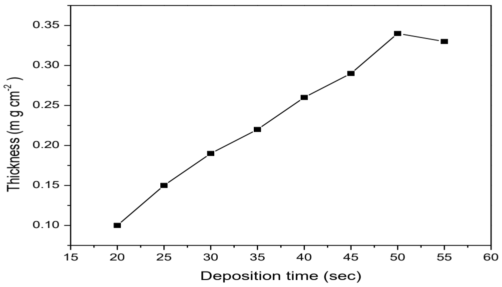


Figure 1: Thickness variation of $NiMnCo_3O_4$ thin film as a function of deposition time from 20 to 55

3. Result and discussion

3.1. Structural analysis

3.1.1 X-ray diffraction technique (XRD)

The crystalline structure and crystalline phase of the prepared samples are analyzed by XRD in the 2θ range of 20°-80°. The figure 2a and 2b shows, $NiMnCo_3O_4$ films deposited on copper and porous copper substrate. $NiMnCo_3O_4$ films deposited on copper substrates exhibit a series of diffraction peaks at 2θ=42.80°, 49.89°, 73.58° which was assigned to the plane (331), (222), and (620) respectively [JCPDS: 73-1704, JCPDS:23-1237] and diffraction peaks of the films on porous copper substrates 2θ=42.67°, 49.79°, 73.44° are assigned to (331), (222), and (620) planes, respectively. This diffraction reveals that the electrodeposited Ni-Mn-Co ternary oxide thin film was nanocrystalline, indicating phase purity of $NiMnCo_3O_4$.

Further, the crystallite size was estimated using Scherrer's formula $D=\frac{0.89\,\lambda}{\beta\cos\theta}$

Where D is crystalline size, K is the shape factor (0.94), λ is the wavelength of Cu Kα radiation (1.5406 Å), β is full width at half maxima; lambda is the wavelength of X-ray used and θ is diffraction angle. The calculated average crystallite size of the $NiMnCo_3O_4$ deposited on copper substrate 39.94 and $NiMnCo_3O_4$ deposited on porous copper substrate 42.90 films.

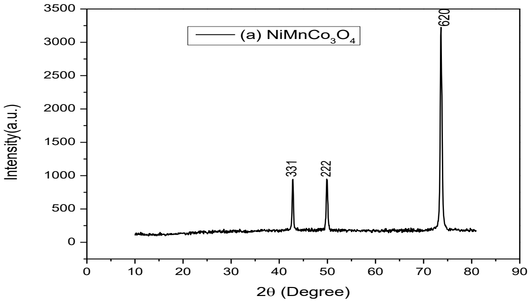


Figure 2a): The XRD Patterns of $NiMnCo_3O_4$ thin film electrode deposited on a copper substrate

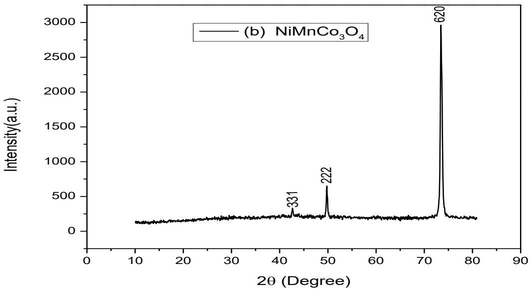


Figure 2b): The XRD Patterns of $NiMnCo_3O_4$ thin film electrode deposited on a porous copper substrate

3.1.2 FTIR Study

FTIR spectra of $NiMnCo_3O_4$ films deposited on a copper substrate and porous copper substrate as shown in Figure 3 (a) and (b) which confirms the presence of relevant functional groups. The bands due to the oxide structure appeared in the region between 800 and 850 cm^{-1}. In both, the samples, the absorption band at 825 cm-1 (around 800-850cm^{-1}) was associated with the Ni-O vibration bond [29]. Two bands observed at 1134 cm^{-1} and1512 $cm^{-1}$are corresponded to the strong C-O stretching vibration, which indicated that the ultrafine powders tend to physically absorb CO_2 molecule from the air. The bands at 2360 and 3475 cm^{-1} (around 3300-2300 cm^{-1}) were due to strong, broad O-H vibration corresponded to the surface absorbed water from the atmosphere. The above information confirmed the formation of $NiMnCo_3O_4$ thin films.

