## One-step Preparation of Binder-free Nickel Containing Graphene Foam Electrode for Supercapacitors

# Sirin SIYAHJANI GULTEKIN<sup>1</sup>, Aziz Ahmad KARIMI<sup>2</sup>, Mustafa CAN<sup>3</sup>, and Serafettin $\rm DEMIC^3$

<sup>1</sup>Canakkale Onsekiz Mart University <sup>2</sup>Ege University Solar Energy Institute <sup>3</sup>Izmir Katip Celebi University

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## Abstract

A nickel hydroxide (Ni(OH) \_2)-modified reduced graphene oxide (rGO) foam electrode for supercapacitor application is presented in this study. The electrode was made without binder through a one step process. In order to compare the supercapacitor performance of as synthesized graphene foam electrode, rGO and rGO:carbon black (CB) standard electrodes with PVDF-HFP binder were also synthesized . All electrodes were then characterized structurally (XPS, EDS, RAMAN, XRD, and FT-IR) and morphologically (SEM). Ni-containing electrodes were found in the  $\alpha$ -Ni(OH)2:rGO structure. NirGO3 has 800 Fg <sup>-1</sup> capacitance, while rGO:CB has 900. Thus NirGO3 has the best capacitive performance among binder-free electrodes, comparable to rGO:CB.

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Sirin SIYAHJANI GULTEKIN<sup>a,b\*</sup>, Aziz Ahmad KARIMI<sup>b,c</sup>, Mustafa CAN<sup>c</sup>, Serafettin DEMIC<sup>c</sup>

<sup>a</sup> Canakkale Onsekiz Mart University, Faculty of Engineering, Department of Chemical Engineering, Canakkale, Turkey

<sup>b</sup>Ege University Solar Energy Institute, Bornova Turkey

<sup>c</sup> Izmir Katip Celebi University, Faculty of Engineering and Architecture, Department of Materials Science and Engineering, Izmir, Turkey

## Abstract

A nickel hydroxide  $(Ni(OH)_2)$ -modified reduced graphene oxide (rGO) foam electrode for supercapacitor application is presented in this study. The electrode was made without binder through a one step process. In order to compare the supercapacitor performance of as synthesized graphene foam electrode, rGO and rGO:carbon black (CB) standard electrodes with PVDF-HFP binder were also synthesized . All electrodes were then characterized structurally (XPS, EDS, RAMAN, XRD, and FT-IR) and morphologically (SEM). Ni-containing electrodes were found in the  $\alpha$ -Ni(OH)2:rGO structure. NirGO3 has 800 Fg<sup>-1</sup> capacitance, while rGO:CB has 900. Thus NirGO3 has the best capacitive performance among binder-free electrodes, comparable to rGO:CB.

