

SYNTHESIS OF A SUPERCAPACITOR BASED ON NANOMATERIALS

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Abstract -

Demand for various energy storage technologies in electronic and electrical devices continuously goes on increasing. In that context, objective of this research work is to develop and test an electrode of a energy storage module (supercapacitor) using nickel hydroxide and carbon-based nanocomposite materials. Electrochemical performance of electrode is enhanced by optimizing synthesis parameters and designing the electrochemical cell. Conventional and all solid-state supercapacitors are developed with notable electrochemical performance. Pure Ni(OH)₂ deposited on 3D networked nickel foam by chemical bath deposition process under thermal treatment to develop electrode. The nanoflower-like structure formed by connecting nanosheets together exhibits porous structure which leads to faster ions diffusion and also shorten diffusion path of electrolyte. Electrochemical characterization has been carried out using cyclic voltammetry and galvanostatic charge-discharge. The specific capacitance of 1065 Fg⁻¹ was observed for Ni(OH)₂/Ni electrode at current density 1 Ag⁻¹. The electrochemical characterization result demonstrates that obtained specific capacitance for nanoflower-like Ni(OH)₂ was far less than the theoretical specific capacitance of Ni(OH)₂ and it is due to the semiconductor nature of nickel hydroxide (poor electrical conductivity ~10-17Scm⁻¹). In order to improve electrical conductivity reduced graphene oxide having good electric conductivity and high surface area (2630 m²g⁻¹) added in pure Ni(OH)₂ to form nanocomposite of Ni(OH)₂/rGO/Ni. The maximum specific capacitance of 1947 Fg⁻¹ was obtained for Ni(OH)₂/rGO/Ni electrode at current density 1 Ag⁻¹. Further, in order to enhance another important parameter stability cobalt is doped in Ni(OH)₂/rGO/Ni. Addition of cobalt increases electrochemical activity by offering rich redox reaction from both nickel and cobalt and also it reduces the electrode resistance and increases the oxygen overpotential.

Keywords: Energy Storage, Nanocomposites, Material Synthesis, Electrode, Electrochemical, Supercapacitors.

1. Introduction

Industrial and economical development massively relies on the availability of fossil fuel resources. The energy demand for fossil fuel for the total world was 13.731 billion tons of oil equivalents (BTOE) as of 2012 and it will increase 18.30 BTOE in 2035[1-2]. But the depletion of natural resources and uneven distribution causes problems like economical imbalance which impact on energy generation and storage, industrial operation and transportation sectors. Apart from this, consumption of fossil fuels generates pollutants such as CO, CO₂, NO_x etc. and they are creating significant environment damage such as the greenhouse effects [3]. In that context, many researchers are looking for the replacement for fossil fuel resources. As a part of this, the development of renewable energy sources such as solar energy, wind energy, tidal energy, geothermal energy etc. has also been pursued extensively [4-7].

Apart from biofuels, major renewable source generated energy is in terms of electricity and to store such generated energy need advanced storage technology. Hence there has been a great demand for electrochemical energy storage devices which are reliable and having excellent electrochemical performance such as batteries, fuel cell, supercapacitors etc. [8]. Among them, supercapacitor attracted more attention due to its characteristics such as fast storage capability, flexible packaging, wide temperature range (-40°C to 70°C), high-security coefficient (long time use with little maintenance), improved cyclic stability and superior lifespan (>1000000) [9]. The performance comparison for battery, supercapacitor and the conventional capacitor is given in

Table 1 which indicates supercapacitor facing major issue regarding poor energy density as compared to battery technology. But, recent advancement in electrode material and electrolytes are able to solve an issue related to the poor energy density [10]. Because of this, year by year research work on supercapacitor goes on increases which indicated by a number of publications accessed on Google scholar on this topic shown in Fig. 1. It also indicates how properties enrichment is done in electrode materials till now [11].

Table 1. Comparison between supercapacitor and battery based on properties.[10]

Parameters	Electrochemical Capacitor	Battery
Energy density	Low	High
Power density	High (1-10KW kg ⁻¹)	Low(150 W kg ⁻¹)
Charge-discharge cycle	10 ⁵ -10 ⁶	500-10 ⁴
Self discharge time at room Temperature	Days-week	Months
Life time at room temperature (years)	5-10	3-5
Cell voltage (Volts)	1.2-3.8	2.5-4.2

The supercapacitor is also known as ultracapacitor, first developed in 1957 by General Electric during the experimentation on porous carbon. General Electric engineers found that porous carbon can store charge by forming a double layer. The same double layer effect rediscovered by researchers at the Oil of Ohio in 1966 when they are working on fuel cell design. In this design, two activated charcoal electrodes separated by thin porous insulator was used, the same mechanical design is used till date for electric double-layer capacitor [12]. The first commercialize supercapacitor given by Sohio. In between 1975 and 1981, Conway proposed a new type of supercapacitor where RuO₂ film was used in aqueous H₂SO₄, which demonstrate charge storage based on surface redox reactions [13]. The Nippon Electric Company (NEC) in 1978 referred term “Supercapacitor” first time and used in practical application as backup power for computer memory [4,14–18].

