

ANNEALING OF ELECTRODEPOSITED NICKEL ON LOW CARBON STEEL FOR SUPERCAPACITOR APPLICATIONS

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Nickel oxide electrodes, which are promising electrodes for use in energy storage devices, are prepared by cathodic deposition in an ionic liquid containing nickel (II) oxide plating solution. Ni coated steel was annealed in a muffle furnace at 700 K for 30, 45 and 90 minutes. Nickel based steel electrodes were oxidised to NiO with heat treatment and they were transferred to KOH electrolyte to test their electrochemical behaviours. Cyclic voltammograms of NiO coated steel electrode in an alkaline electrolyte have exhibited both rectangular shape and the faradaic peaks between -0.1 V and 0.5 V vs Ag/AgCl reference electrode at sweep rates up to 200 mV s⁻¹. Specific capacitance of nickel film annealed for 45 minutes was greater than that for 30 and 90 minutes. 45 minutes annealed nickel oxide, evaluated by cyclic voltammetry at a scan rate of 10 mV s⁻¹, illustrates a maximum specific capacitance of 105 mF cm⁻².

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1. Introduction

Increased depletion rate of fossil-fuels is a problem and researchers aim to find alternative sustainable energy types. Energy storage from renewable energy sources is also another problem for governments and industry. Energy storage devices providing high power and energy density are required to be able to fulfill the energy demand of some applications such as automotive industry and household devices. Some of these energy storage devices are supercapacitors and batteries. Supercapacitors generally have high power density as they can charge-discharge in a short timescale. Therefore, supercapacitors could be charged more quickly than batteries and besides supercapacitors can be able to store a great deal of energy than electrolytic capacitor types.

Supercapacitor could be a promising energy storage device in order to satisfy people's demand in the long term with its high power density, quick charge and discharge time and longer life time. Ordinarily supercapacitors are not expected to store much energy when they are compared with lithium-ion batteries. Supercapacitors are potential energy storage electrode for car companies looking for short charge and discharge time of energy storage devices in order to power the electrical cars. A supercapacitor can be charged/discharged more than 100,000 times with more than 95 % capacitance retention [1]. While fossil fuel operated cars and supercapacitor powered cars can be charged more or less at the same time interval, cars using supercapacitors cannot harmful to the nature [2,3]. However, supercapacitors have a self-discharge rate that it is not very beneficial to be left too long without working. Throught the last decade, energy deposition area has risen up with a great attention that researchers have started to study combining different electrodes and electrolytes in order to obtain supercapacitors which could have high power density, long effective life durations and less charge and discharge times [4].

Supercapacitor could have a redox type or electrical double layer capacitor (EDLC). Redox type supercapacitor known as pseudocapacitor or faradaic type capacitor stores energy thanks to the redox reactions happening between an electrolyte and an electrode (anode or

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cathode). Basically energy generation is provided with the movement of electrons in these layers via an external wire. EDLC type supercapacitors storing energy electrostatically consist of carbon based electrodes [5]. However, pseudocapacitor electrodes are based on conducting polymers or metal oxides/hydroxides or their mixture [6]. To be able to produce a supercapacitor could be an easy process but in order to obtain sustainable and inexpensive electrode-electrolyte combination is required.

One of the biggest problems for producing supercapacitor electrode is to find a suitable electrode that researchers generally have faced. Thin film coatings are commonly obtained for pseudocapacitor modified electrode. Metal oxides including cobalt [7], copper [8], manganese [9], tin [10] and nickel [11] have been obtained electrochemically or by thermal oxidation on various current collectors (such as copper, aluminium, stainless steel or graphite) for supercapacitor applications [12,13]. Nickel oxide could have different morphologies depending on growth conditions and thus a high specific capacitance [14]. NiO is chemically stable that making it a proper electrode candidate for supercapacitors [15].