Keywords: foam electrode, supercapacitor, self-templated, nickel hydroxide

1. IntroductionSupercapacitors (SCs), as environmentally friendly and renewable energy storage technology, have recently become popular in the scientific community. When compared to conventional batteries, their relatively long lifetime and higher power density makes them good candidates for electrical application. A typical supercapacitor contains positive and negative electrodes separated by an ion-conducting electrolyte [1]. As a critical component of SCs, the electrodes are prepared by the slurry casting method that needs adding some high conducting material and/or a binder (generally a polymer). The function of conductive (and porous) additives is to improve the interaction at the current collector and the electrode material interface to reduce the series resistance of the device. However, additives and insulating binders have some disadvantages, such as aggregation or clogging pores of active material resulting in loss of volume and relatively lower volumetric and gravimetric capacitance of electrodes [2, 3]. In SC applications, carbonaceous materials, conductive polymers, and metal oxides/hydroxides have generally been used as electrode materials. Particularly, graphene-based composites have commonly been used in those applications due to their large surface area (theoretical surface area up to 2630 m<sup>2</sup> g<sup>-1</sup>), high electronic conductivity, mechanical flexibility and excellent thermal stability [4-7]. However,  $\pi$ - $\pi$  interactions and weak van der Waals forces lead graphene nanosheets to aggregate to be stacked back into graphite, resulting in decreased accessible surface area and a limited electrolyte ion diffusion rate. To overcome this problem, some other carbon-based materials (carbon black (CB), carbon nanotube (CNT), etc.) or metal oxide/hydroxides nanoparticles (Ni(OH)<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, etc.) have been inserted into the electrode structure [8-11]. Although high capacitance values (maximum theoretical capacitance: 2082 F g<sup>-1</sup>) can be achieved with electrodes prepared, a decrease in conductivity may occur due to the introduction of impurities into the structure and the increase in the distances between the lamellas [8, 9]. From this perspective, binder-free, lightweight graphene foams (GF) with porous structure and high surface area have recently emerged as an essential development [12-14]. 3D GF is a hierarchical material with a porous structure exhibiting suitable properties such as a highly conductive path, extensive surface area, improved charge-carrying mobility, and lower resistance [15]. Electrons can be transferred efficiently in the system with low resistance because of the ideal interconnected network and 3D macrostructure. Moreover, it is possible to obtain more functional structures for various applications by making GF composites with different nanoparticles or semiconductor metal oxides/hydroxides[16-22]. In the literature, the most viable and efficient methods proposed for the preparation of 3D GF and GF-based hybrid structures are hydrothermal, chemical vapor deposition, template, freeze drying, and electrochemical preparation. [23-26]. For instant, it was reported that an Au and rGO based 3D composite material was coated on a carbon electrode surface by electrochemical deposition [27]. This method formed a three-dimensional structure with an interconnected network having relatively larger surface area and higher conductivity. It was also determined that the layer distances of the rGO nanolayer were increased by the presence of Au nanoparticles, providing a biocompatible interface. In another study, the  $GF-TiO_2$  composite was obtained by a procedure called one-step-hydrothermal method at 180 °C in an autoclave for wastewater treatment. Wang and co-workers reported that the hybrid nanosheet they prepared exhibited much superior performance for removing methylene blue (MB) and chromium (VI) than individual pure graphene foam or pure  $TiO_2$  sheets [28]. Similar structures containing Ni, NiO, and Ni(OH)<sub>2</sub> have been obtained to be used in supercapacitor applications. Huang et al. reported a graphene/NiO-based film through various preparation processes. The prepared graphene/NiO film achieved a specific 540 F g<sup>-1</sup> at 2 A g<sup>-1</sup> and kept 80% of initial capacitance for 2000 CDC [29]. On the other hand, Pore et al. also proposed another method to obtain a graphene/NiO foam. In that procedure, the electrode material was prepared with a hydrothermal method by annealing at 400°C. A specific capacitance of 727.1 F  $g^{-1}$  at 1mA cm<sup>-2</sup> was achieved with a stability over 80% after about 9000 cycles [3][26]. In addition, an electrode based on  $Ni(OH)_2$  for supercapacitor application was reported by Viswanathan and coworkers [8]. As well known,  $Ni(OH)_2$  has good solubility in acids such as  $H_2SO_4$ . A chemical reduction method was achieved to obtain insoluble rGO/Ni(OH)<sub>2</sub> structure showing a specific capacitance value over 130 F g<sup>-1</sup> in 1M H<sub>2</sub>SO<sub>4</sub> electrolyte. This current study developed a self-templated foam based on Ni and rGO, and its structural analyses was carried out. The prepared foams in different weight ratios of Ni and rGO were directly grown on the current collector. These electrodes were electrochemically characterized as supercapacitor electrodes in aqueous electrolytes and compared with standard rGO and rGO:CB reference electrodes.

2. Experimental Section

## 3. Preparation of electrode material and fabrication of PSC

The Hummer's method was modified to synthesize GO efficiently and a chemical reduction method was applied to obtain rGO [30]. In order to determine effects of both foam structure and Nickel derivative, three types of electrode composition were prepared. The standard electrode (rGO) was obtained by mixing rGO and binder PVDF at a ratio of 95:5 (w/w) in acetone. The standard secondary electrode (rGO:CB) was obtained by mixing rGO, CB and binder PVDF in the ratio of 80:15:5 (w/w) in acetone. Both reference electrodes were coated on current collector  $(1*1 \text{ cm}^2)$  by drop casting method. Initially, rGO powder (10 mg) and nickel nitrate hexahydrate in the various weight ratio of 1:3, 1:6 and 1:12 was added into 2.5 mL ethylene glycol, and then the mixtures were sonicated for 3 h (presented weight ratios of starting materials are optimized values). Subsequently, the resulting dispersions were cast onto a 250 degC pre-heated graphite sheet (the active material is 1.0-1.3 mg in 1\*1 cm<sup>2</sup> surface area). Adding reactant dispersion onto the hot graphite sheet causes NOx gas's evolution, and binder-free NirGO foam forms on the current collector. Consequently, these electrodes were used as working electrode and characterised electrochemically in the electrochemical cell system to determine their capacitive performances.

