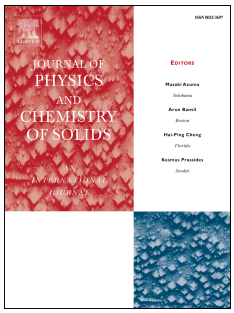
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Electrodeposition of zinc and reduced graphene oxide on porous nickel electrodes for high performance supercapacitors

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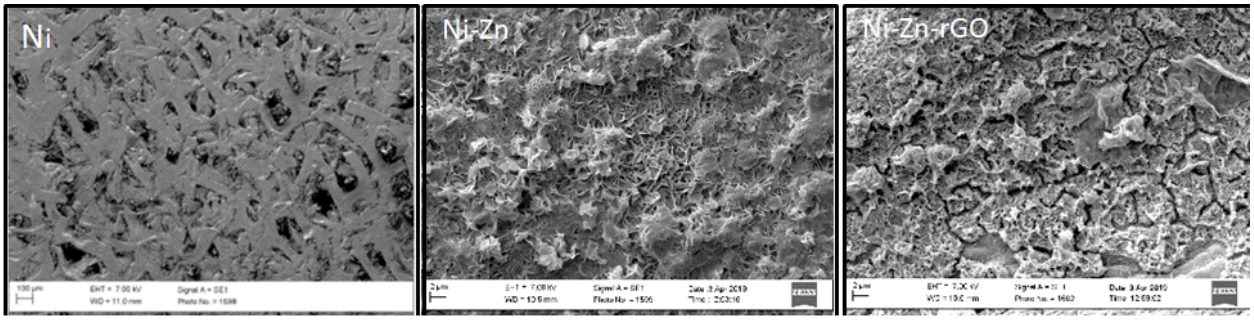
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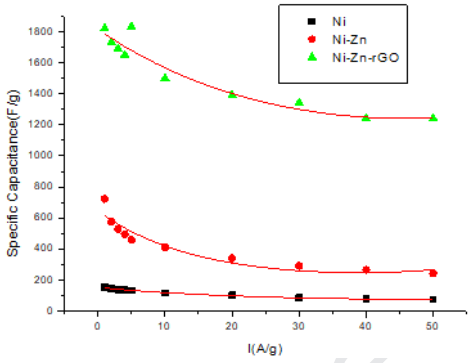
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Ni
Ni-Zn
Ni-Zn-rGO


Ni
Ni-Zn
Ni-Zn-rGO
Specific Capacitance(F/g)
I(A/g)
0
200
400
600
800
1000
1200
1400
1600
1800
0
10
20
30
40
50

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Electrodeposition of Zinc and Reduced Graphene Oxide on Porous Nickel Electrodes for High Performance Supercapacitors

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ABSTRACT

Electrochemical properties of porous nickel (Ni) foam, electrodeposited zinc (Zn) on Ni foam (Ni-Zn) and electrodeposited reduced graphene oxide (rGO) on Ni-Zn foam electrodes (Ni-Zn-rGO) in 6M KOH electrolyte were investigated. Cyclic voltammetry (CV) and galvanostatic charge–discharge cycling (GCD) techniques were used to carry out the redox interactions, and cycling capacitive properties of the electrodes in KOH solution. Platinum (Pt) and gold (Au) foil were used as a counter electrode and the current collector in the electrochemical measurements, respectively. The specific capacitances of the electrodes were found from the GCD measurements as 155, 722 and 1820 F/g for Ni, Ni-Zn and Ni-Zn/rGO electrodes at the current density of 1 A/g, respectively. Scanning electron microscope (SEM) images of the three electrodes were also taken into account to associate all the electrochemical measurements. These results clearly show that specific capacitance values highly increased after the deposition of Zn and rGO to Ni electrode.

Keywords: Nickel, Zinc, Reduced Graphene Oxide, Supercapacitor, Electrodes

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1. INTRODUCTION

Supercapacitors have quite good properties for energy storage such as high power density, strong stability for long-term usage and they are very fast for charging and discharging. Supercapacitors have much higher power density than that of batteries in the same volume [1]. However, their energy densities are usually 3 to 30 times lowers [2]. Since they have high power density, they are used in various fields such as forklifts, load cranes, electric vehicles, propagation of wearable or paper electronics in biomedical, consumer electronics, military applications and power back-up industries [3, 4].