The supercapacitor is an energy storage device having very high power density and low internal resistance, these properties make them able to store and deliver energy at higher rates than the battery. Supercapacitor consists of two electrodes separated by the dielectric film in an electrolyte. Electrode and electrolyte material is the most important parameter for electrochemical performance of supercapacitor [8].

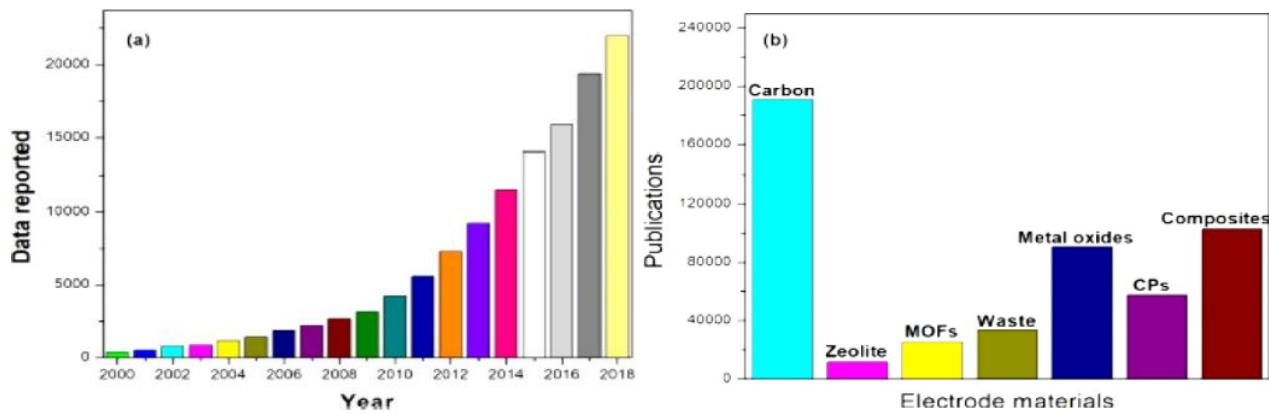


Figure 1 Statistical survey on the research activities toward supercapacitor: a) presents the number of publications including articles, books, and other authentic open literature (2000–2018 (predicted)) from a search using supercapacitor as a keyword in

1.1. Fundamentals of Supercapacitor

For supercapacitor various parameters are playing important role in deciding final performance. In this section all such parameters affecting on electrochemical performance are discussed.

1.2 Types of Supercapacitors

Based on energy storage mechanism supercapacitors are grouped into the three categories electrochemical double layer capacitor, pseudocapacitor and hybrid capacitor (fig 2).

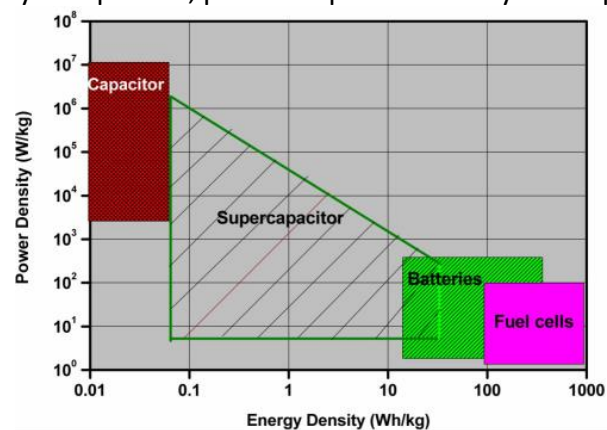


Figure 2 Ragone plot for various electrical energy storage devices (specific power against specific energy).

1.3. Electrochemical double layer capacitor (EDLC)

In EDLC charge storage mechanism is based on nano-scale charge separation at the electrochemical interface between electrolyte and electrode. The charge storage mechanism is totally non-faradaic, non-occurrence of an oxidation-reduction reaction. Due to no charge transfer between electrodes, EDLC has superior life cycle [19-25]. The material having high surface area such as activated carbon, graphene, carbon aerogel etc. (carbon-based material) shows EDLC type behavior. EDLC constructed using two carbon-based electrodes, electrolyte and separator. When voltage is applied, there is an accumulation of charge on the electrode surface, due to potential difference opposite charged electrolyte ions are attracted towards respective electrodes and forms double layer (fig 3). To avoid recombination, double layer is formed and this double layer increases with increasing specific surface area and decreasing with distance between two electrodes [4].