Metals/alloys deposition on a substrate is an important step to obtain modified electrode. Ionic liquids have been studied recently for electrodeposition of metals. Deep Eutectic solvents (DESs) share similar properties of ionic liquids. DESs are inexpensive, non-toxic and easy to prepare compared with ionic liquids. Basically DESs can be prepared with an exact amount of quaternary ammonium salt which is choline chloride in this study and a hydrogen bond donor (HBD) which is ethylene glycol here [16].

The main aim of this study is to design an efficient and sustainable electrode in order to increase the performance, stability and workability of supercapacitor applications. It is also aimed to understand the stability and capacitive performance depending on charging timescale during reduction and oxidation reactions. Ni coated electrodes were electrodeposited cathodically from a deep eutectic media on an inexpensive steel substrate and then nickel coating was thermally oxidised to NiO. Specific capacitance of modified electrodes was measured by means of cyclic voltammetry.

2. Experimental

100 mM Nickel II Chloride (NiCl_2 , 99 % purity) dissolved in Ethaline was used as deposition electrolyte. No other purification method was applied to deposition and cycling electrolytes. Ethaline was prepared by mixing two parts of choline chloride with one part of ethylene glycol. The mixture was heated to 50 ° C until a homogenous solution was obtained (about 30 minutes). Heating can also remove water molecules inside the solution. The mixture became a homogenous green colour in the presence of Nickel (II) chloride powder. 4 cm² steel was grinded with the emery papers (200 grids to 800 grids) to clean the impurities of the surface. To be able to deposit the nickel on steel at room temperature three-electrode system which 6 cm² titanium coated platinum as a counter electrode, silver (Ag/AgCl) wire as a reference electrode and steel itself as a working electrode were used. The reason why bigger size platinum was chosen is that not to limit redox reactions of counter is required to coat film on a steel working electrode. As long as a small size of platinum counter electrode is used, the rate of redox reaction on platinum could limit redox reaction of working electrode and therefore the reaction of counter electrode could not be on desired level. Nickel was electrodeposited on steel by using conventional three-electrode cell (AMETEK VersaSTAT 3 potentiostat) by applying constant potential of -1.0 V for 300 seconds at 65 ° C. Nickel coated steel was washed up with pure water and dried with hot air. It was then splitted into 3 equal pieces in order to be annealed in a furnace for 30, 45 and 90 minutes. Heat treatment was applied at 700 K to observe distinct structure of nickel film coating. All films annealed at 700 K were transferred to 1 M KOH for polarisation. Bare steel was also cycled in KOH media to compare with nickel based electrodes in terms of electrochemical behaviour. Electrochemical properties of electrodes were elucidated in 1M KOH with three-electrode system to observe their electroactive potential range. According to electroinactive potential range of bare steel, nickel based films on steel annealed for 30, 45 and 90 minutes were

scanned in 1M KOH between -0.1 V and 0.5 V at the scan rate of 200 mV s⁻¹, 100 mV s⁻¹, 50 mV s⁻¹, 20 mV s⁻¹ and 10 mV s⁻¹, respectively.

3. Results and discussion

Cyclic voltammogram of Ethaline containing NiCl₂ was studied at room temperature (22 ± 2 °C) and at 65 °C. Their cyclic voltammogram responses are compared in Fig. 1. A reduction started at around -1.05 V when cyclic voltammogram was conducted at room temperature. However a reduction reaction was observed at around -0.55 V at 65 °C in the presence of NiCl₂ in Ethaline, which belongs to the reduction of Ni²⁺ to nickel metal. As reduction current of Ethaline containing NiCl₂ at 65 °C is higher than at room temperature, reduction of Ni²⁺ is more possible at high temperature. Therefore, nickel growth was obtained at higher temperatures. An oxidation of Ethaline having 0.1 M ZnCl₂ occurred at around -0.2 V at room temperature. It could be either oxidation of iron or oxidation of Ni²⁺ to Ni³⁺. The main objective here is to electrodeposite nickel on steel. For this reason cyclic voltammetric study was conducted to select deposition potential depending on temperature. Dissolution of electrode could be found in the literature [17]. A reduction peak of Ethaline having NiCl₂ salt on steel at 65 °C observed at around -0.75 V can be associated with reduction of Ni²⁺. As potential window of ionic liquids is generally wide, hydrogen evolution of Ethaline cannot be observed at this potential. The second reduction started at around -1.0 V is related to hydrogen evolution because bubbles were covered at the steel surface. Nickel included Ethaline was cycled at 65 °C until -1.2 V because the current density was high enough (around 40 mA cm⁻²) to compare with cyclic voltammogram of Ethaline containing NiCl₂ at room temperature. Dissolution charge (integration of current time) of nickel deposited on steel at 65 °C was also higher than that at room temperature. Deposition and dissolution of nickel was anticipated because viscosity of a deep eutectic solvent decreases upon increasing temperature [18]. As the viscosity of deposition electrolyte decreases, the rate of mass diffusion to electrode surface increases during polarisation [19].