Main components of a typical supercapacitor are cathode electrode, anode electrode, electrolyte and a separator. The electrodes have porous structure for increasing the surface area. The electrolyte is used as a source of ions which are used during the charge and discharge process. The separator has an ion-permeable property and it is used for both transferring the ions through the electrodes and preventing the electrical contact between the electrodes [2]. Supercapacitors can be classified as symmetric, in which identical electrodes are used, and asymmetric, in which different electrodes are used depending on the types of the electrodes. In addition, depending on the ion behavior at the electrodes, the supercapacitors are classified as electric double layer (EDL), pseudocapacitance and hybrid structures. In EDL no reaction occurs between the ions and the electrodes but in pseudocapacitance faradaic reaction occurs at the electrodes. [5-7]

A pseudo-capacitor metals have high specific capacitance, but due to their low conductivity, the cyclic stability is lower than that of EDLC capacitors. The problem can be reduced If they are added into a layer with a too thin thickness [8]. Therefore, EDLC and a pseudo-capacitor hybridized to increase the energy and power densities of the super capacitors [9-11].

For EDL type supercapacitors, mostly graphene-based electrodes are used [12-14] and for pseudocapacitors mostly metal oxides such as Nickel oxides (NiO) and cobalt oxides (Co_3O_4)

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ruthenium oxides (RuO_2), manganese dioxides (MnO_2) are used [15-21]. The specific capacitance for manganese oxides ranges from 360 to 394 F/g regardless of the preparation methods, Ruoff also reported graphene based electrodes for the supercapacitors [22]. The specific capacitance was found around 100 F/g at a current density of 1A/g in KOH electrolyte. Another value was reported as 400 F/g at 0.3 A/g using rGO-RuO_2 symmetric electrodes [23]. In this work, the specific capacitance values of (Ni, Ni-Zn, and Ni-Zn-rGO) three electrodes were calculated from GCD curves and they were found to be 155, 722 and 1820 F/g, in 6M KOH electrolyte, respectively.

However it is reported that nickel–cobalt based materials is still poor in terms of rate capability, because that have low electronic conductivity. Recently, porous nickel foam (NF) has attracted great attention for current conductors due to their availability, low cost, good electrical conductivity, and corrosion resistance [24], Ni-based materials for conductors such as NiO nanosheets, [25-29]

However, for most Ni oxide-based electrodes are still unsatisfactory, their long-term stability are insufficient at high current densities and they have poor conductivity. The energy density achieved ranges from several to several dozens of Wh/kg. The power density ranges from 0.1 to100 kW/ kg for Nickel based electrodes. The grafting of pseudo active materials was always a big problem for handling homogeneous distribution on the Nickel electrodes. In this study, the distribution problem has been solved in a very short time and very homogeneously using the electrodeposition method for the grafting materials, Zn and rGO.

In this work, three different electrodes from the simplest to the advanced electrode were used to determine the electrochemical properties. Ni foam which behaves as pseudo capacitor with an average pore size of 80 μm, electrodeposited Zn on Ni foam (Ni-Zn) and electrodeposited rGO on Ni-Zn foam electrodes (Ni-Zn-rGO) were investigated in terms of the electrochemical properties. A gold foil and a commercial ion permeable polyethylene separator were used as

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a current collector and as a separator between the electrodes, respectively. The electrochemical measurements were performed in 6 M KOH electrolyte at different scan rates by CV and at different current densities by GCD methods. The specific capacitance values of these three electrodes (Ni, Ni-Zn, and Ni-Zn-rGO) were calculated from GCD curves and they were found to be 155, 722 and 1820 F/g, respectively. The base material was chosen as Ni electrode for the excellent electrochemical performance of supercapacitor because of low density and very high porosity which covers 75–95% of the volume with void spaces. It is used in variety of rechargeable battery applications, such as Ni–Cd and Ni–H rechargeable batteries and hydrogen storage units [30]. Ni foam has also high conductivity, good chemical stability, wide potential window, good mechanical strength and low-cost [31]. Deposition of Zn and rGO to the base Ni electrode material enhance the properties of electrochemical performance considerably for the supercapacitor applications and the results show also the specific energy values obtained with these modified electrodes are higher than those of similar systems.

2. Experimental

2.1. Reduced Graphene Oxide Sheets

Reduced graphene oxide (rGO) sheets used in this study were synthesized previously by our group. Detailed information about the synthesis can be found in [32].

