Wet Chemical Synthesis of Graphene Containing Co / Mn Co-Doped NiONanocrystalline Materials: Efficient Electrode for Electrochemical Supercapacitors

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ABSTRACT: *Graphene containing Co and Mn co-doped NiOnanocrystallinematerials (with composition graphene - $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$) were synthesized by chemical synthesis route and studied for potential application as electrode material for supercapacitors. The phase structure of the materials was characterized by XRD technique and the crystallographic parameters were found out and reported. FT-IR spectroscopy revealed the presence of M-O bond in the materials. The morphological phenomenon of the materials was studied by SEM and the particles were found to be spherical with an average grain size of 14 – 28 nm. EDAX analysis confirmed the presence of appropriate levels of elements in the samples. The in-depth morphological characteristics were also studied by HR-TEM (High-Resolution Tunneling Electron Microscopy). Cyclic Voltammetry (CV), charge-discharge, and electrochemical impedance measurements were carried out in an aqueous electrolyte (6 mol/L KOH) to investigate the electrochemical performance of the graphene containing Co and Mn co-doped NiOnanocrystallinebased electrode materials and the material found to exhibit a specific capacitance of 1243 F/g at a current density of 0.5 A/g and hence these electrode materials can be used in electrochemical supercapacitors.*

KEYWORDS: *Doped NiO with graphene, Chemical synthesis, Electrode material, Electrochemical supercapacitor applications.*

INTRODUCTION

Supercapacitors, otherwise called ultracapacitors, an important energy storage devices that possess high specific power density, fast charge, and discharge rate, and long cycle life [1-2]. Supercapacitors have a great demand in the market and extensive research is being pursued a wide range of materials has been proposed as an alternate in the field of electrode materials for supercapacitors and device fabrication [3]. With the growth of nanotechnology, electrode materials for supercapacitors and their performance. Metal oxides have been the most employed active electrode materials for supercapacitor applications [4, 5]. The transition metal oxides have been shown to exhibit

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pseudocapacitance. It was reported that ruthenium oxide in aqueous sulphuric acid exhibited a specific capacitance of 720 F/g [6], which is connected with redox reactions that go beyond the surface and enter into the bulk of these materials. However, RuO_2 based materials are found to be toxic and highly expensive [7]. Apart from this, other metal oxide-based materials, such as, MnO_2, CoO_x, NiO, Fe_2O_3, etc., and conducting polymers, such as polypyrrole, polyaniline, poly (3,4-ethylenedioxythiophene, etc. have been studied as alternate electrode materials by many researchers [8–11]. *KuaibingWang et.al.*have synthesized NiO nanoparticles by simple calcination of Ni-based co-ordination polymer precursors. These materials have resulted in a specific capacitance of 140 F/g [12]. *Vijakumar et al.* have synthesized NiOnanoflakes at different calcination processes temperatures by CTAB surfactant and it exhibited maximum specific capacitance of 401 F/g at a current density of 0.5 mA/cm [13]. Nickel oxide nanoparticles were synthesized by combustion route in presence of organic fuels such as glycine, glucose, and urea. It resulted in capacitance of ~ 300F/g [14]. NiO@graphene composite modified electrodes were prepared by *Hui et. al* with an electrophoretic deposition process and they reached the capacitance value of 1258 F/g with the longest discharge time at the current density of 5 A/g [15]. In our previous study, we reported a specific capacitance of 673.33 F/g for the $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$nanomaterial prepared by the co-precipitation method[11]. The objective of the present research work is to evaluate the physico-chemical/electrochemical performance of the $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ (NCMO) nanomaterial in presence of rGO in order to use this electrode composition for application in electrochemical capacitors. In the first part of the study, the structural, functional, and particulate characteristics of NCMO –rGO have been studied. In the second part, the electrochemical performance of NCMO-rGO has been evaluated. The obtained results were discussed systematically in comparison with the reported data.

EXPERIMENTAL SECTION

Chemicals

The chemicals such as nickel nitrate hexahydrate (98%, LobaChemie, India), cobalt nitrate hexahydrate (97%, Merck, India), manganese nitrate tetrahydrate (97%, LobaChemie, India), sodium hydroxide (≥ 97%, Merck, India), graphite (extra pure, LobaChemie, India), Potassium permanganate(98.5%, Merck, India), sulphuric acid (98%, Merck, India), Hydrogen peroxide (30% w/v purified, SD Fine, India), ethanol (99.9%, Changshu Yangyuan, China), N,N di-methyl-acetamide (99%, LobaChemie, India) and polyvinylidene fluoride (PVDF) were as used in the experiment. All the chemicals were used as such without any further purification.

