Synthesis and electrochemical performance of cobalt oxide deposited on nickel-foam for energy storage devices

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Abstract. Efficient and flexible energy storage materials are the future of energy technology. Among the various energy storage devices supercapacitor which stores electrochemical energy with higher power density than battery and higher energy density than capacitor is a potential device. In the supercapacitor, electrode active material plays very important role for storage and transportation of electrolytic ions. Herein, we have synthesized substrate free cobalt oxide deposited nickel-foam with the help of microwave-assisted hydrothermal technique, which is novel and faster synthesis process than conventional synthesis processes. Morphological characterization of as-synthesized samples was investigated with FESEM. Electrochemical performance with specific capacitance ($C_s$) value of 98.31 F g\textsuperscript{-1} at 0.25 A g\textsuperscript{-1} current density and 93.59 F g\textsuperscript{-1} at 1 mV s\textsuperscript{-1} scan rate obtained from galvanostatic charge/discharge and cyclic voltammetry curves.

1. Introduction

In the present time, the major source of energy is based on fossil fuel, which is depleting day-by-day and responsible for environmental pollution and global warming by emission of toxic gases. To overcome this effect energy storage from renewable energy sources such as solar, wind and tidal energy can be efficiently stored in electrochemical energy storage (EES) devices or supercapacitors [1]. This stored energy can be transported easily and used for flexible electronics to datacenters to hybrid vehicles. Supercapacitors have been further classified based on electric double layer capacitor (EDLC) and pseudocapacitor. EDLC stores charges/ions by adsorption/desorption between interface of electrode active material and electrolyte. While pseudocapacitor stores charges/ions by faradic redox reactions. Supercapacitors having the combined effect of EDLC and pseudocapacitance provides the high energy and power density. Which is the combined effect of capacitors (high power density) and batteries (high energy density). High potential window, fast charging/discharging and cycle stability of supercapacitors are the very important characteristics applicable for future portable, flexible and stable power electronic devices. Advancement of energy storage devices over the century has been depicted in figure 1 from primary cell, secondary cell, through advancement of some other battery technology to Li-ion batteries and supercapacitors for efficient utilization of energy generation [2, 3].
Figure 1. History of evolution of energy storage devices.

To improve the supercapacitor performance, various advancements have been done in the field of microstructure of active electrode materials for effective utilization of electrolytic ions/charges. In this direction, supercapacitor performance was analyzed with transition metal oxides i.e., RuO$_2$, MnO$_2$, MoS$_2$, CoO, Nb$_2$O$_5$, TiO$_2$, WO$_3$, CeO$_2$ etc. with conducting activated carbon, graphene oxide or conducting polymers [4,5]. Doping of metallic elements (Ag, Au, Pt, etc.) and small charges (Li$^+$, Na$^+$, K$^+$, etc.) have particular impact on electrical conductivity thereby raising supercapacitor performance. Various research have also been conducted for substrate free electrode to achieve better energy storage performance [6, 7, 8]. In the present research, we have demonstrated the effect of cobalt oxide deposited on porous nickel foam for enhancing the supercapacitor performance. This has been analyzed by the different morphology or microstructure in relation with electrochemical performance. We hope this finding could lead the scientific community for some better understanding and development of supercapacitor device.

2. Experimental section

2.1. Chemicals.

Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O), ammonium fluoride (NH$_4$F), Urea (CO(NH$_2$)$_2$), potassium hydroxide (KOH), hydrochloric acid (HCl), and all other chemicals were purchased from Merck (India) and used without further purification.

2.2. Synthesis of cobalt oxide deposited nickel-foam microstructures.

Synthesis of cobalt oxide deposited Nickel foam (Co-oxide/Ni-foam) has been carried out by microwave-assisted hydrothermal method followed by annealing in muffle furnace. At first, impurities and oxide layer of Ni-foam were removed by ultrasonication for 10 minutes using solution of 10 mL HCl and 10 mL deionized water in a beaker. Further, the Ni-foam was washed with deionized water three times to remove acid. Thus cleaned two pieces of Ni-foam of 1x2 cm$^2$ dimensions was put into two different prepared solutions containing varying concentration of Co(NO$_3$)$_2$·6H$_2$O as 0.25 and 0.5 mmol with 4 mmol NH$_4$F and 5 mmol urea in deionized water. Further, this mixture solution was transferred into a teflon pressure vessel (NXH100), sealed and maintained at 130 °C for 15 min under microwave irradiation of 250 W power in a Multiwave PRO microwave synthesizer (Anton Paar). After cooling down the final product was washed with deionized water three times to remove impurities and then dried in an oven overnight at 80 °C. Thus obtained cobalt oxide deposited Nickel foam samples were annealed in muffle furnace at 450 °C for 4 hours. The samples with varying concentration of Co(NO$_3$)$_2$·6H$_2$O as 0.25 and 0.5 mmol labelled as CN0.25 and CN0.5, respectively.

The surface morphology and microstructure of CN0.25 and CN0.5 samples were analyzed with field emission scanning electron microscopy (ZEISS EVO 60 FESEM). The electrochemical charge storage performance of as-synthesized samples were carried out using three-electrode configuration of
saturated calomel electrode (SCE), Pt wire and cobalt oxide deposited Nickel foam electrode as reference, counter and working electrode, respectively. The tests were performed by using cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques in 3 M KOH electrolyte using a CHI 760D electrochemical workstation (CH Instruments, Inc.).