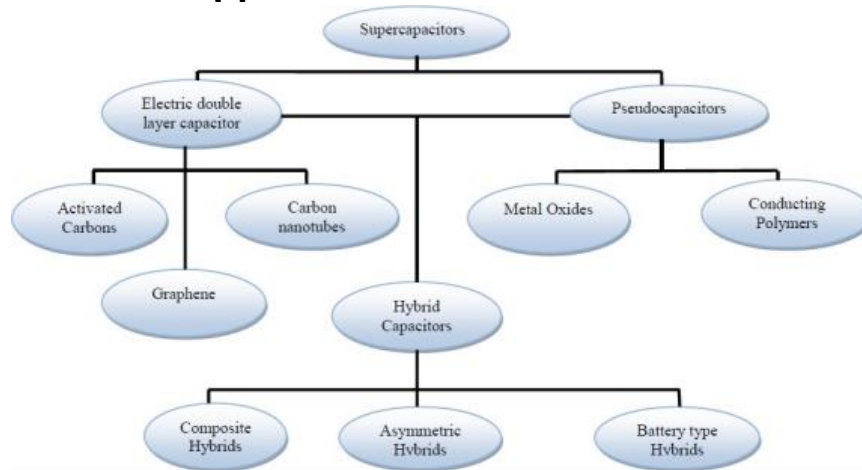


Figure 3 Taxonomy of supercapacitor

The charge storage mechanism of EDLC allows fast energy uptake and delivery lead to superior power performance. Also due to absence of chemical reaction, it avoids swelling which is generally observed in battery electrodes. Electrostatic surface charge mechanism experience limited energy density of EDLC and hence more research is focused on enhancing EDLC electrodes energy density and operating temperature range [6].

1.4 Pseudocapacitor

In the case of pseudocapacitor, charges are stored through a faradaic process where charges transferred across the electrodes. When potential applied to pseudocapacitor redox reaction (oxidation-reduction) occurred at electrodes where charges pass across the double layer and faradaic current passes through the cell. Due to the reversible faradaic process, supercapacitor allows the more specific capacitance and energy density as compared to EDLC. Transition metal oxide, conducting polymer exhibited pseudocapacitive behaviour. Even though superior energy density of pseudocapacitor materials, it suffer from poor stability and lower power density because reversible faradaic reaction generates swelling of electrode [16-17].

1.5. Hybrid capacitor

Hybrid capacitors are developed to combine advantages of EDLC and pseudocapacitor. As we know, EDLC possess excellent stability and superior power density while pseudocapacitor possesses higher energy density. Hybrid capacitor acquires all these characteristics. Hybrid capacitor combines energy source from a battery-like electrode and power source from the capacitor-like electrode. By using an appropriate combination of these two electrodes, it is possible to achieve a high-performance hybrid system. Several combinations have been tested till now as a positive and negative electrode in various types of electrolytes such as aqueous, inorganic and ionic [18]. Currently, major research has been focused on three types of system as follow:

- Composite:** Composite electrodes are combines EDLC material with pseudocapacitive materials in single electrode for example $\text{RuO}_2/\text{graphene}$. Both physical and chemical storage mechanism is involved in a single electrode [26-30]. The carbon-based material offers double-layer charge and high specific area which enhances contact between pseudocapacitive material and electrolyte while reversible faradaic reaction enhances the capacitance of composite material. Currently, binary and ternary type of composite electrodes has been used in the supercapacitor.
- Asymmetric:** The asymmetric supercapacitor couples EDLC type electrode with pseudocapacitive type electrode in a single cell. This system combines a faradaic process with non-faradaic reaction where carbon-based material coupled with a metal oxide or conducting polymer.
- Battery Type:** In battery type hybrid system two different types of electrodes combine together to form a cell. Supercapacitor type electrode is combined with a battery type electrode. In this way, both battery and supercapacitors properties can be utilized (fig 4).

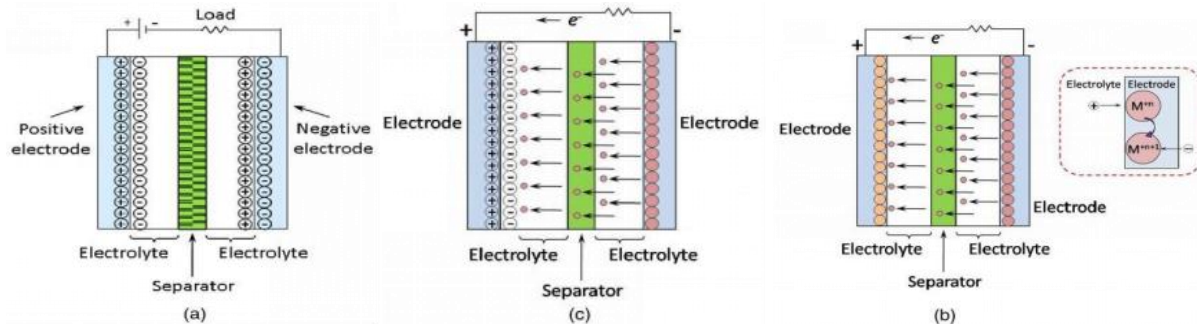


Figure 4 Schematic representation of supercapacitor types: (a) EDLC type; (b) Pseudo capacitor type; (c) Hybrid capacitor type (the figure is not to scale). [18]

2. Electrochemical Modelling

The mathematical modelling and numerical solutions are playing a vital role in design and estimation of performance of advanced energy storage systems such as batteries, supercapacitor etc. However, there are challenges in deriving and solving this model analytically and numerically such as a model that intends to cover all physical and chemical factor has to consider, conversion of charge, species and energy along with appropriate relationship for double-layer charging and redox reaction. And also, it should be applicable for all the functional layers and groups within the cell at different scales like macroscale or microscale [12]. The characteristics obtained in the process are closely related to the parameters used in the process and mainly depend on the physical, chemical, electrochemical, electrical and crystallographic parameters of electrode and electrolyte materials, design parameters of its component and supercapacitor as whole (fig 5). Hence for modelling of supercapacitor and predicting

performance such as energy, capacitance etc. proper knowledge of its component parameters are necessary [13].