2.2 Preparation of the Ni-Zn Electrodes

Preparation of supercapacitor cathode electrodes is performed in two stages in general. In the first stage, nucleation of Ni and Zn atoms takes place and then crystallization of Ni-Zn particles with a maximum size of 40 nm on nickel foam occurs. Nickel foam used as a cathode base has a surface density of 350 g/m^2, a thickness of 0.08 mm, a purity of >99.99%, and a porosity of 70-80%. Ni-Zn alloys were collected on NF by electrodeposition technique

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at constant current (galvanostatic). 0.3 M zinc sulfate heptahydrate; 0.71 M nickelsulfate heptahydrate; 0.25 M nickel chloride hexahydrate and 1 M sodium chloride aqueous solution was prepared. After the solution was mixed at room temperature for 1 hour, sodium dodecyl sulfate was added as an active ingredient with a weight of 0.2%. Pt wire electrode was used as an anti-electrode, as a nickel foam working electrode with an exposed surface area of 1 cm^2. All changes in the potential read against time at every 1 second through galvanostatic scanning technique software. The photographs of the experimental setup and the electrodes after the deposition of Zn are seen in Fig 1 .

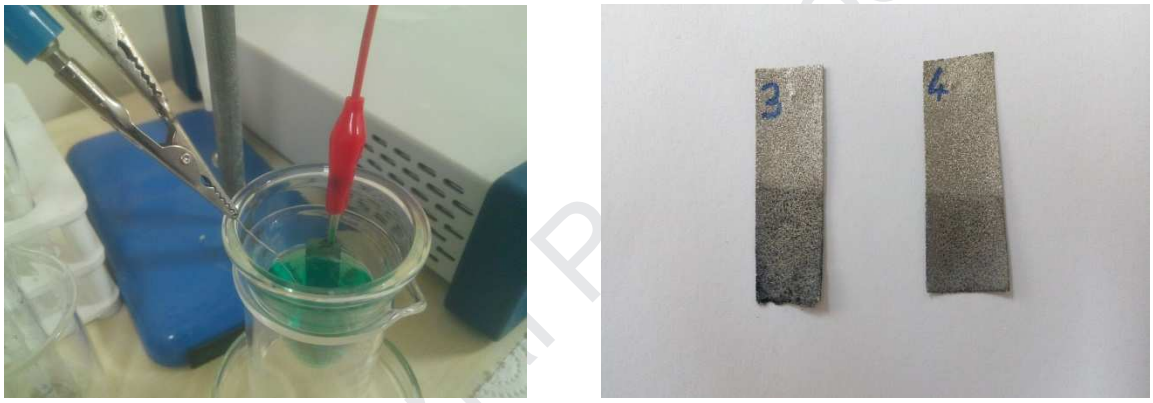


Fig 1: (a) Experimental setup for the electrodeposition of Zn on Ni foam, **(b)** photographs of the Zn

2.3 Preperation of Ni-Zn-rGO Electrodes

A Pt wire, and Ag/AgCl separated from the bulk of the solution by a double bridge were used as counter and reference electrodes respectively. $LiClO_4$ in ultra-pure water was the supporting electrolyte at a concentration of 0.10 mol dm^{-3}. Repeating 50 cycles in cyclic voltametry between −1.20V and + 1.20V in $LiClO_4/H_2O$ electrolyte system were employed to reduce GO-N_3 and to form rGO-N_3 on Ni-Zn electrode. Then Ni-Zn-rGO electrode was dried in vacuum at 70 ^oC for 20 min. Finally, Ni-Zn-rGO electrode rinsed several times with water.