#### Structural Characterization of Electrode Materials Methods

X-Ray Diffraction (XRD, Rigaku Ultima IV), depth profiling Raman spectroscopy (XploRA Raman Microscope), Fourier-transform infrared spectroscopy (FT-IR, Nicolet iS50 FTIR), energy dispersive spectroscopy (EDS, JEOL JSM-7100-F), and X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha), methods were used for the structural characterization of rGO and NirGO composites. Moreover, scanning electron microscopy (SEM, JEOL JSM-7100-F) analyses were carried out to take micrographs of all electrodes for morphological analyses.

XRD patterns were recorded to analyse phase compositions of NirGO3 and rGO with Cu K $\alpha$  radiation ( $\lambda = 1.54$  Å), while step size and scan rate are 0.02° and 2°/min, respectively, in a 2 $\vartheta$  range from 3° to 95. Furthermore, Raman spectra of rGO and NirGO3 were used to determine the intensity and position changes in the D and G bands of rGO and the Raman shift peaks of Ni(OH)<sub>2</sub> in the 400-2500 cm<sup>-1</sup>. Furthermore, the phase of Ni(OH)<sub>2</sub> and its interaction with rGO through the functional groups was also clarified by carrying out FT-IR analyses in the range from 400 to 4000 cm<sup>-1</sup>.

SEM analyses of rGO, rGO-CB and NirGO3 electrode materials were performed to examine their morphology. The 250X and 50kX magnitude micrographs were recorded with secondary electrons detector (SE). In addition, EDS analyses were used to determine the composite electrodes' chemical composition (amount of C, Ni and O). XPS analysis was carried out for a detailed characterization of the composition. In the complete spectrum of the XPS survey, elements of Ni, C, and O were detected clearly. Moreover, their chemical states were confirmed by the deconvolution of Cs1, Os1, and Ni 2p.

## **Electrochemical Characterization of Prepared Supercapacitors**

As it was mentioned above, CV, EIS and CDC techniques were carried out for determining the capacitive performance of SC cells by using a CH Instrument CHI 660B electrochemical workstation. Three NirGO electrodes with different weight ratios and two rGO and rGO: CB reference electrodes were performed in the three-electrode system. In the electrochemical cell, an aqueous solution of  $1M H_2SO_4$  was used as the electrolyte, while platinum (Pt) wire and Ag/AgCl were used counter as and reference electrodes, respectively. As stated in section 2.1., rGO:Binder was used as the standard electrode structure. In addition, a second standard electrode with a higher surface area was prepared by adding CB to the rGO:Binder mixture.

It was aimed to compare the capacitive performances of NirGO-based foamed electrodes and the standard electrodes according to their CV analysis results. All voltammograms were recorded between -0.4 V and

The specific capacitance  $(C_{sp})$  of NirGO1, NirGO3 and NirGO6-based electrodes were calculated by using the equation below [31].

$$C_{\rm sp} = \frac{i}{\rm ms}$$

In the equation, *i*, *m*, and *s* represent the average current, the average mass of electrode materials (binder and additive), and the scan rate  $(\Delta V/\Delta t)$ , respectively.

With EIS analysis, it is possible to determine the resistance across the entire device, electrode (related to its bulk resistance), and electrode-electrolyte interface (related to the charge transfer). All spectra were obtained with the measurements taken in the 10 MHz-100 kHz. The bulk ( $R_b$ ) and the charge transfer ( $R_{ct}$ ) resistance values were calculated from these spectra.