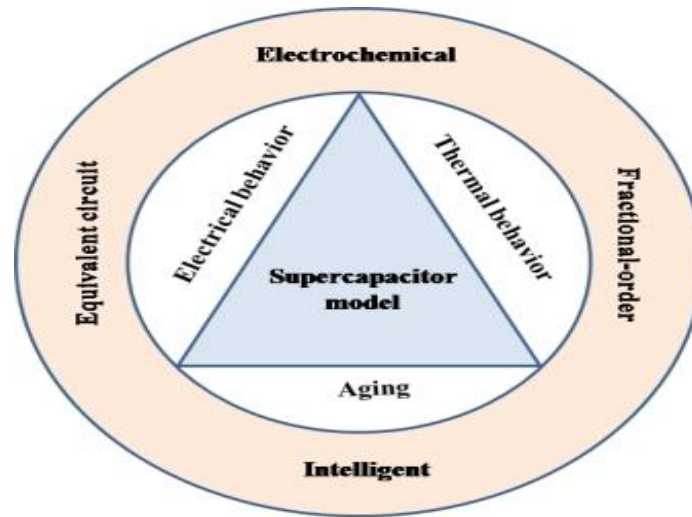


Figure 5 Various models available for Supercapacitor modelling.

2.1 Artificial Neural Network (ANN)

The mathematical model and electrical model obtained the best performance report but sometimes it becomes very cumbersome for example, in case of mathematical modelling for non-linear equation formulation become very difficult. In that case, ANN can be used for any linear or non-linear system [13]. ANN can be applicable in a wide variety of scientific and engineering applications such as control, modelling and identification [14]. Recently, ANN has been used for predicting the performance of supercapacitors and batteries [15]. The structural unit of ANN is identical as biological neurons where inputs are weighted, summed and transformed as output. A set of processing elements in ANN is called neurons (Fig. 6). Every neuron corresponds to function from one or more input to a single output. The principle behind ANN is instead of programming they learn to make a prediction.

ANN composed of three elements: input layer, hidden layer and output layer [15]. The information transmitted to the node (neurons) in the hidden layer is amplified by weight W_{ij} and piece of information coming to each node is summed and transformed and redistributed to further hidden node or output layer. The schematic diagram of an artificial neural network shown in Fig. 7 Let $S = (S_1, S_2, S_3 \dots S_n)$ represents the n inputs applied to the system [31-36].

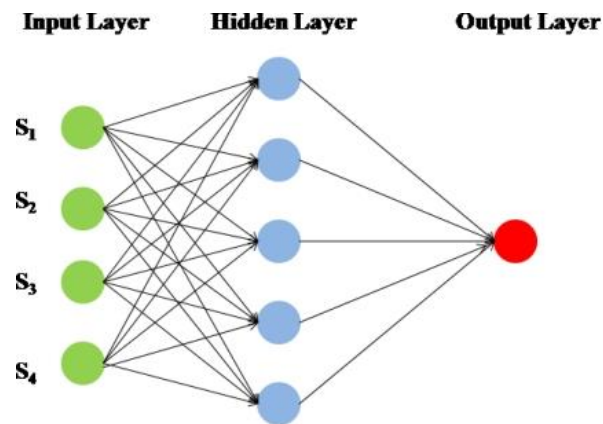


Figure 6 Artificial neural network with single hidden layer

2.2 Parameter Selection

The present model focuses on the modelling of cyclic voltammetry behavior for prediction of specific capacitance. The multilayer perceptron concept is base for present ANN model. The scripting is done in MATLAB 2016 R1. Various learning algorithms are used in the training network; this work is trained using Levenberg–Marquart back-propagation algorithm (BP). The model of three layers of feed-forward ANN consists of input layer, hidden layer and output layer (table 2). The number of neurons in the hidden layer is decided by the number of an input neurons as per rule of thumb (size of hidden neurons roughly twice the size of input neurons). The Sigmoid function is used as an activation function or transfer function for further improvement in performance [37-42].

Table 2 Artificial neural network parameters and architecture.

ANN parameters	Number/ Type
Number of neuron at Input	2
Number of neuron at Output	1
Number of neuron at Hidden Layer	10
Activation function	Sigmoid function
Learning Rule	Levenberg-Marquardt back propagation algorithm

In this modelling data generated from cyclic voltammetry characterization for Ni(OH)₂ is used for training and testing ANN model. The current density is obtained for within potential scan window for forward oxidation and reverse reduction cycle. The potential scan and cycle were used as input parameters for ANN while obtained current as output. Among the data used, 80 percent data used for training while 20 percent data was used for testing purpose. More than 1000 iterations were used to achieve correct output [43-48].