Chemical synthesis of graphene containing $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$nanocrystalline materials

Initially, the Graphene Oxide (GO) was prepared by a modified Hummer's as reported in the literature [16]. The prepared 20mg of GO powder was ultrasonicated with 100mL of deionized water for about 1 hr to get exfoliated GO suspension. After making this suspension, a known amount of precipitating agent (NaOH) was added and dissolved in it. Then, appropriate concentrations of $Ni(NO_3)_2$, $Co(NO_3)_2$, and $Mn(NO_3)_2$solutions were prepared in deionized water (100 mL each) and they were added dropwise to the already prepared GO containing NaOH solution. The entire reaction mixture was stirred thoroughly by a magnetic stirring apparatus (1500 rpm) at room temperature for about 30 minutes. The pH was maintained above 10 during the experiment. The resultant GO containing metal hydroxide precipitate ($(Ni(OH)_2 + Co(OH)_2 + Mn(OH)_2$) was filtered off and washed thoroughly with deionized water. The product was dried at 60 - 70 °C for about 6 hours in a hot air oven. The resultant material was calcined at 250 °C for 3 hours in the air to get a reduced Graphene Oxide (rGO) containing Co/Mn co-doped with NiO(NCMO)nanocrystalline material.The number of precursor materials used for the preparation of rGO-$Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ based nanocomposite materials is indicated in Table 1.

Characterizations

Physico-chemical characterization of materials

The heat-treated nanocrystalline materials were characterized by Shimadzu XRD6000 XRD instrument using CuKα radiation. The lattice parameters were calculated by the least square fitting method using DOS computer programming. The theoretical density of the powders was calculated with the obtained XRD data. The crystallite sizes of the powder were calculated by

Table 1: Amount of precursor materials (dissolved in 100mL of water each) used for the preparation of rGO-NiO based electrode materials.

Sample	Concentration of $Ni(NO_3)_2$ / Wt (g)	Concentration of $Co(NO_3)_2$ / Wt (g)	Concentration of $Mn(NO_3)_2$ / Wt (g)	Concentration ofNaOH / Wt (g)	Amount ofGO Wt (g)
rGO-$Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$	0.095 M/ 2.762	0.0025 M/ 0.0727	0.0025 M/ 0.0627	0.2M/ 0.8	0.020

Scherrer's formula. Shimadzu IR Prestige – 21 model FTIR spectrometer was employed to record the FT-IR spectra of materials in the range of 4000 – 400 cm^{-1}. The particle size of the powder was measured using Malvern Particle Size Analyzer using triple distilled water as a medium. The surface morphology of the particles was studied by means of JEOL Model JSM-6360 scanning electron microscope. EDAX analysis was also performed with JEOL Model JSM-6360 to find out the atomic weight percentage of elements present in the samples. The HR TEM of the samples was measured by HR TEM - JEOL JEM 2100 model.

Electrochemical characterization of materials

The electrochemical measurements were performed in a three-electrode electrochemical cell with a Saturated Calomel Electrode (SCE) as a reference electrode, a platinum wire as a counter electrode, and a graphene-containing NCMOworking electrode in 6 M KOH using a CH1660C electrochemical work station.

To fabricate a working electrode, the prepared material and a binder (PVDF) mixed together (9:1 wt. ratio)with N,N di-methyl-acetamide (~15 mL solvent) to form a slurry. The above mixture was stirred for about 12 to 16 h in a magnetic stirrer (1500 rpm) to ensure homogeneity at room temperature. Then, the slurry was coated with a doctor's blade onto a thin graphite sheet (having a specific area of 1 x 1 cm^2). The fabricated electrode was then dried at 50° C for about 2 h in a hot air oven in order to remove the organics present in the micropores of the electrode. The mass loading of the active materials on the graphite sheet was found to be around 0.5 mg/cm^2 in the fabricated electrode.