The galvanostatic CDC curves of all electrodes were recorded between -0.4V and +0.6 V potential range under 1 mA current. From these graphs, the specific capacitances (c, F g<sup>-1</sup>) were calculated for each electrode using the formula below.

$$\mathbf{C} = \frac{I * t}{m * V}$$

In the equation, I, the discharge current (A), is multiplied by [?]t, the discharge time (s). This value is then divided by the product of [?]V, the potential operating window (V), and m, the mass of the electrode material (g). Besides, CDC plots were also used to calculate the energy density (E, Wh kg<sup>-1</sup>) and the power density (P, W kg<sup>-1</sup>) by using the following equations:

 $E = \frac{1}{2}C_{\rm sp}V^2$ 

$$P = \frac{E}{\Delta \tau}$$

In the first equation, the calculated specific capacitance,  $C_{sp}$  (F g<sup>-1</sup>) is multiplied by the potential operating window, V (V), while in the second equation, the calculated Energy Density, E, is divided by the discharging time,  $\Delta \tau$  (s) represent.

## **Results and discussion**

## Structural Characterization of Electrode material

Raman spectroscopy, X-ray diffraction, FT-IR, XPS and EDX analyses were used to elucidate the structure of the composite materials. Due to the best overall capacitive performance achieved by NirGO3, some structural and morphological analyses were reported and evaluated for that active material.

The Raman spectra exhibited in Fig. 1(a) belong to rGO and NirGO3 electrode materials. In the spectra of rGO and NirGO3, the D band corresponding to the defects and the disorders, while the G band corresponding to the vibration of carbon atoms (sp<sup>2</sup>-bonded) in the hexagonal lattice were observed at 1320 and 1596 cm<sup>-1</sup>, respectively [32]. Furthermore, peaks at around 545 and 781 cm<sup>-1</sup>, which correspond to the Ni—OH bond, were also observed in the NirGO3 spectrum. These results indicated that the composite contains oxide/hydroxide forms of Ni rather than Ni(NO<sub>3</sub>)<sub>2</sub> [33].

Fig. 1(b) shows the XRD graph of reference rGO gave a compatible pattern with the literature [31, 34]. The broad peak of (002) graphitic crystal planes in rGO was observed between 20-30°, while the peak belonging to the (100) plane,  $\pi$ - $\pi$  stacking of graphene, appeared at 44.2° as evidence for the formation of rGO. Ni(OH)<sub>2</sub>

has two phases,  $\alpha$  and  $\beta$ , in the layered hexagonal structure. Although the structure occurred in the  $\beta$ -phase form has high crystallinity and more stability, the large surface area of the  $\alpha$ -phase shows better capacitive performance due to its low crystallinity. In the pattern of NirGO, four characteristic peaks appeared at 10.95°, 33.76°, 45.21° and 59.08° belonging to (003), (016), (018), and (110) planes, respectively, belong to the  $\alpha$ -phase of Ni(OH)<sub>2</sub>. However, the peak which must be observed at 20.59° originating from the (006) plane of Ni(OH)<sub>2</sub> could not be detected because the graphitic crystal peak in the same region covers it. Furthermore, the disappearance of the sharp peak of the (100) graphene plane and the observed broad peaks of  $\alpha$ -Ni(OH)<sub>2</sub> indicate that the obtained composite has a highly amorphous character [33, 35]. Increasing the amorphous form in the structure provides higher capacitance with Ni-based composite electrodes. It has also been previously reported that the  $\alpha$ -crystal phase gives better capacitive performance [36]. Therefore, it can be stated that the prepared material is suitable for supercapacitor applications in terms of its crystal structure.

Fig. 1(c) illustrates the FT-IR spectra of rGO and NirGO3. rGO presents several oxygen functionalities remaining in rGO [37]. In addition, both electrode materials show very similarly shaped FT-IR spectra, as they have almost the same functional groups except for the Ni—O—H structure. Due to the hydrogen bond-free nature of  $\beta$ -Ni(OH)<sub>2</sub>, gives a sharp vibration peak at about 3645 cm<sup>-1</sup> corresponding to stretching vibration of O—H. However, for the FT-IR spectrum of  $\alpha$ -Ni(OH)<sub>2</sub>, this peak is either unobservable or rarely detectable as a shoulder due to the high rate of hydrogen bond signal [38, 39]. In the spectrum of NirGO3, there is a relatively broader O—H band, between 3100 cm<sup>-1</sup> and 3650 cm<sup>-1</sup>, attributed to stretching vibration belong to hydroxyl groups of  $\alpha$ -Ni(OH)<sub>2</sub> with hydrogen-bonded and H<sub>2</sub>O intercalated in between rGO layers[26]. In addition, a noticeable redshift was observed for FT-IR peaks of NirGO3, particularly in the strong vibrations of the C—O, C=O and —OH bond, compared to that of rGO. On the other hand, in the rGO's spectrum, the peaks at 1557 (C—C stretch) and 1627 cm<sup>-1</sup> (C=C stretch) are fused in the FT-IR spectrum NirGO, forming a broad peak appeared around 1614 cm<sup>-1</sup> due to the interaction between rGO and Ni(OH)<sub>2</sub>. The peaks at about 1384, 1081, and 1042 cm<sup>-1</sup> belong to C—C, C—O, and C—O—C bonds, respectively[26, 35]. These results also support the Raman analyses.