3. Model Analysis

In this model, two input neurons, potential and redox cycle (oxidation and reduction), approx ten hidden layers and one output layer as a current density are used which is shown in Fig. 7

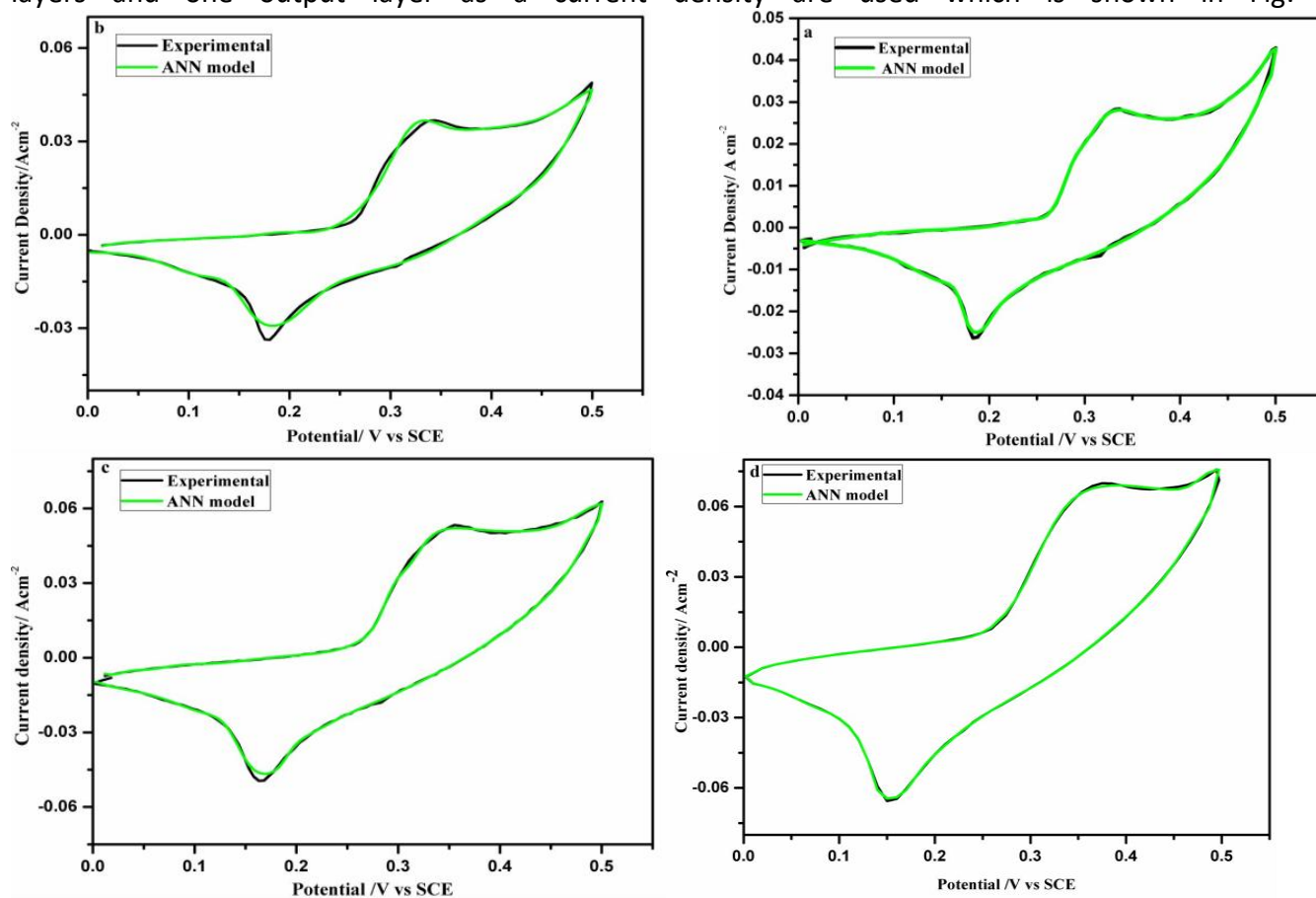


Figure 7 Comparison between CV curve obtained from experimentation and ANN modeling at a. 10mVs-1 b. 20 mVs-1 c. 30 mVs-1 d. 40 mVs-1 obtained from three electrode workstation.

Table 3. Comparison of result obtained from ANN model and Experiments.

Scan rate (mVs ⁻¹)	Experimental capacitance (Fg ⁻¹)	ANN predicted capacitance (Fg ⁻¹)	Error in %
10	958	954	0.41
20	656	652.3	0.56
30	645	641.4	0.55
40	639	636.2	0.43

The obtained error values are very small which indicates ANN can predict appropriate specific capacitance once it is thought how to predict current density (table 3). If we know then the potential for specific material, we can predict current density and which leads to the calculation of specific capacitance by putting value in the model. Such ANN model can be used for prediction of specific capacitance, energy density and power density using various materials properties. The data generated from electrochemical characterization can be used for training model and such prepared model can save the time required for rigorous experimentation.

4. Development of Energy Storage Module

4.1. Negative Electrode Preparation

4.1.1. Selection of Material

Asymmetric supercapacitor composed of one battery-type faradaic electrode (higher energy density) and one capacitor-type electrode (higher power density) can exhibit superior energy density, power density and cycle life [14]. An asymmetric supercapacitor can make full use of the differential potential window for the electrode's materials, and accordingly provide a maximum potential window for the cell. Hence selection of proper materials for a negative electrode as per positive electrode used to assemble a high-performance asymmetric supercapacitor is critical [14,15].