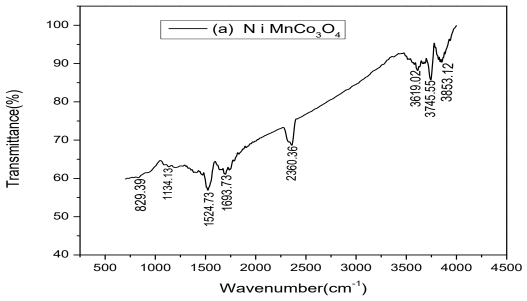


Figure 3a): FTIR spectrum of $NiMnCo_3O_4$ thin film electrode deposited on a copper substrate

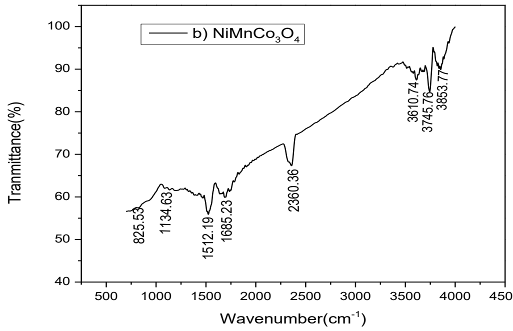


Figure 3b): FTIR spectrum of $NiMnCo_3O_4$ thin film electrode deposited on a porous copper substrate

3.2. Field Emission Scanning Electron microscopy (FE-SEM)

The FE-SEM micrographs were adopted to confirm the surface morphologies of $NiMnCo_3O_4$ films and Porous formation in copper which is shown in figure 4(a), (b) and (c). FE-SEM micrograph of porous copper confirms the formation of porous in Nano range. Figure b) shows $NiMnCo_3O_4$ film deposited on a copper substrate reveals the spherical shaped smaller grains. The formation of these grains was dense, uniform, homogeneous and covered well with the substrate. The $NiMnCo_3O_4$ film deposited on copper porous was shown in Figure (c) which reveals that the films were roughly deposited with microcracks.