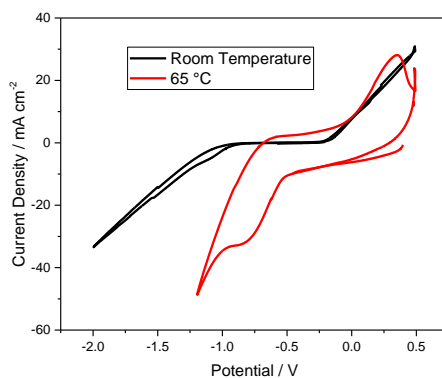


Fig. 1. Cyclic voltammograms of Ethaline having 0.1 M NiCl₂ at room temperature (black line) and at 65 °C (red line) at the scan rate of 20 mV s⁻¹. Steel working electrode, platinum coated titanium counter electrode and Ag wire reference electrode were used.

As Fig. 1 illustrates that nickel coating could be obtained at 65 °C from choline chloride and ethylene glycol based electrode containing NiCl₂ by applying a potential more negative than -0.6 V. Nickel film was deposited potentiostatically onto a low carbon steel by applying -1.0 V. Fig. 2 presents chronoamperometric (black line) and chronocoulometric (red line) responses of nickel deposition from Ethaline on a bare steel shown in the inset of Fig. 1a. Electrodeposited nickel on steel is presented in the inset of Fig. 1b. Hydrogen evolution occurs during nickel deposition in ionic liquid which could change the surface morphology of coating. When the potential of -1 V was directly applied, sudden decrease of current (around 0.07 mA cm⁻²) was observed because

nickel deposition started. The application of constant potential after 50 second causes less current density (around 0.025 mA cm^{-2}). However, charge plot (red line of Fig. 2) is almost linear because deposition of nickel occurred with hydrogen evolution reaction.

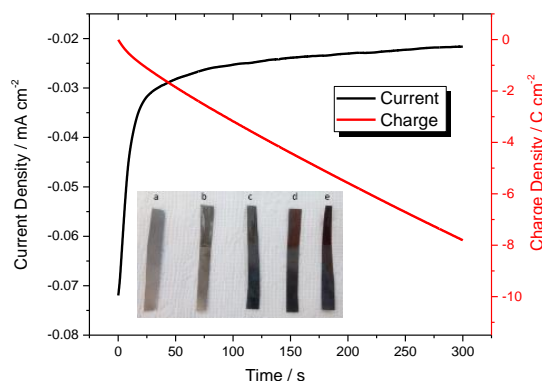
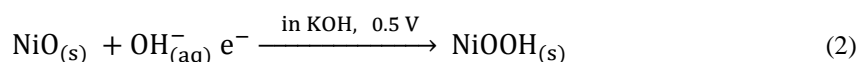
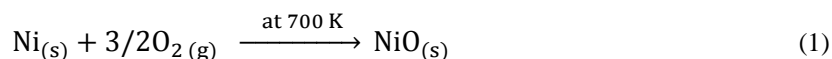


Fig. 2. Chronoamperometry and chronocoloumetry data of nickel deposition on a steel substrate from choline chloride based ionic liquid containing 0.1 M NiCl_2 by applying constant potential of -1 V . Inlet: images of a) bare steel; b) nickel coated steel; c) annealed nickel for 30 minutes; d) annealed nickel for 45 minutes e) annealed nickel for 90 minutes.