RESULTS AND DISCUSSION

XRD studies

The XRD pattern obtained on graphene containing $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ (NCMO) nanocrystalline material is shown in Fig.1. In the sample, five diffraction peaks appeared which could be indexed to the (111), (200), (220), (311), and (222) crystal planes of face-centered cubic of NiO (JCPDS no: 71-1179), respectively. The peak (insert line) that appeared at 2θ=24° reveals the presence of graphene which was actually overlapped with the peak of NiO-based materials in the sample inferring the formation of the graphene containing NCMO nanocrystalline materials. No additional peaks other than graphene and NiOwere appeared in the sample, suggesting that no NiO insertion into graphene matrix. The crystallographic parameters obtained on graphene containing $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$are reported in Table -2 in comparison with our already published data for $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$. It was reported that NiOwas prepared by the thermal conversion method indexed in a face-centered cubic lattice with a unit cell parameter of 4.177 Å [17].

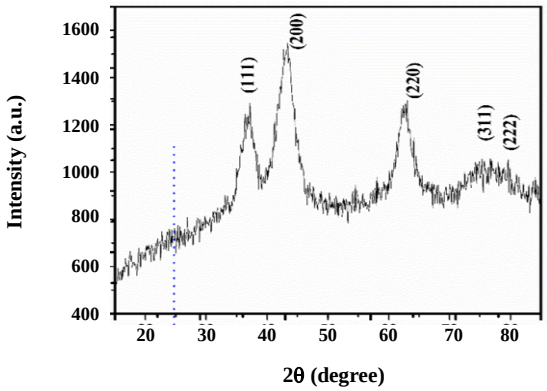

Fig.1: XRD pattern obtained on graphene containing $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ (NCMO) nanocrystalline material.

FT-IR studies

The FT-IR spectra obtained on graphene containing $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ (NCMO) nanocrystalline material are shown in Fig.2.The peaks that appeared at 450.40 to 596.99 cm^{-1} in the samples may be attributed to metal oxide stretching vibrations**.** The bands that appeared at 1383.02 cm^{-1} may be assigned to the C-O-H deformation peaks. The broad spectra appeared at 3453.37 cm^{-1}belongs to water molecules present in the atmosphere or hydroxyl groups.

Table 2:Crystallographic parameters obtained on Graphene containing $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ (NCMO) nanocrystalline material.

Sample	Crystal structure	Unit Cellparameter 'a' (Å)	Unit cell volume (Å^3)	Crystallitesize (nm)	Theoretical density (g/cc)
Standard NiO (JCPDS No. 71-1179)	Cubic (F.C.)	4.178	72.92	--	6.80
Graphene containing $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$	Cubic (F.C.)	4.173	72.67	13.86	6.81
$Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ [11]	Cubic (F.C.)	4.190	73.56	13.0	6.73

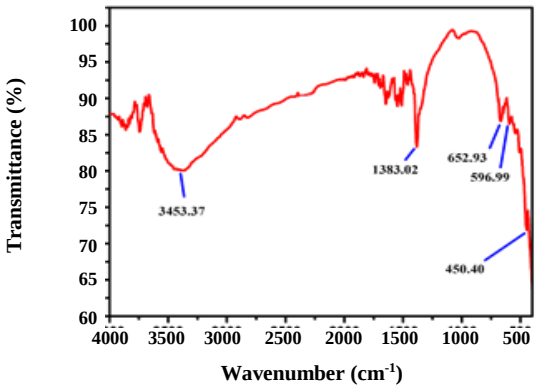

Fig. 2: FTIR spectra obtained on graphene containing $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ (NCMO) nanocrystalline material.

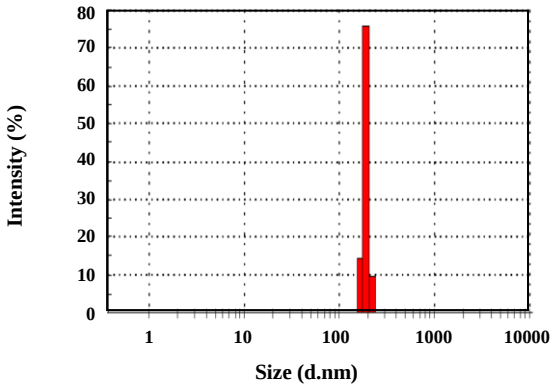

Fig. 3:Particle size analysis obtained on graphene containing $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ (NCMO) nanocrystalline material.

It was reported thatnanoparticles may have a tendency to absorb moisture from the atmospheric air [18].