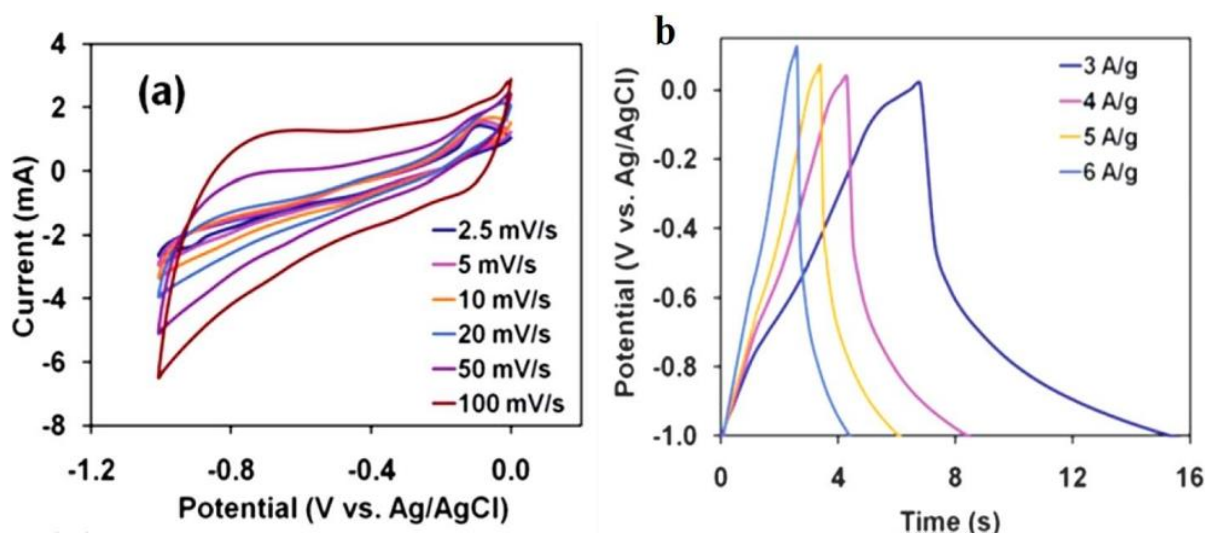


Figure 8.

Cyclic voltammetry of Fe₂O₃ at scan rates 2.5, 5, 10, 20, 50, 100 mVs⁻¹ b. GCD

In this research Fe₂O₃ deposited on nickel is selected as the negative electrode. Among the metal oxides used as negative electrode, Fe₂O₃ is attracted attention due to its characteristics such as high theoretical capacitance, ideal potential window, low cost and environmental friendliness [38,47]. The cyclic voltammetry curve is shown in Fig. 8, the potential window obtained for Fe₂O₃ is -0.85V to 0.0V[39]. For synthesized positive electrode Ni.Co LDH/rGO exhibited potential window of 0.0 V to 0.5 V hence after

assembling these two electrodes together as an asymmetric supercapacitor, the overall cell voltage can cross 2.5 V limit.

4.1.2. Synthesis Process

Nanostructured Fe_2O_3 is deposited on nickel foam by using simple successive ionic layer adsorption and reaction (SILAR) method with four beakers explained schematically in Fig. 9. The solution of 0.01M FeCl_3 and 1M NaOH as a cationic precursor and anionic precursor are used respectively. The piece of nickel foam (3 cm*2 cm) is cleaned with dilute HCL solution to remove oxides and dirt present on the substrate. The cleaned nickel foam initially dipped in cationic solution for 10s so Fe^{+3} ions can be adsorbed on the surface of the nickel foam. Next, this substrate is dipped in DI water to remove loosely bounded species.

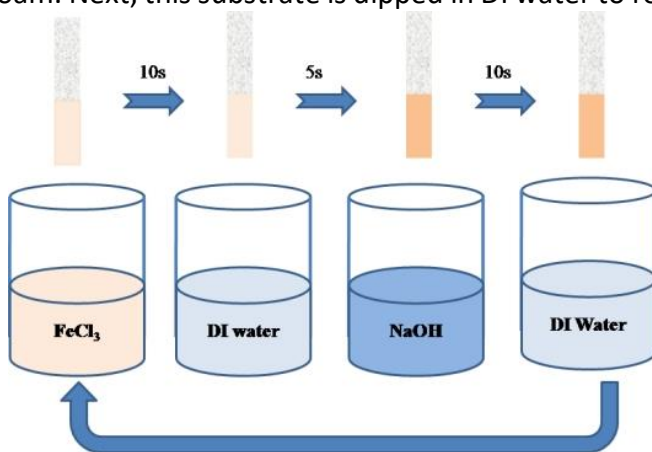


Figure 9 Schematic process of successive ionic layered adsorption and reaction (SILAR)

After that, substrate is dipped in anionic solution for 10s where OH^- ions are reacted with Fe^{+3} to form Fe_2O_3 . Finally, substrate dipped in DI water for 5s so that loosely bounded species removed. Such 150 cycles can be repeated to obtain the required layer thickness of Fe_2O_3 .