2.4. Electrochemical Performance

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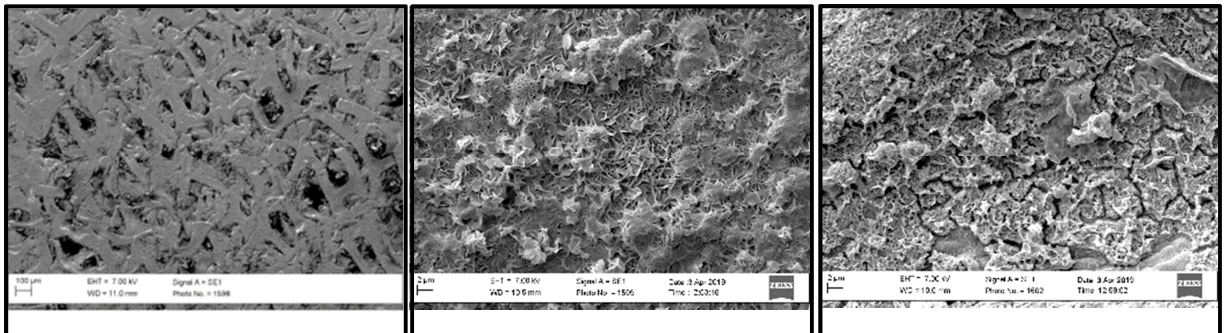
The electrochemical performance of Ni, Ni-Zn and Ni-Zn-rGO electrodes were determined by CV at different scan rates and different current densities for GCD methods in 6M aqueous KOH solution. The scan rates and the current densities were chosen as 5, 10, 20, 50, 100, 200 $mV.s^{-1}$ and 1, 2, 3, 5, 10 A/g for CV and GCD measurements, respectively. Galvano static charge-discharge performance was carried out to obtain specific capacitances, power energy and energy densities. Potential window was determined from -0.3 to 0.55 V for Ni, Ni-Zn and -0.3 to 0.5 V for Ni-Zn-rGO of electrodes.

2.5. *SEM imaging*

Scanning electron microscopy (SEM) analysis was used to investigate the surface morphology and the microstructure of Ni, Ni-Zn and Ni-Zn-rGO electrodes Non-conductive specimens were mounted on aluminum stubs using carbon tape and they are coated with gold by using a LEICA ACE600 Sputter in vacuum before the examination in the SEM. The surface morphology of the first two electrodes (Ni, Ni-Zn) and the last electrode (Ni-Zn-rGO) was examined by ZEISS LS10, at 7 kV and QUANTA FEG 450 at 15 kV, respectively. In addition, elemental analysis of the Ni, Ni-Zn and Ni-Zn-rGO electrodes was done by QUANTA FEG 450 and represented in Fig 2

3. Results and Discussions

rGO which was used in this study was characterized in the previous work of our group and it was found that the diffraction peak, the interlayer spacing, the number of layers and the size of the crystallites are 25.16°, 3.5 Å, 1-2, and 0.45 nm, respectively [32]. These values clearly show that rGO could be obtained successfully.



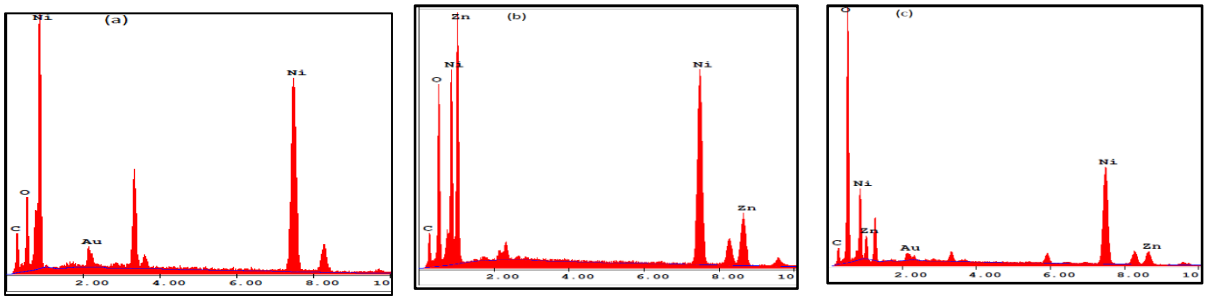


Figure 2: SEM images results of EDS analysis of a) Ni b) Ni-Zn and c) Ni-Zn-rGO electrodes before charging

SEM images of the Ni, Ni-Zn, and Ni-Zn-rGO electrodes before charging were represented in Fig. 2. Deposition of Zn and rGO on Ni electrode abruptly affected the surface morphology of the Ni electrode as seen in Fig. 2(b-c). The main effect observed after all of these processes is changing the pore structure of the surface: from macro holes to submicron pores. These submicron pores allow the diffusion of more ions through the electrodes which results in more capacity. After depositing rGO on Ni-Zn foam surface on which rGO particles are clearly visible, we obtained more homogeneous surface including pores as seen in Fig. 2 (c). In addition, from EDS analysis, it is clearly seen that the deposition of Zn and rGO on the electrodes were successfully performed.