Particle size measurements

In particle size analysis, 0.001 g of material was sonicated in about 5 mL double distilled water for about 30 minutes and after which the sample was subjected for particle size analysis. The particle size pattern obtained on graphene containing $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$(NCMO) nanocrystalline material is shown in Fig.3. Particle size analysis of graphene-based nanocrystalline materials has not been much reported in the literature because the graphene-based materials may tend to exfoliate during the sonication process in water. The particle of the sample is reported to be 1131 nm which may be due to the exfoliation of graphene in water. The particle size of pure $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ nanocrystalline powder was found to be291.5 nm [11].

Morphological and EDAX studies

From SEM image(Fig. 4 –a&b), the presence of RG along with NCMO has been identified. Also, the grains were like flakes. The HR-TEM and SAED images (Fig. 4 (c) and (d)) revealed the presence of graphene consisting of thin stacked flakes of shapes and having well-defined multilayer structures at the edge. HR-TEM image revealed that the NCMO nanoparticles are homogeneously anchored on the graphene sheets. It is clearly seen that even after the strong sonication most of the particles still remain on the graphene layers indicating that a relatively strong interaction between NCMO and graphene. The obtained SAED pattern shows polycrystalline in nature which is in good accordance with the obtained XRD data. EDX spectrum in Fig 4(e) confirmed the presence of carbon because of the existence of graphene along with other elements such as Ni, Co, and Mn in the sample. The elemental composition data are presented in Table 3. From the data, it was found that the presence of appropriate elements in an appropriate amount in the final sample.

Electrochemical measurements

The Cyclic Voltammograms (CV) of graphene - $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ (NCMO) electrode has been taken

Table 3 - Elemental composition data obtained on the graphene containing $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ (NCMO) nanocrystalline material.