5. Results for Electrochemical Performance

The excellent performance of Ni.Co LDH/rGO deposited on nickel foam, it used for fabrication of all-solid-state asymmetric supercapacitor with Fe_2O_3 deposited on Ni foam. In this module Ni.Co LDH/rGO act as a positive electrode and Fe_2O_3 used as a negative electrode. The PVA/KOH gel was used as electrolyte as well as separator. The assembled all-solid-state asymmetric supercapacitor is electrochemically tested using cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) techniques. Fig. 10 shows the cyclic voltammetry (CV) curve for asymmetric cell Ni.Co LDH/rGO/Ni// Fe_2O_3 /Ni at scan rates 10, 20, 40, 60, 80 and 100 mVs^{-1} .

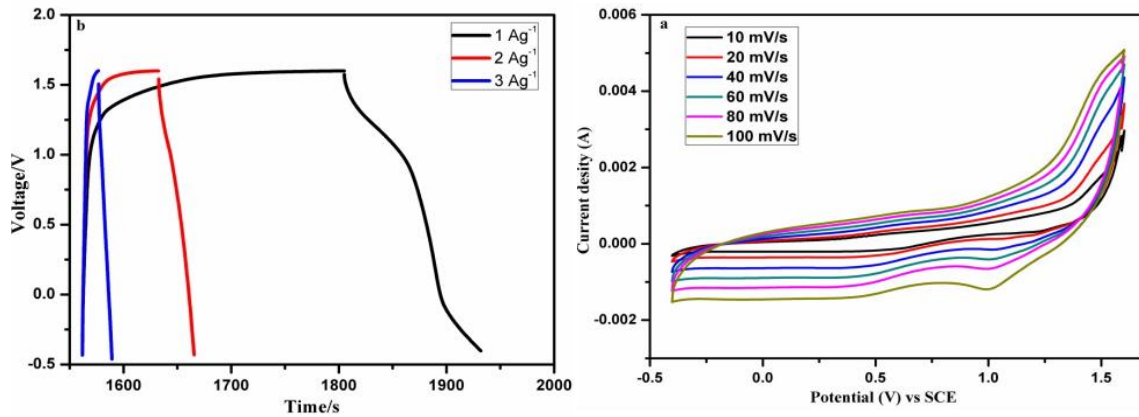


Figure 10 a. Cyclic voltammetry of Ni.Co LDH/rGO/Ni//Fe₂O₃/Ni at scan rates 10, 20, 40, 60, 80 and 100 mVs⁻¹ b. Galvanostatic charge-discharge of Ni.Co LDH/rGO/Ni// Fe₂O₃/Ni at current density 1, 2 and 3 Ag⁻¹.

The overall voltage window obtained for CV curve is -0.5V to 1.6 V. The CV profile demonstrates hybridized capacitance obtained from electrical double-layer capacitance and pseudocapacitance. The overall potential obtained for assembled asymmetric supercapacitor is 2.1 V and which is higher than the conventional battery (1.5V) for a single cell. The asymmetric cell developed Ni.Co LDH/rGO/Ni//Fe₂O₃/Ni exhibited potential window of 2.1 V while specific capacitance of 90.20 Fg⁻¹ is calculated from CV profile at scan rate 10 mVs⁻¹(fig 10 a). Fig. 10.b represents galvanostatic charge-discharge (GCD) profile for Ni.Co LDH/rGO/Ni//Fe₂O₃/Ni assembled asymmetric supercapacitor at current density 1, 2 and 3 Ag⁻¹. The nonlinear correlation with the potential obtained from GCD curve suggests pseudocapacitive behaviour for module.

Calculation for single module:

Discharge time $\Delta t = 129$ s

Active mass = 0.566 g (0.5016 + 0.0544) Voltage window = 2.1 V

$C_s = 129 \times 1 / (2.1 \times 0.566) = 110.48$ Fg⁻¹ $E = 110.20 \times 2.1^2 / 7.2 = 67.669$ Wh Kg⁻¹

$P = E \times 3600 / \Delta t = 64.32 \times 3600 / 129 = 1888.43$ W kg⁻¹

Fig. 11 a shows the variation in specific capacitance with current density for device fabricated Ni.Co LDH/rGO with Fe₂O₃ negative electrode and demonstrated specific capacitance is decreased slowly with increasing current density which indicates that the excellent rate capability of the assembled device. The cyclability of the prepared device is evaluated at 5000 cycles. Fig. 11 b represents the curve of specific capacitance versus cycles. The obtained curve demonstrated that specific capacitance goes on increasing till 1000 cycle's approx may due to availability of intrinsic active mass at nickel foam 3D network. After 1000 cycles specific capacitance decreases and make stable at 2000 cycles and after that decreases slowly. The obtained graph shows that developed cell not only exhibited excellent energy density and power density but also superior cycle life.