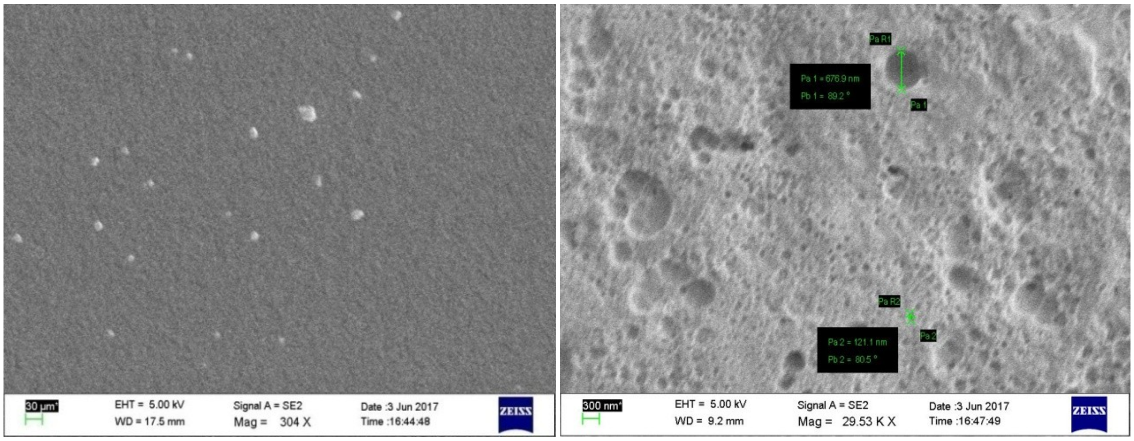


Figure 4a: The scanning electron micrographs of the porous copper substrate

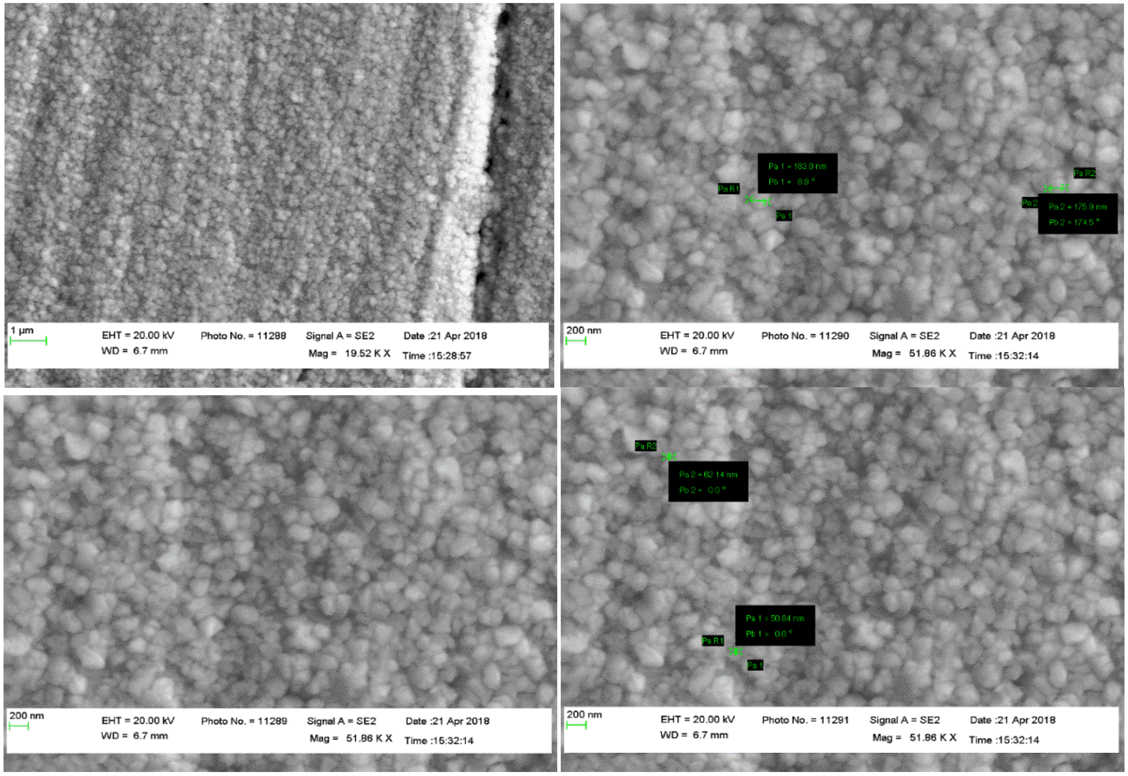


Figure 4 b): The scanning electron micrographs of $NiMnCo_3O_4$ thin film electrode deposited on copper substrate annealed at 300°C for 2 hrs