3. Results and discussion

3.1. Morphology and microstructure

![Figure 2. FESEM images of CN0.25 (a & b) and CN0.5 (c & d) samples.](image)

The morphology of as-synthesized samples were examined with the help of FESEM as shown in figure 2. The different concentration of Co(NO₃)₂·6H₂O plays important role for alteration of morphology. The morphology evolved with 0.25 mmol Co(NO₃)₂·6H₂O sample (CN0.25) as shown in figure 2 (a & b) with gear like morphology of diameter about 4 to 7 μm having cut teeth like structures of diameter ranging from 100 to 400 nm. Further, with increased concentration as 0.5 mmol Co(NO₃)₂·6H₂O (CN0.5) sample the obtained branched morphology having diameter ranging from 500 to 700 nm with outer very thin flexible layer as shown in figure 2 (c & d). Thus, obtained porous morphology is responsible for high electrochemical performance by providing easy access to electrolytic ions.

3.2. Electrochemical energy storage study

Electrochemical energy storage or supercapacitor performance was analyzed with three electrode system in the 3M KOH electrolyte solution and potential window of 0.0 to 0.4 V with GCD and CV profile according to figure 3. Comparative GCD study of specific capacitance of samples CN0.25 and CN0.5 at different current densities at 0.5 and 1 A g⁻¹ was observed in figure 3 (a). CN0.5 sample deliver higher supercapacitance performance as indicated by higher discharge time than CN0.25 by providing more open space with multiple branching as confirmed by FESEM images. The specific capacitance (Cs) calculation was carried out using equation (1) and (2) from GCD and CV profile, respectively [9].
\[ C_s = \frac{I \cdot \Delta t}{m \cdot \Delta V} \]  

(1)

\[ C_s = \frac{\int I \, dV}{m \cdot \nu \cdot \Delta V} \]  

(2)

where, \( I \) is applied current, \( \Delta t \) is discharge time, \( m \) is the mass of active material, \( \Delta V \) is the potential window, \( \int I \, dV \) is the area under CV curve and \( \nu \) is the scan rate. The specific capacitance value obtained from GCD profile for CN0.5 sample shown in figure 3 (b) and maximum of 98.31 F g\(^{-1}\) obtained at 0.25 A g\(^{-1}\) current density as depicted in Table 1. Further from the CV profile at different scan rate as shown in figure 3 (c), the maximum specific capacitance of 93.59 F g\(^{-1}\) obtained at 1 mV s\(^{-1}\) scan rate. With increasing the scan rate up to 100 mV s\(^{-1}\) the specific capacitance value reduced up to 19.72 F g\(^{-1}\) as depicted in Table 2. This reduction in specific capacitance value at higher scan rate is due to less effective insertion of electrolytic ions. The EIS study was conducted for CN0.25 and CN0.5 samples to determine capacitive behavior and solution resistance of flow of ions to electrode surface as shown by Nyquist plot in figure 4. In the plot a straight line in low frequency region depicts capacitive behavior while semicircle in high frequency region depicts solution resistance [10].

![Figure 3. (a) Comparative GCD profile of CN0.25 and CN0.5 samples at 0.5 and 1 A g\(^{-1}\) current densities, (b) GCD profile of CN0.5 sample at different current densities, and (c) CV profile of CN0.5 sample at different scan rate](#)

Figure 3. (a) Comparative GCD profile of CN0.25 and CN0.5 samples at 0.5 and 1 A g\(^{-1}\) current densities, (b) GCD profile of CN0.5 sample at different current densities, and (c) CV profile of CN0.5 sample at different scan rate
Figure 4. Nyquist plot of CN0.25 and CN0.5 samples in the frequency range of 0.01 Hz to 1 M Hz.

Table 1. Sp. capacitance value obtained from GCD curve of CN0.5 sample at current density.

| Current Density (I/m) in A g⁻¹ | 0.25 | 0.5  | 1   |
|-------------------------------|------|------|-----|
| Sp. Capacitance (C_s) in F g⁻¹| 98.31| 86.87| 34.50|

Table 2. Sp. capacitance value obtained from CV curve of CN0.5 sample at different scan rate.

| Scan Rate (v) in mV s⁻¹ | 100 | 50  | 20  | 10  | 5   | 2   | 1   |
|-------------------------|-----|-----|-----|-----|-----|-----|-----|
| Sp. Capacitance (C_s) in F g⁻¹ | 19.72| 27.07| 39.47| 50.71| 62.79| 77.94| 93.59|

4. Conclusions

In the present finding, we have synthesized cobalt oxide deposited Nickel foam (Co-oxide/Ni-foam) for electrochemical energy storage electrode materials. Morphology of as-synthesized samples of CN0.5 with diameter ranging from 500 to 700 nm with outer very thin flexible layer obtained from microwave-assisted hydrothermal synthesis method. Thus, obtained sample has shown a maximum specific capacitance of 98.31 F g⁻¹ at a current density of 0.25 A g⁻¹ from GCD curve and 93.59 F g⁻¹ at a scan rate of 1 mV s⁻¹ from CV curve. The facile and fast synthesis of cobalt oxide deposited Nickel foam with moderate electrochemical performance suggests the importance of the work.
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