From the SEM images of rGO, rGO-CB and NirGO3 electrode materials, it was determined that the porous structure of NirGO3 was more evident than that of rGO (Fig. 2(a)-(f)). Although it could not be determined numerically, the pore size distribution of NirGO3 material was more uniform than that of other materials. As a result, it can be proposed that the foam (or sponge) structured morphology is obtained, and the surface area is increased while preparing the electrode material composed from NirGO3. On the other hand, looking at the 50kX image of the rGO electrode material modified with CB, it could be noticed that the morphology was similar to that of rGO. In 250X extended images, however, it was clear that the CB containing sample was more porous than pure rGO. This is because CB is deposited between the rGO sheets, reducing  $\pi$ - $\pi$  stacking. In the lower (NirGO1) and higher (NirGO6) concentrations of Ni(NO<sub>3</sub>)<sub>2</sub>, organic and inorganic phases were separated, and the formation of an ideal foam structure did not occur (Fig. S1(a-d)). In conclusion, SEM analyses show that NirGO3 material has a morphologically significant advantage in capacitor applications.

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image3.emf available at https://authorea.com/users/657349/articles/662186-one-steppreparation-of-binder-free-nickel-containing-graphene-foam-electrode-for-supercapacitors Fig. 1. (a) Raman shift spectra, (b) XRD patterns (# refers to rGO crystalline signals, \* refers to Ni(OH)<sub>2</sub> crystalline signals) and (c) FT-IR spectra of electrode materials.

In the EDS spectrum (Fig. 2(g)) of Ni-rGO, as expected, there is a Ni atom in the structure accompanied by C and O. Although  $Ni(NO_3)_2$  was used as the reactant at the beginning of the reaction, the absence of the signal of the N atom in the spectrum indicates that the starting material is fully reacted, and as a result of this process, oxide/hydroxide derivatives of Ni are eventually formed.





Fig. 2. (a) 50kX, (b) 250X micrographs of rGO, (c) 50kX and (d) 250X micrographs of rGO:CB, (e) 50kX and (f) 250X micrographs of NirGO3 materials and (g) EDS spectrum of NirGO3.

In the Cs1 spectrum of the XPS survey (Fig. 3(b)), peaks at 285.00, 286.67, and 288.90 eV were related to C=C, C—OH and C=O bonds, respectively. The peaks belonging to O=C/O—Ni and HO—C were observed at 533.04 and 531.56 eV in the Os1 spectrum (Fig. 3(c)), respectively. Furthermore, in the Ni2p spectrum (Fig. 3(d)), two typical peaks at 855.80 and 873.40 eV are referred to as Ni2p<sub>3/2</sub> and Ni2p<sub>1/2</sub>, respectively. Spin-energy separation was calculated as 17.60 eV as the individual indicator for Ni (OH)<sub>2</sub> phase (Fig. 3(a)). Besides, satellite signals are defined as two extra peaks at 861.50 and 879.00 eV, which close the Ni2p<sub>3/2</sub> and Ni2p<sub>1/2</sub>. XPS results agree with XRD and FT-IR analyses and indicate that the electrode material of NirGO3 is consisting of rGO and Ni(OH)<sub>2</sub>.

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**Fig. 3.** XPS analysis of NirGO3 material: (a) complete XPS survey spectrum, deconvoluted spectra of (b) C1s, (c) O1s, and (d) Ni2p.