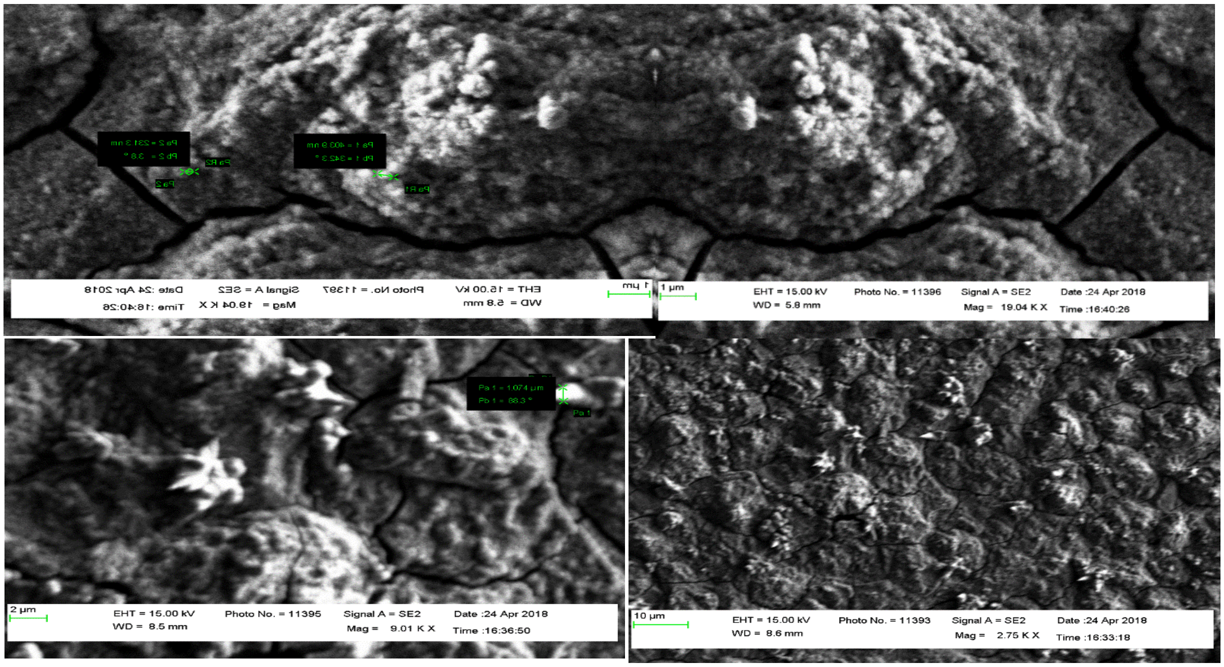


Figure 4c: The scanning electron micrographs of $NiMnCo_3O_4$ thin film electrode deposited on porous copper substrate annealed at $300^{\circ}C$ for 2 hrs

3.3Elemental composition and identification study (EDAX)

The elemental composition of prepared samples has been identified and confirmed by using (EDAX) pattern. Figure 5 a & b shows the EDAX study for $NiMnCo_3O_4$ electrode deposited on both copper and porous copper substrate. From the analysis, the presence of Ni, Mn, Co, and O was confirmed along with the substrate peak copper (Cu). This analysis clearly confirms the presence of Ni, Mn, Co atoms is higher when the film deposited on a copper substrate.

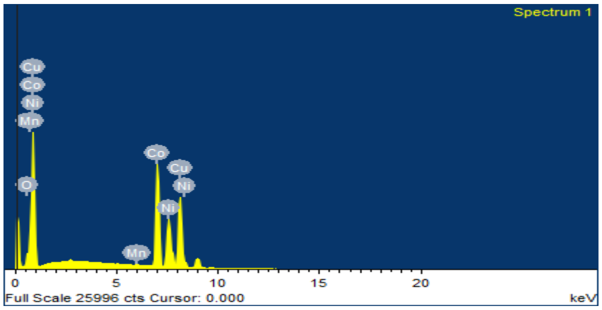


Figure 5a: Energy ray dispersive analysis of $NiMnCo_3O_4$ thin film electrode deposited on a copper substrate

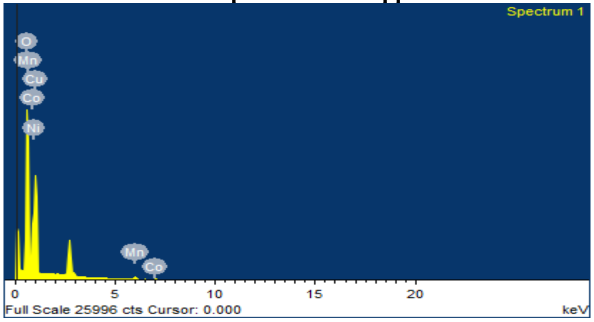


Figure 5b: Energy ray dispersive analysis of $NiMnCo_3O_4$thin film electrode deposited on a porous copper substrate

3.4. Supercapacitive study

3.4.1 Cyclic voltammetry (CV)

Capacitive behavior of the prepared electrode material was characterized using cyclic voltammogram. Comparisons of CV measurements at 10, 20, 30, 40, 50 and 100 mVs^{-1} between $NiMnCo_3O_4$ electrode deposited on copper and porous copper substrates. Obviously, the area surrounded by the CV curve $NiMnCo_3O_4$ electrodes deposited on porous copper is considerably larger than the $NiMnCo_3O_4$ electrode deposited on a copper substrate and also exhibit the higher redox current demonstrating much more advanced supercapacitive performance of $NiMnCo_3O_4$ electrode deposited on a porous copper substrate. The maximum specific capacitances are calculated to be 947 Fg^{-1} for the $NiMnCo_3O_4$ film deposited on a porous copper substrate.