Atomic weight % of the elements				
Ni	Mn	Co	C	O
18.26	0.99	0.72	40.45	39.58

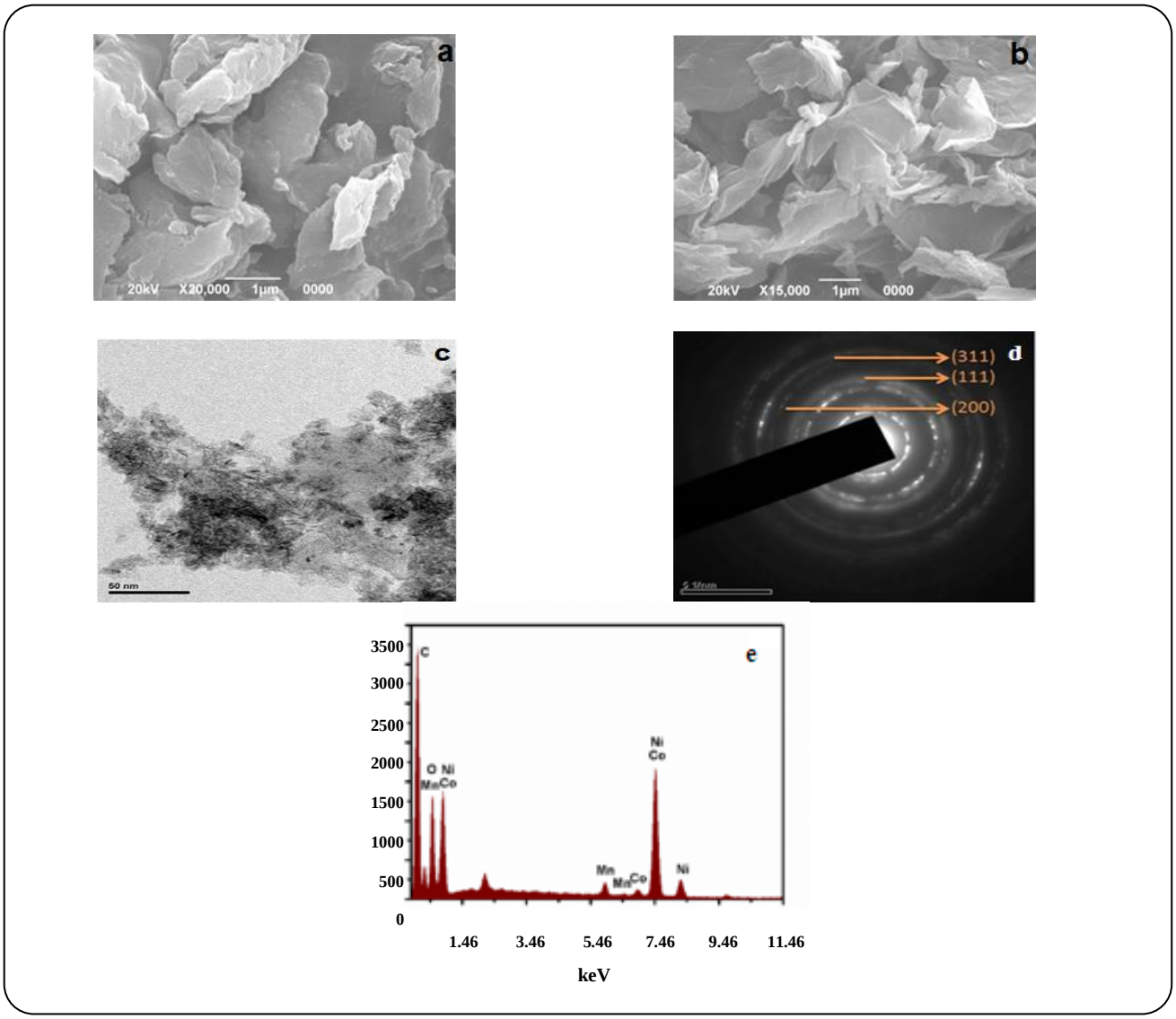

Fig. 4: (a, b)SEM image of graphene - $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ (NCMO) nanocrystalline material (c, d) HR-TEM image and SAED pattern of graphene - $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ (NCMO) nanocrystalline material and (e) EDX spectrum of graphene-$Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$.

in the potential range of 0.4 V to -0.9 V and it has been presented in Fig. 5a. From the CV curves (Fig. 5a), it was clearly seen that the prepared graphene containing $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ (NCMO) revealed a slightly distorted rectangular shape with no other redox peaks, showing a good double-layer capacitive behavior [19]. Also, in all the curves the peak current increased with an increase in the scan rate. Because of this, the shape of the CV curves slightly changes indicating the small equivalent series resistance and weak polarization of the electrodes.