CV of the electrodes, Ni, Ni-Zn, and Ni-Zn-rGO are represented in Fig. 3. The CV behaviors of all electrodes are similar to each other and all curves have two redox peaks. All of the electrodes exhibit pseudocapacitive behavior due to the Ni used in these electrodes and it is well known that Ni causes reversible faradaic reactions on the surface of the electrodes [33-35]. The peaks observed in CV are the results of the faradaic oxidation and reduction processes as given by the following reaction

$$NiO + OH^- \leftrightarrow NiOOH + e^- \quad (1)$$

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The voltages of the reduction and the oxidation, and the potential windows are 0.2 V, 0.5 V, 0.7V; 0.1 V, 0.7 V, 1.1 V; and -0.1 V, 0.8 V, 1.8 V for Ni, Ni-Zn and Ni-Zn-rGO electrodes, respectively at the scan rate of 200 mV/s. This result clearly shows that, when the Ni electrode is deposited by Zn and Zn-rGO, the potential window is extended which leads to higher capacitance values.

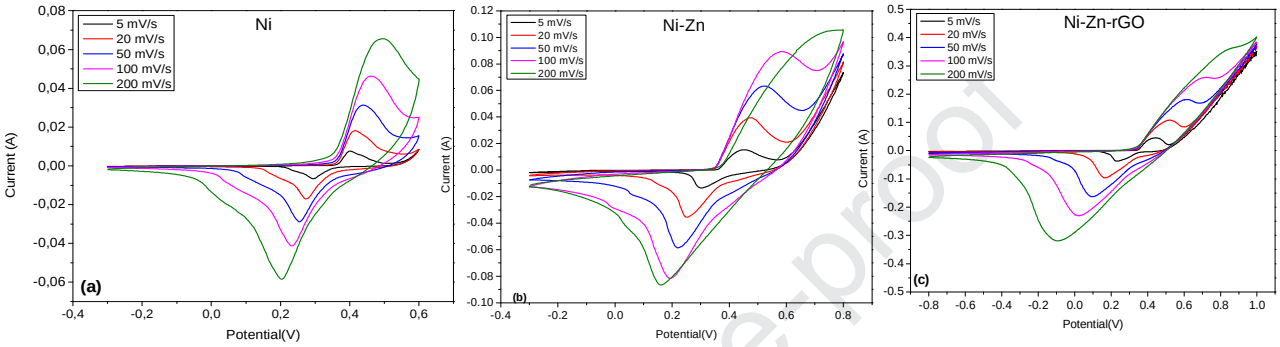


Figure 3: CV behavior of (a) Ni, (b) Ni-Zn, (c) Ni-Zn-rGO electrodes in 6M KOH solution at different scan rates.

Charge and discharge curves at the current densities of 1, 2, 3, 5 and 10 A/g were represented in Fig. 4. The slopes of the curves on the left and right sides of the peaks are not identical which is the result of the redox reactions between the electrode and electrolyte and thus only a quasi-symmetrical peaks were observed. This is due to the pseudo-capacitive property of the capacitor designed in this study.

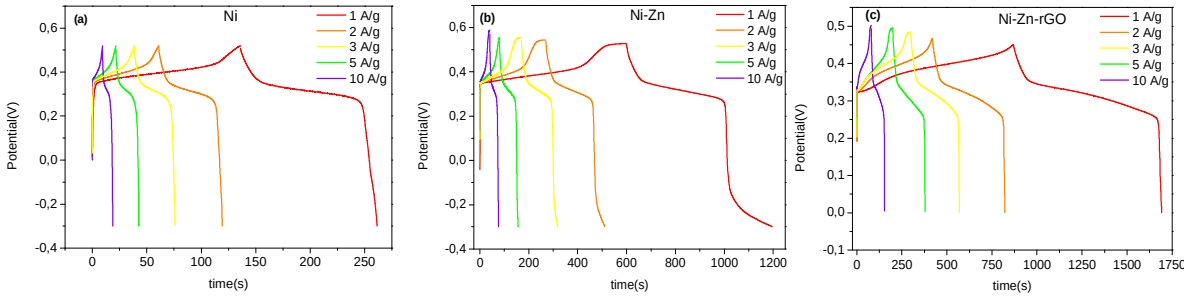


Figure 4: Charge and discharge curves of the a) Ni b) Ni-Zn and c) Ni-Zn-rGO electrodes for the different current densities.