The curve of both $NiMnCo_3O_4$ electrode under various scan rate are shown in figure 6 (a) and (b). Figure 7 shows a comparison of variations of specific capacitance of (a) $NiMnCo_3O_4$ thin films deposited on the copper substrate (b) $NiMnCo_3O_4$ thin films deposited on the porous copper substrate at different scan rate in 1M KOH electrolyte.

The energy storage mechanism of the $NiMnCo_3O_4$ electrode can be assigned to the following equations.

$$MnNiCo + H_2O + OH^- \rightarrow MnOOH + NiOOH + CoOOH + e^-$$

$$MnOOH + NiOOH + CoOOH + OH^- \rightarrow NiO_2 + MnO_2 + CoO_2 + H_2O + e^-$$

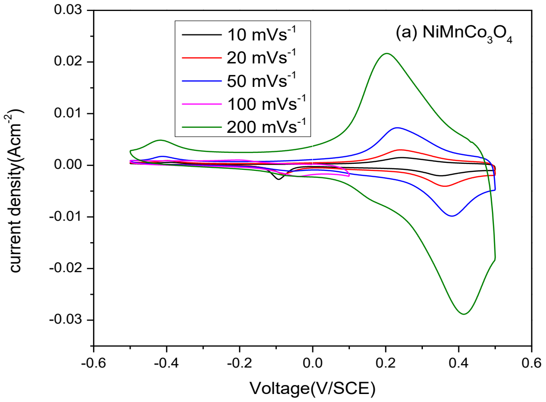


Figure 6 (a): The curve of $NiMnCo_3O_4$ thin film electrode deposited on copper substrate at different scan rate in 1M KOH electrolyte

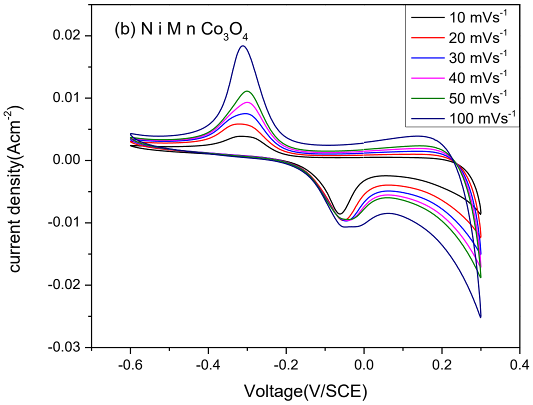


Figure 6 (b): The curve of $NiMnFeCo_3O_4$ thin film electrode deposited on the porous copper substrate at different scan rate in 1M KOH electrolyte

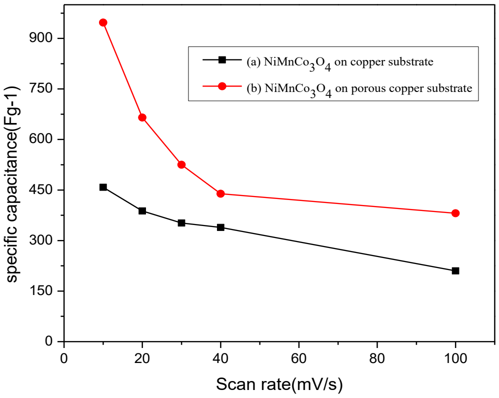


Figure 7: The variations of specific capacitance of (a) $NiMnCo_3O_4$ thin films deposited on the copper substrate (b) $NiMnCo_3O_4$ thin films deposited on the porous copper substrate at different scan rate in 1M KOH electrolyte.