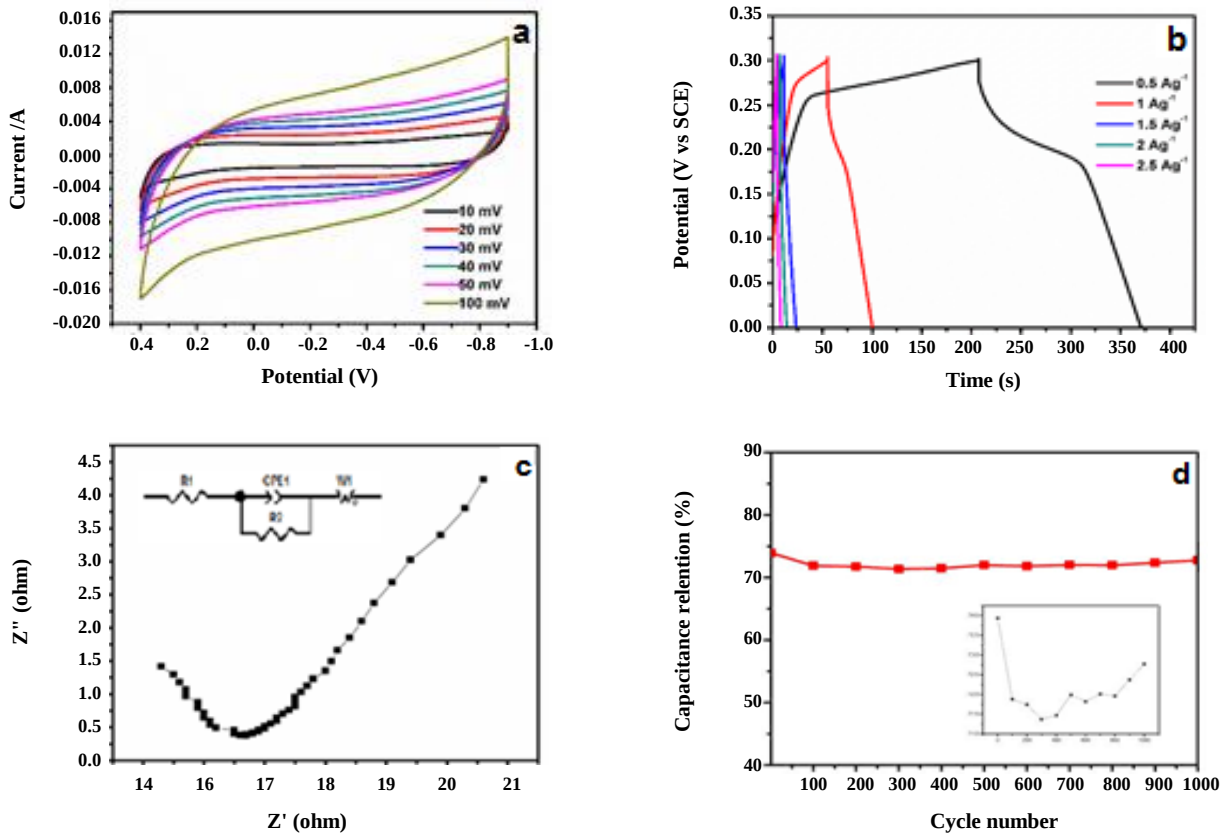

Fig. 5:a) Cyclic voltammograms obtained on graphene - $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ (NCMO) in the potential range of 0.4- -0.9V, (b) charge- discharge curves of graphene - $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ (NCMO) in the applied potential of 0 – 0.3V at various current densities (c) impedance analysis of the graphene-$Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$, (d) capacitance retention of the prepared graphene-$Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$.

Fig.5b shows the charge-discharge curves with a good symmetrical triangle shape which implies an ideal capacitive behavior [20]. From the result, it was found that graphene-$Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$nanocrystalline material exhibiting more charge-discharge duration time. The enhanced electrochemical performance of the graphene-based electrode materials may be due to high electronic conductivity and excellent interfacial contact between Co- and Mn- co-doped NiO and graphene. This results in the fast transportation of electrons throughout the entire electrode matrix. The specific capacitance values were calculated by the following equation,

$$C_s = \frac{I \times \Delta t}{m \Delta V} \quad (1)$$

Where *I* is the discharge current (A), Δ*t*is the discharge time (s), *m* is the mass of the electroactive material (g) and Δ*V* is the potential difference (V). The prepared graphene-$Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ sample exhibited a specific capacitance value of 1243.9 F/gat a current density of 0.5 A/gwhich is found to be in the higher-order than the reported values.

However, pure $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ nanocrystalline electrode exhibited 673.73 F/gat the current density of 0.5 A/g[11]. Fig. 5c shows the Nyquist plots for the graphene - $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ carried out in the frequency range of 1Hz to 100 MHz at the amplitude of 5mV/sin 6M KOH electrolyte solution. All the plots displayed a distorted semicircle in the high-frequency region and a straight line in the low-frequency region. The straight line in the low-frequency range, called Warburg resistance, is caused by the ion diffusion or transport of ions from the electrolyte to the electrode surface region. The arc-like semicircle in the high-frequency range attributes to the charge transfer resistance at a contact between the interface regions between

the electrode/electrolyte solution [21].Hydrous RuO_2 exhibited a high specific capacitance value exceeding 1000 F/g. But its high cost and toxic nature restrict its commercial application [22]. The capacity retention value of 94.05% was reported for rGO/Ag/Co_3O_4 nanocrystalline electrode material after 1000 cycles [23]. The hydrothermally pre-processed bagasse-derived carbon (BHAC) electrode exhibited 90% of the capacity retention at a current density of 10 A/g up to 1000 cycles [24]. In our research activity, the graphene - $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ electrode material exhibited an excellent long-term cyclic stability which is shown in Fig. 5d. This is investigated by repeating the cyclic voltammetry experiments for 1000 cycles at 100 mV/s in the potential range of 0.4 to -0.9V. The results obtained are in line with the reported literature [25]. It is suggested from the experiment that Co/Mn co-doped NiO can be studied as alternate electrode materials in electrochemical capacitors.

CONCLUSIONS

Graphene containing $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$materials were prepared by a simple chemical synthesis route. The physical characterization revealed that the sample is in high purity form with polycrystalline behavior and the presence of GO sheets in the sample. The electrochemical measurement has exhibited a good specific capacitance of 1243.9 F/gfor graphene - $Ni_{0.95}Co_{0.025}Mn_{0.025}O_{1-\delta}$ and the prepared material has shown an excellent cyclic response over 1000 cycles. Based on this result, it is suggested that graphene containing Co/Mn co-doped NiO may be a promising electrode material for electrochemical capacitors.

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