Electrodeposited nickel was heated at 700 K in a pre-heated furnace in order to obtain NiO coatings. The process of nickel oxidation at high temperature was discussed elsewhere [20]. Nickel coated steels were annealed for different times and their photos were taken after annealing (presented inlet of Fig. 1). Colour of nickel coating was greenish grey, brown and black after 30, 45 and 90 minutes annealing processed at 700 K , respectively as shown in Fig. 1. Colour of steel also was different after annealing. Reaction of nickel oxidation in a furnace is given as Equation 1.



Nickel was electrodeposited from one of the deep eutectic solvents (Ethaline) containing Ni^{2+} ions on steel. Nickel coated steel was oxidised in a muffle furnace to have NiO. Resulting electrodes were transferred to KOH media for cycling. NiO coated steel was cycled in KOH between -0.1 V and 0.5 V at the scan rate of 20 mV s^{-1} . Cyclic voltammetry response of NiO coated steel annealed for 90 minutes is given in Fig. 3a. NiO coated steel film can be evolved after 2nd cycle. When deposition and cycling electrolytes are different, evolution of electrode could require large timescale (typically 20 scans) [21]. Cyclic voltammetry shows that NiO modified electrodes annealed at 700 K can reach an equilibrium point after only two scans.

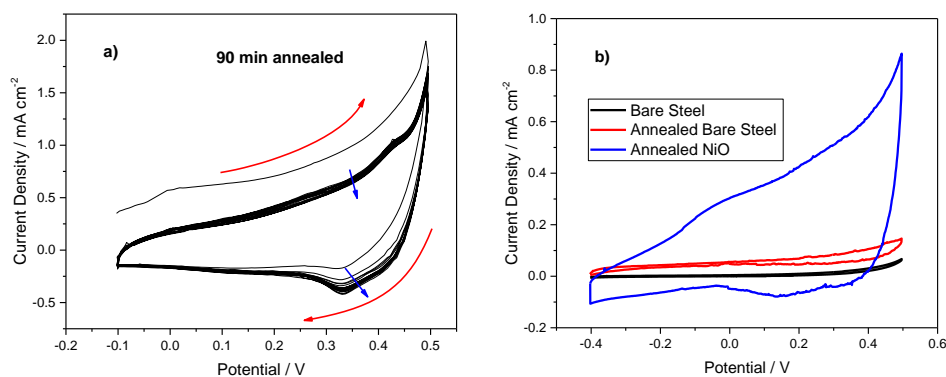


Fig. 3. First 20 cyclic voltammogram curves of NiO thin films annealed for 90 minutes. b) Cyclic voltammogram of bare steel (black line), annealed bare steel and annealed nickel oxide in 1 M KOH at the scan rate of 20 mV s^{-1} .

Electrochemical performance of NiO coated steel was compared with bare steel and annealed bare steel in KOH electrolyte (see Fig. 3b) in order to observe the effect of annealing. Bare steel is electroinactive in KOH between -0.4 V and 0.5 V in comparison with annealed nickel film on steel. Charge of annealed bare steel was slightly higher than bare steel without heat treatment. However, charge of annealed nickel coated electrode increased significantly. The reaction mechanism of NiO in KOH has been studied [22,23] and its equation is given in Equation 2.