3.4.2 Galvanostatic charge-discharge study

The Galvanostatic charge-discharge measurement of the $NiMnCo_3O_4$ electrode deposited on the copper and porous copper substrate was studied using charge-discharge curves and shown in figure 8, 9. It is studied based on the transition of metal oxides in 1 MKOH electrolyte between the potential range -0.2 and 0.6 V at current densities of 1, 3, and 5 mA cm^{-2}. The observations of the nearly symmetric potential-time curves indicate the high charge-discharge of the $NiMnCo_3O_4$ electrode. The specific capacitance can be calculated by the following equation:

$$C = I \Delta t / m \Delta V$$

Where C (F g^{-1}) is the specific capacitance of the electrode, I (A) is the discharge current, Δt (s) is the discharge time, m (g) is the mass of active material, and ΔV (V) is the potential window. The specific capacitances are calculated to be 176, 456 and 610 Fg^{-1} for the $NiMnCo_3O_4$ film deposited on a copper substrate and 234,567,793Fg^{-1} for the $NiMnCo_3O_4$ film deposited on a porous copper substrate, respectively, at the current density of 1, 3, 5 mA g^{-1}. These results clearly indicate that the specific capacitance of $NiMnCo_3O_4$ electrode deposited on the porous copper substrate is much higher than that of the $NiMnCo_3O_4$ deposited on copper substrate electrodes, well consistent with the CV results. This result can be attributed to the synergetic effect of Mn-Ni–Co species and the high electroactivity of the $NiMnCo_3O_4$ porous electrode systems. Due to the more difficult penetration and diffusion of the electrolyte under a high current density, the specific capacitance of all samples decreased with the increase of current densities.

Furthermore, the results showed that the $NiMnCo_3O_4$ system still has the highest specific capacitance. This phenomenon can be attributed to the porous structure of the present electrode which it allows to facile insertion extraction and diffusion of $OH^-$from the electrolyte, resulting in the improving the electrochemical performance. In addition, ternary oxides $NiMnCo_3O_4$ may afford a richer variety of redox reactions (contributed by $Mn3^+$, Ni3+, and $Co3^+$ ions) and a much higher electrical conductivity than both of the binary and monometallic oxide materials [30,31].

The cycling stability of $NiMnCo_3O_4$ is shown in figure 10, with high retention of 90.2 % even after 3000 cycles, indicating the good cycling stability and excellent electrochemical performances of this electrode for supercapacitor application. Moreover, the effect of scan rate on the specific capacitances of the electrodes was studied within the ranges of 10 to 100 mV s^{-1}.

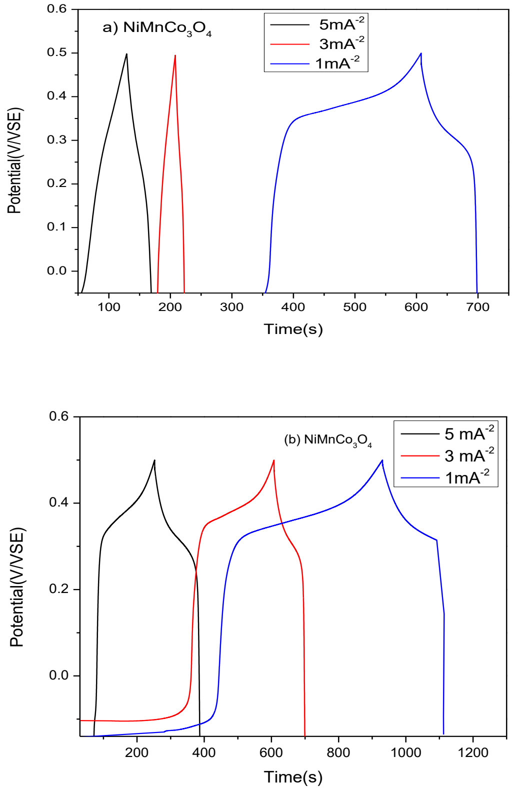


Figure 8 a) & b) Galvanostatic charge-discharge curves of NiMnCo$_3$O$_4$ deposited on copper and porous substrate at various current densities in 1M KOH electrolyte.