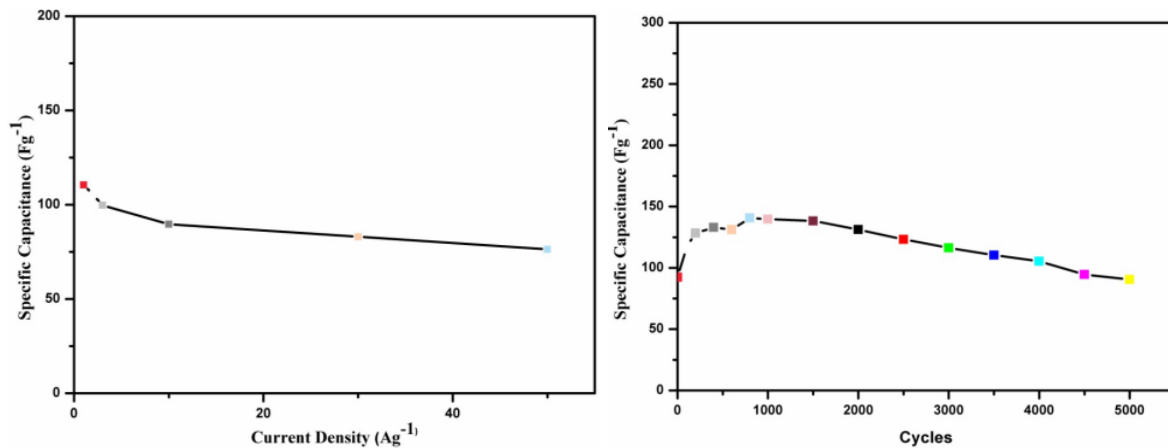


Figure 11a. Specific capacitance vs current density b. Cycle vs specific capacitance for energy storage module prepared from Ni.Co LDH/rGO/Ni//Fe2O3/Ni.

6. Conclusions

- On the basis of higher theoretical specific capacitance, and environmental friendliness nickel hydroxide- $\text{Ni}(\text{OH})_2$ based materials selected. Achieved expected electrochemical performance, intrinsic properties of electrode material through chemical bath deposition synthesis process. This process also found to be useful to fabricate binder-free electrode by direct depositing material on the substrate. The electrochemical performance measured for $\text{Ni}(\text{OH})_2$ deposited on nickel foam, exhibited a specific capacitance of 1065 Fg^{-1} at current density 1 Ag^{-1} .
- Due to semiconductor nature of $\text{Ni}(\text{OH})_2$, possess lower electrical conductivity hence in order to enhance the electrical conductivity of $\text{Ni}(\text{OH})_2$, highly conductive reduced graphene oxide combined with nickel hydroxide which not only improve electrical conductivity but also specific surface area.
- nanosheet of $\text{Ni}(\text{OH})_2$ grown on rGO sheet uniformly spread on nickel foam network exhibited higher porosity which allows easy access to the electrolyte. The specific capacitance obtained for $\text{Ni}(\text{OH})_2/\text{rGO}$ is 1947 Fg^{-1} .
- Further due to cobalt doping in $\text{Ni}(\text{OH})_2$ stability of composite improved throughout. Due to addition of cobalt, nanosheets morphology get transferred into nanorods and Ni.Co LDH nanorods grown vertically on rGO sheet which was uniformly spread on nickel foam which further increases porosity and specific surface area of electrode. The synthesized sample showed the superior specific capacitance of 2957 Fg^{-1} which is nearly equal to the theoretical specific capacitance of $\text{Ni}(\text{OH})_2$ ($\sim 3000 \text{ Fg}^{-1}$). This nanomaterial found to be more suitable for electrodes.
- Electrochemical model is developed in artificial neural network (ANN) from cyclic behavior of material in order to predict the specific capacitance of nickel hydroxide - $\text{Ni}(\text{OH})_2$ based nanomaterials. The specific capacitance measured from ANN model and in experiments shows deviation within 1%. Thus developed model can be used for prediction of capacitance from available data and will reduce experimental work, time and cost in further research
- In order to verify the electrochemical performance of synthesized electrode Ni.Co LDH/rGO, all-solid-state asymmetric supercapacitor (energy storage module) successfully developed with

Ni.Co LDH/rGO/Ni as a positive electrode and Fe₂O₃/Ni as a negative electrode. The negative electrode Fe₂O₃/Ni exhibited differential potential window and which is reflected in developed cell Ni.Co LDH/rGO/Ni// Fe₂O₃/Ni overall voltage as 2.1 V.

- The PVA/KOH gel used as the electrolyte is worked successfully as electrolyte and separator. The specific capacitance for energy storage module measured from the GCD curve delivered 110.9 Fg⁻¹ at a current density of 1 Ag⁻¹ which is higher than the values obtained in the literature.

7. Future Scope

- Nanomaterials with three metal oxide combinations can be tested for electrode material.

Apart from nano-flower and nanorods other nanostructure with high surface area and porosity maybe obtained by changing synthesis process parameters or process. Electrochemical ANN model based on parameters such as surface to volume ratio, pore size, scan rate can be developed for prediction of electrochemical performance.

- Asymmetric cell can be developed using ionic electrolyte or redox electrolyte so that voltage may reach up to 4V. Negative electrode materials other than Fe₂O₃ may synthesize to achieve higher active mass. Design of asymmetric supercapacitor can be modified such as sandwich, layer by layer etc.

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