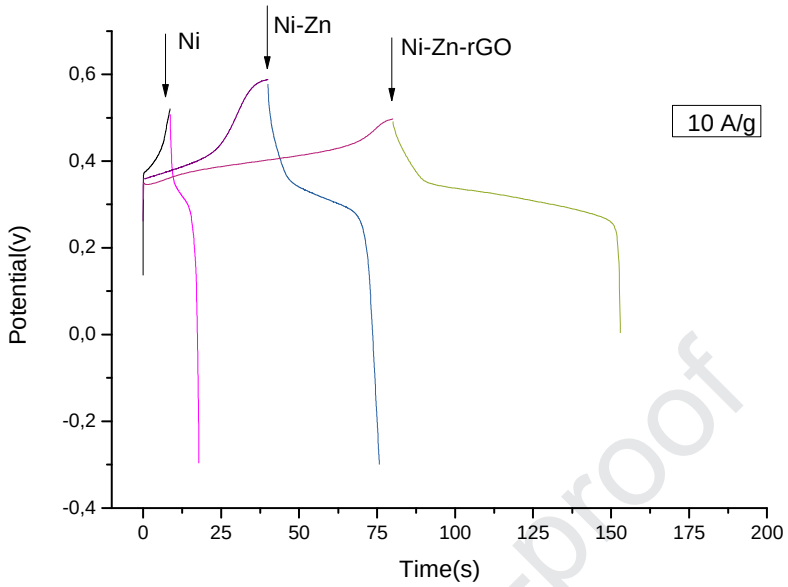


Figure 5: Charge and discharge curves of the a) Ni b) Ni-Zn and c) Ni-Zn-rGO electrodes at the current density of 10 A/g.

As it is clearly seen from the Fig 5, one cycling period takes 15, 75 and 150 seconds for the Ni, Ni-Zn, and Ni-Zn-rGO electrodes at 10 A/g, respectively. In other words, longer cycling time for the galvanostatic curves means that the capacitance value is also higher for these electrodes. The following equation can be used for computing the capacitance values [36]

$$C = (\frac{I}{m})\Delta t \Delta V \quad (2)$$

Here, I/m, Δt, ΔV are the discharge current density, the discharge time and the potential window, respectively. As it is seen from Table 1, the specific capacitance values at 1 A/g, are 155, 722 and 1820 F/g for Ni, Ni-Zn and Ni-Zn-rGO electrodes, respectively. These results show that the Ni-Zn electrode is about 6 times and the Ni-Zn-rGO electrode is about 10 times higher than that of Ni electrode. The main reason for the high capacitance values is attributed to the porous structure of the Ni-Zn and Ni-Zn-rGO electrodes which allows the diffusion of

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more ions easily. As can be seen from the Fig. 6 and Table 1, these specific capacitances decreased with the increasing current densities. This is due to the increasing internal resistance at high current densities and this resistance causes low conductivity and thus low capacitance.

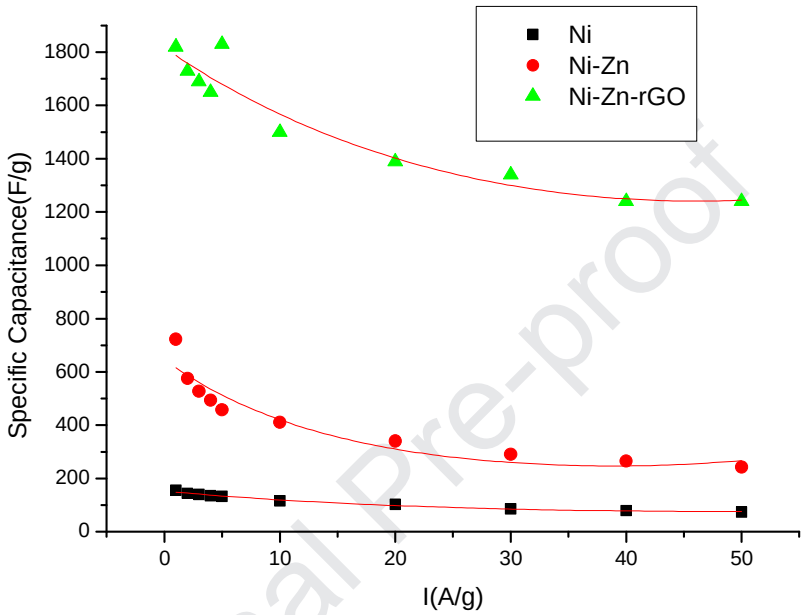


Figure 6: The change of specific capacitances according to current densities of Ni, Ni-Zn and Ni-Zn-rGO electrodes for discharge process.