## Electrochemical performance of supercapacitor cells

## Cyclic voltammetry

As seen from the voltammograms, the capacitive performance of the reference rGO electrode (containing binder) was limited because of its relatively high resistance and low surface area (Fig. 4a). When CB was added to the mixture, a decrease in the capacitance was observed because of the increase in the surface area of the electrode. Besides, as it is well known, the square-like shape of the voltammogram indicates an ideal capacitive behaviour in a device. However, the rGO-CB graph was not square, indicating high resistance related to the binder. When the voltammograms of the binder-free NirGO foamed electrodes are examined, it is noticed that the graphs are relatively closer to the square-like shape than those of rGO and rGO: CB. The oxidation peak of Ni(OH)<sub>2</sub> at 0.3 V, which was expected in NirGO voltammograms, could not be observed very clearly. This is due to a phenomenon called the surface-based faradaic process. In this process, a capacitive faradaic activity is exhibited on the surface thanks to the delocalized electrons on the electrode. Therefore, square-like voltammograms were obtained at [40]. Since there was no binder in these electrodes, the resistance in the electrode was relatively lower. In addition, the square-like graphs showed that the pore sizes and ion sizes were compatible.

The capacitive performance of NirGO3 is comparable to that of rGO:CB based electrode (900 F g<sup>-1</sup>). The results regarding porosity and surface areas were in agreement with the results obtained from SEM studies. Furthermore, voltammograms were recorded at different scanning rates (Fig. 4(b), (c) and Fig. S2) to compare pore size-ion diameter match and resistances at the electrolyte-electrode interface. When the graphs of rGO:CB and NirGO3, which showed the relatively best performance, were examined, it was observed that the voltammograms of NirGO3 obtained at different scan rates were less distorted than those of rGO:CB as the speed increased (Fig. 4(b)). In the device prepared with NirGO3 electrode material, this shows that ions move more efficiently during entry and exit into the pores than in devices prepared with other electrode materials.

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**Fig. 4.** (a) Comparison of cyclic voltammograms of all electrodes (scan rate: 50 mV s<sup>-1</sup>). Cyclic Voltammograms of rGO:CB, (b) and NirGO3 at various scan rates (c). Variation of specific capacitance calculated from CV with scan rate for all electrodes (d). specific capacitance vs scan rate graphs of all electrodes.

## 3.2.2. Electrochemical impedance spectroscopy (EIS)

In the EIS spectrum, the bulk resistance  $(R_b)$  is related to the interruption on the real axis at high frequency. At the same time, the semicircle at the mid-frequency zone corresponds to the charge transfer resistance  $(R_{ct})$  at the electrolyte/electrode interface, which is strongly related to the capability of ion transfer into the pores of an electrode (Table 1). As seen in Fig. 5, the device based on NirGO3 has the lowest bulk resistance (2) and the charge transfer resistance (1 Ohm) compared to other devices. This is because the  $\pi$ - $\pi$  agglomeration in bare rGO is less in NirGO-based electrodes. During the formation of the foam structure, this agglomeration was prevented, and thus lower resistance was obtained. Although CB prevents this agglomeration, there is an increase in bulk resistance due to the usage of a dielectric binder. Among the NirGOs, the highest resistance was observed in NirGO6. As seen in the SEM images, the reason is that as the Ni ratio increases, the regular agglomeration and the formation of porous structure between the rGO layers deteriorates (Fig. S1). Therefore, the bulk resistance (11) at the electrode and the charge transfer resistance (4) between the electrolyte and the electrode also increases.

## 3.2.3. Galvanostatic charge-discharge (CDC) characteristics

The capacitance of each electrode materials was also calculated by using the galvanostatic CDC curves (Fig. 6 (a)). Calculated capacitance of rGO, rGO:CB, NirGO1, NirGO3, and NirGO6, were 606, 1000, 714, 833, and 270 Fg<sup>-1</sup>, respectively (Table 1). When the IR (current-resistance) drops in each electrode are examined, it is seen that they are very close to each other but slightly higher than that of NirGO6 (0.3 Ohm). This shows that the total resistances in the devices are close to each other. Then, CDC curves were obtained for all electrode materials at different currents between 1-5 mA. In this way, charge transfer and interaction between electrode and electrolyte were investigated. All devices retained their capacitive behaviour even though their capacitance values decreased with the current increase.