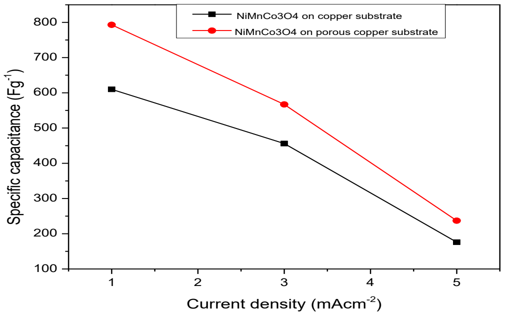


Figure 9: Discharge curves at different discharge current densities corresponding specific capacitance

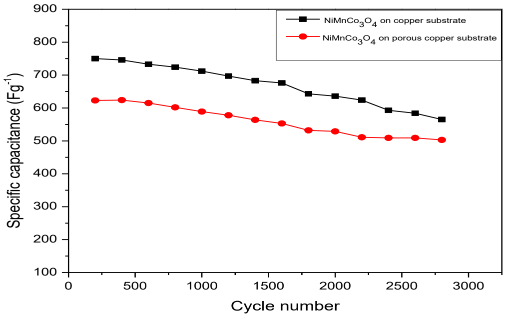


Figure 10: Relationship between the specific capacitance and cycle number

3.4.3 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) data were adopted to quantify the electronic and ionic conductivities and diffusive behavior of NiMnCo$_3$O$_4$ thin films. Nyquist plots of annealed NiMnCo$_3$O$_4$ electrode samples were elucidated in 1M KOH electrolyte over the frequency range of 100 kHz to 0.01 Hz and shown in figure 11 (a) & (b).

The Nyquist plots of NiMnCo$_3$O$_4$ electrodes are closer to an ideal supercapacitor, all plots show a part of the semicircle in the high-frequency region and a straight line in the low-frequency region, which corresponds to the electron-transfer processes and diffusion, processes, respectively. In the low-frequency area, the slope of the curves related to the Warburg resistance (W) for all electrode materials is almost the same and sharp, indicating the similar diffusion resistance [32].

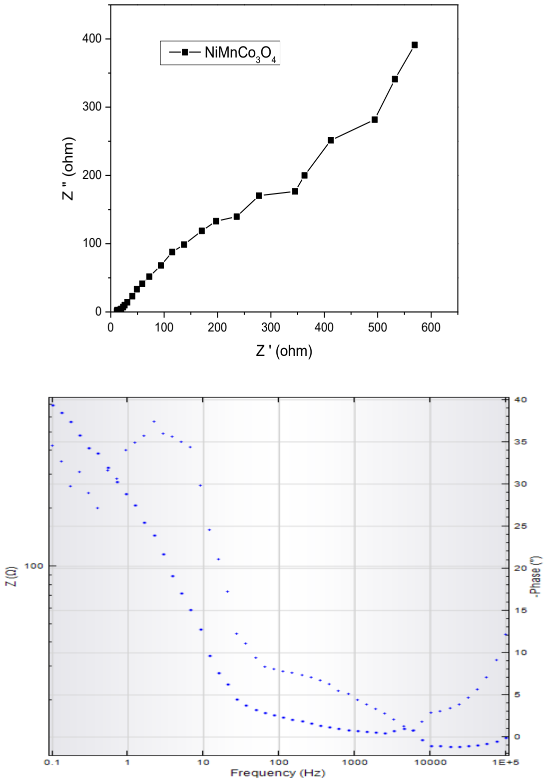


Figure 11 a) & b) The electrochemical impedance spectroscopy curve of NiMnCo$_3$O$_4$ thin film electrode deposited on the copper substrate at different scan rate in 1M KOH electrolyte

4. Conclusion

In summary, NiMnCo$_3$O$_4$ electrodes were successfully deposited on copper and porous copper substrate by electrodeposition method. The prepared sample was annealed at 300ºC for 2 hrs. The results possess a noticeable pseudo-capacitive performance in comparison with NiMnCo$_3$O$_4$ electrode deposited on both substrates.

Specifically, the $NiMnCo_3O_4$ film deposited on porous copper substrate exhibits a high specific capacitance of 947 F/g at 10 mV/s, which is good capacitance retention of 90.2% at a high current density of1mA g^{-1}after 3000 cycles. The $NiMnCo_3O_4$electrode is expected to be a promising candidate to be used in high-performance electrochemical capacitors with high energy and power densities.

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