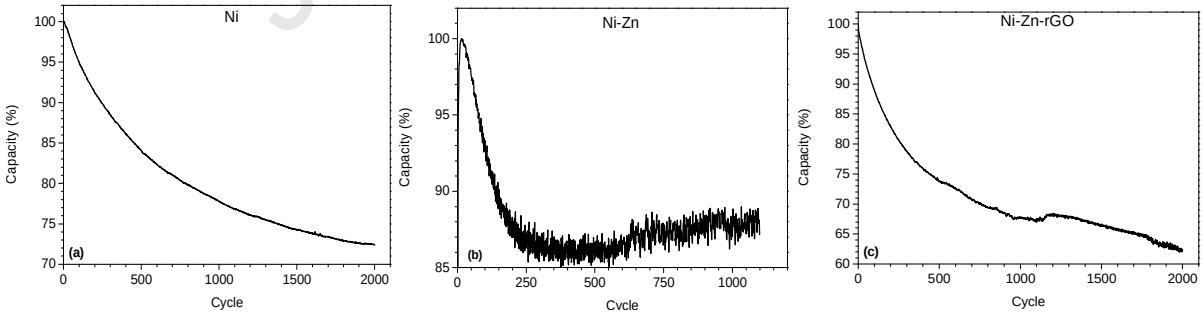


Figure 7: Capacitive retention of a) Ni, b) Ni-Zn and c) Ni-Zn-rGO electrodes

Capacitive retention properties of all electrodes were also measured to see the cycling performance and it was presented in Fig. 7. Three electrodes charged and discharged 2000 times in 6M KOH at 10 A/g for this purpose. Capacitive performance was still 70-75 % for

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Ni, 85-90% for Ni-Zn and 65-70% for Ni-Zn-rGO electrodes after 2000 times cycling. Ordinary Ni nano porous foam structure allows the uniform deposition of Zn particles on the surface which enhance mechanical strength and causes longer time cycling for Ni-Zn electrode. The reason for the shorter cycling stability of Ni-Zn-rGO electrodes can be attributed to agglomeration in the composite matrix after the addition of rGO sheets. This situation creates more voids and breaks partly the interaction with rGO and electrode. As a result, rGO cannot be stable as much as Ni-Zn electrodes. Although these decreasing rates are quite good and acceptable, it is expected to obtain more cycling retention for the lower current densities. When three electrodes are compared, the highest cycling capability value was observed for Ni-Zn electrode while the biggest capacitance was for Ni-Zn-rGO electrodes. The biggest capacitance for Ni-Zn-rGO and the highest cycling capability for Ni-Zn are due to the more porous structure and more chemical and mechanical durability, respectively.

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Table 1: Specific Capacitance values of Ni, Ni-Zn and Ni-Zn-rGO electrodes at the different current densities for charge and discharge

I(A/g)	Ni Specific Capacitance (F/g)		Ni-Zn Specific Capacitance(F/g)		Ni-Zn-rGO Specific Capacitance(F/g)	
Current Density	Charge	Discharge	Charge	Discharge	Charge	Discharge
1	281	155	1060	722	3360	1820
2	243	144	961	575	3070	1730
3	238	139	1120	527	3200	1690
4	224	135	1040	493	3110	1650
5	214	132	884	458	3870	1830
10	180	115	891	411	3310	1500

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20	168	102	649	340	3730	1390
30	130	85	580	291	3470	1340
40	128	79	536	265	3420	1240
50	111	73	520	242	3430	1240

Results showed that all of the electrodes exhibited good capacitive performance at the current density of 10A/g and even after 2000 cycle. Ragone plot is an efficient way to observe capacitive performance of supercapacitor devices considering power and energy densities. The values of specific power and energy density can be calculated using the following equations [37-39].

$$E = \mathrm{C}\Delta V^2/7.2 \tag{3}$$

$$P = 3600E/t \tag{4}$$

Where, E is the specific energy density (Wh/kg), P is the specific power density (kW/kg), C is the specific capacitance, ΔV is the potential window for the discharge, and t is the discharge time.