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Fig. 5. Electrochemical impedance spectra of electrodes (f=10 mHz-100kHz).

Table 1. Calculated electrochemical parameters of all electrodes by using EIS and CDC results.

Device	<b>R</b> ь ()	${ m R_{ct}}$ ()	${ m C_{SP}\ EIS\ (F\ g^{-1})}$	$C_{SP} CDC (F g^{-1})$	Energy Density <sup>1</sup> (Wh kg <sup>-1</sup> )	Power Density <sup>1</sup> (W kg <sup>-1</sup> )
rGO	12.0	3.0	476	606	83.3	500.0
rGO-CB	3.5	3.0	800	1000	136.1	490.0

Device	<b>R</b> ь ()	$\mathrm{R_{ct}}$ ()	${ m C_{SP}\ EIS\ (F\ g^{-1})}$	$C_{SP} CDC (F g^{-1})$	Energy Density <sup>1</sup> (Wh kg <sup>-1</sup> )	Power Density <sup>1</sup> (W kg <sup>-1</sup> )
NirGO1	4.0	2.0	628	714	97.0	499.0
NirGO3	1.5	1.5	888	833	113.3	509.9
NirGO6	10.0	4.0	272	270	35.8	1795

<sup>1</sup>Calculated from CDC data (applied current: 1A)

Furthermore, looking at the discharge current vs. specific capacitance plot (Fig. 6(d)), the capacitance drop due to the current increase in foamed electrodes is slightly less than those in rGO and rGO:CB. This may be due to the incompatibility of the pore size of the rGO and rGO:CB materials and the ion diameters in the electrolyte. Also, when considering the decrease in capacitance due to the increase in current, it is clear that the curve of NirGO3 is more linear, and there is less drop in the rGO:CB and NirGO3, in which NirGO3 shows higher performance than the other electrodes. This is because although CB increases the surface area of the electrode material, it causes an irregularity in the pore structure due to its structure. The accumulation and release of ions in the electrolyte decrease at high currents. In addition, specific energy and power values of the electrodes at different currents were determined from CDC graphs to obtain the Ragone Plot. The Ragone plot, which has power density and energy density axes, helps to illustrate the electrochemical performance of the device. In studies conducted at 5 different current values between 1-5 A g<sup>-1</sup>, the energy density values of standard electrodes decrease dramatically with the increase of current density, although their power densities increase. However, the decrease of energy density in foamed electrodes is less than those of reference electrodes. It was observed that the foamed electrodes retain their specific energy more than those of rGO and rGO:CB at high specific power values (Fig. 6(e)). As mentioned above, the ion paths are short and favourable for the diffusion of ions throughout the foam-structured Ni-based electrodes [36].

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Fig. 6. (a) Galvanostatic CDC curves of all electrodes (applied current: 1 mA), (b) CDC curves of rGO:CB electrode under different currents, (c) CDC curves of NirGO3 electrode under different currents, (d) specific capacitance (F  $g^{-1}$ ) vs. discharge current (1-5 A  $g^{-1}$ ) and (e) energy density (Wh k $g^{-1}$ ) vs. power density (W k $g^{-1}$ ) plots for all electrodes.

## Conclusion

Composite electrodes with three Ni/rGO ratios were made without a binder in one step. The structural characterisation of NirGO1, NirGO3, and NirGO6 electrodes revealed that the nickel metal present in the electrodes,  $\alpha$ -Ni(OH)2, demonstrated improved capacitive behavior. The study found that the capacitance values of binder-free NirGO1, NirGO3, and NirGO6 were 720, 800, and 310 F g<sup>-1</sup> respectively in 1M H<sub>2</sub>SO<sub>4</sub> electrode solution using a three-electrode method. Unlike the reference electrode rGO:CB, its capacitance value was computed as 900 F g<sup>-1</sup>. According to capacitance tests NirGO3 current decay was less than rGO:CB owing to homogeneous pore structure of NirGO3.

## **CRediT** authors' contribution statement

Sirin SIYAHJANI GULTEKIN: Conceptualization, Methodology, Investigation, Writing- Original draft preparation, Aziz Ahmad KARIMI: Validation, Investigation, Visualization, Mustafa CAN:Resources, Writing - Review & Editing, Serafettin DEMIC:Resources, Supervision, Writing - Review & Editing

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