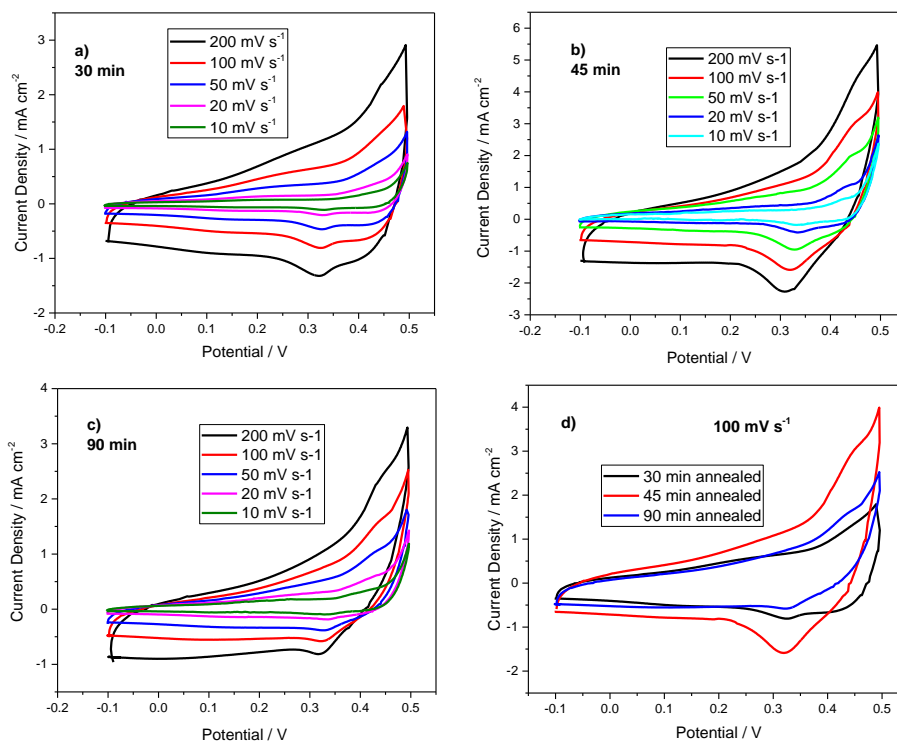


Fig. 4. Cyclic voltammogram of annealed nickel based electrode for a) 30 minutes; b) 45 minutes; c) 90 minutes in 1 M KOH electrolyte at various scan rates. d) Cyclic voltammogram of NiO annealed for different times at the scan rate of 100 mV s^{-1} .

Fig. 4 illustrates the cyclic voltammetry curves of annealed nickel film for different times in 1 M KOH electrolyte. Cathodic peaks generally do not shift significantly. Cyclic voltammetric

responses of nickel based electrode on steel have both quasi-rectangular shape and faradaic redox shape. NiO/NiOOH reaction cannot be ascribed purely to the EDLC. Rectangular shape of cyclic voltammogram is dominant for nickel based electrode annealed for 30 and 90 minutes. They both also have faradaic reduction peaks at around 0.3 V. Reduction peaks of NiO film on steel annealed for 45 minutes are greater than that of NiO films on steel annealed for 30 and 90 minutes. As redox peaks of nickel based film heated at 700 K for 45 minutes is greater than that for 30 and 90 minutes, its capacitance was greater than others (presented in Table 1). Cyclic voltammetric responses of the coatings, annealed for different times, in KOH electrolyte at the scan rate of 100 mV s⁻¹ are given in Fig. 4d. Charge (differential of current vs. time) of the film annealed for 45 minutes is larger than other films. Specific capacitance calculated from raw data of Fig. 4 is tabulated in Table 1. Specific capacitance of the film annealed for 45 minutes is twice and three times greater than the film annealed for 90 minutes and 30 minutes respectively because of probable microstructure differences depending on heating time. The specific capacitance of nickel based steel electrode was calculated according to the equation of

$$C = \frac{\int I dV}{v}$$

where I is the current density response in A cm⁻², V is the potential in V and v is the scan rate in V s⁻¹.