In this work, the maximum specific power densities at 50 A/g were found to be 13.1, 14.1 and 12.8 kW/kg for the Ni, Ni-Zn and Ni-Zn-rGO electrodes, respectively. Although the specific power density values are close to each other, Ni-Zn electrode is slightly higher than the other two Ni and Ni-Zn-rGO electrodes. The maximum specific energy densities for the Ni, Ni-Zn and Ni-Zn-rGO electrodes were measured as 3.83, 14.27 and 45.5 Wh/kg at 50 A/g current density, and 9.5, 36.3 and 71.3 wh/kg at 1 A/g current density(see Fig 8). As it is clearly seen that the specific energy values are highly increased with the deposition of Zn and rGO on the porous Ni foam electrode. The remarkable improvement of the energy densities with the addition of Zn and rGO are attributed to the increased porosity and enlarged potential window since the energy density is written in terms of the square of the potential window as given in Eq.3. Results clearly shows that the specific energy values obtained in this study are higher

than those of similar systems [40, 41] and the results show it is quite possible to enhance energy and power densities of supercapacitors.

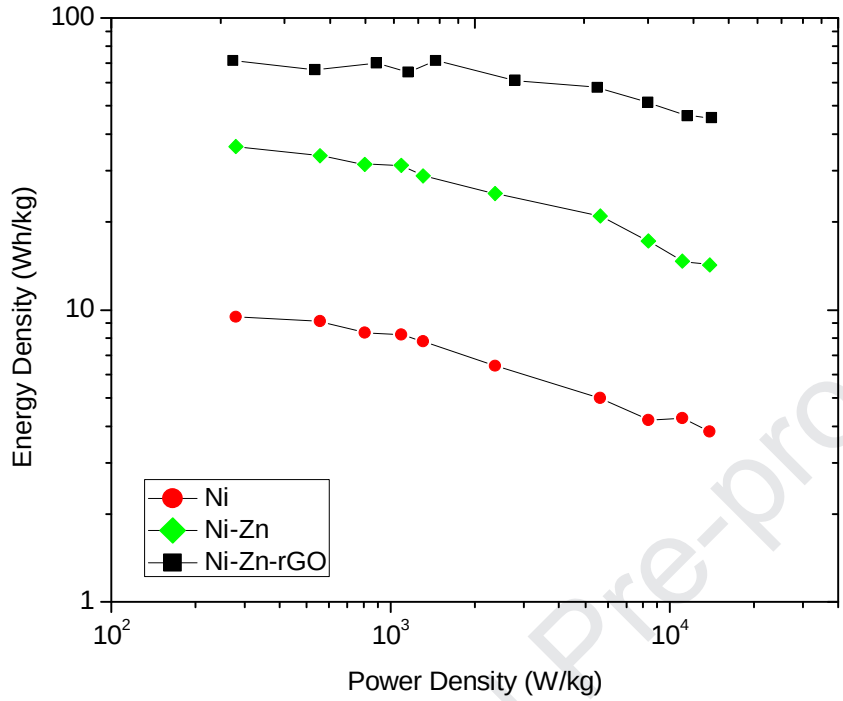


Figure 8: The change of power density according to energy density values for the Ni, Ni-Zn and Ni-Zn-rGO electrodes at the current density of 1 A/g.

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4. Conclusions

In summary, we systematically studied the chemical and electrochemical properties of porous Ni foam and the deposition of Zn and rGO to the Ni foam in different concentrations and scan rates of KOH electrolyte. The maximum specific energy densities for the Ni, Ni-Zn and Ni-Zn-rGO electrodes were measured as 3.83, 14.27 and 45.5 Wh/kg at 50 A/g current density, and 9.5, 36.3 and 71.3 wh/kg at 1 A/g current density. This study shows that deposition of Zn and rGO to the base Ni electrode material enhance the properties of electrochemical performance considerably for the supercapacitor applications and the results show also the specific energy values obtained with these modified electrodes are higher than those of similar

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systems. In addition, these modified electrodes showed high cycling performance and low retention.

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HIGLIGHTS

1) Reinforced electrodes for supercapacitor applications
2) Electrical deposition of zinc and graphene oxide
3) Remarkable improvement of the energy and power densities
4) Low retention and high cycling performence

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Sample CRediT author statement

Onder Yargi, Utkan Sahinturk: Conceptualization, Methodology

Ali Gelir: Methodology

Utkan Sahinturk : Resources, Methodology

Oguz Kaan Ozdemir, İbrahim Yılmaz: Investigation

Onder Yargi, Ali Gelir: Writing - Review & Editing

Onder Yargi : Supervision

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