*Table 1 Specific capacitance of nickel based film annealed at different times.
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Fig..*

	Scan rates				
	200 mV s ⁻¹	100 mV s ⁻¹	50 mV s ⁻¹	20 mV s ⁻¹	10 mV s ⁻¹
NiOx on Steel anneald for 30 min	12.5 mF cm ⁻²	15.5 mF cm ⁻²	19 mF cm ⁻²	24.6 mF cm ⁻²	30.5 mF cm ⁻²
NiOx on Steel anneald for 45 min	20.4 mF cm ⁻²	30.5 mF cm ⁻²	45.5 mF cm ⁻²	70 mF cm ⁻²	105 mF cm ⁻²
NiOx on Steel anneald for 90 min	12.1 mF cm ⁻²	22.5 mF cm ⁻²	24.6 mF cm ⁻²	40.5 mF cm ⁻²	56.5 mF cm ⁻²

Specific capacitance of bare steel and annealed NiO coated steels as a function of scan rates is presented in Fig. 5. The specific capacitance of bare steel is much lower than that of nickel based material on steel at the same scan rates. The specific capacitance of 105 mF cm⁻² for NiO/NiOOH coated steel annealed for 45 minutes was calculated at a scan rate of 10 mV s⁻¹. Specific capacitance of nickel based coating annealed for 30 minutes and 90 minutes is much lower as they are 30.5 and 56.5 respectively at the scan rate of 10 mV s⁻¹. High area of electrode-electrolyte interfaces can provide high electroactive coverage and short diffusion length. Results showed that nickel coated steel annealed at 700 K for 45 minutes must have enhanced interface areas between nickel based electrode and alkaline electrolyte.

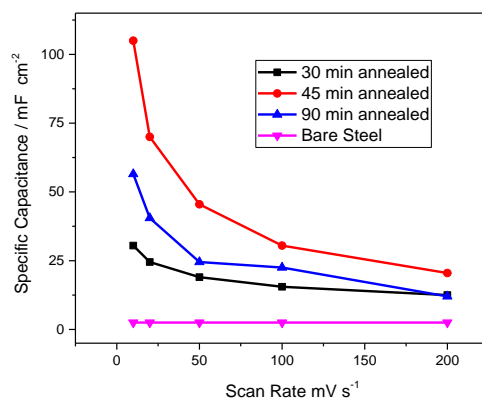


Fig. 5. Specific capacitance as a function of scan rate of nickel oxide films annealed at 700 K for various time.

4. Conclusion

Cyclic voltammogram of from choline chloride and ethylene glycol based deep eutectic solvent containing NiCl_2 proves that nickel can be electrodeposited at the temperature of 65 °C by applying a potential more negative than -0.6 V. Nickel film was electrodeposited potentiostatically onto a low carbon steel by applying constant potential of -1.0 V. Nickel coated steel electrodes were heated at 700 K in a muffle furnace to oxidise nickel film to NiO for 30, 45 and 90 minutes. NiO coated low carbon steel electrodes were transferred to KOH electrolyte to cycle between -0.1 V and 0.5 V. Nickel based film on steel can be evolved after quickly in KOH electrolyte (after typically two cycles).

Capacitance performance of annealed nickel coated steel was compared with bare steel and annealed bare steel in KOH electrolyte. Bare steel was electroinactive in KOH between -0.4 V and 0.5 V and capacitance of bare steel and annealed bare steel was less than that of NiO coated steel. The reaction mechanism of modified electrode in KOH electrolyte is between NiO and NiOOH. Cathodic peaks in the cyclic voltammetry curves of annealed nickel film generally do not shift significantly in 1 M KOH electrolyte. Quasi-rectangular shape and faradaic redox shape of cyclic voltammetric responses of nickel based electrode on steel were observed. NiO/NiOOH reaction is ascribed to both electrical double layer capacitance and pseudocapacitance behaviour. Specific capacitance of NiO film on steel annealed for 45 minutes are greater than that of NiO films on steel annealed for 30 and 90 minutes. The specific capacitance of nickel based material on steel is much greater than that of bare steel at the same scan rates. The maximum specific capacitance of 105 mF cm^{-2} was calculated for NiO/NiOOH coated steel annealed for 45 minutes at a scan rate of 10 mV s^{-1} .

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