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RESEARCH REPORT

A facile method for fabricating porous Ni/NiO nanocomposites for supercapacitor applications

by

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Abstract

As the requirements for energy storage increased, electrochemical capacitors (ECs) enjoy the popularity nowadays. Compared to batteries, ECs have faster charge/discharge rate, higher reliability, and relatively higher specific power density. This work focused on the fabrication of NiO/Ni composite with a facile method, including electrochemical co-deposition, dealloying, and annealing steps. Notwithstanding its synthesis simplicity, the porous structure yielded very high capacitance of ca. 930 F g⁻¹ at the current density of 1 A g⁻¹, together with good cycling stability. In this report, the synthesis and electrochemical properties of NiO/Ni electrode are described. It was found that during synthesis, annealing temperature has a direct effect on the structure, as well as the component of composite framework. The electrode annealed at 300 °C exhibited the pseudocapacitor (redox-capacitor) behavior. Films treated with higher temperature shows poor capacitive behavior, as more nickel oxide generated on electrode surface layer, isolating the porous metal core network, leading to the increased resistivity of electrode.

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Chapter 1 – Introduction

Climate change is highly addressed now, due to the continuously decreasing amount of fossil fuel, and moves the whole society towards the development of friendly sustainable energy. Solar cell, wind energy, geothermal energy, as well as renewable electric cell, are all included in the research agenda. However, even if large amount of energy is produced by these new systems, the storage of which is also crucial. Hence energy storage device [1] is a key element in collecting the wasted kinetic energy, also useful as buffer for electricity supply.

For electrical energy storage, batteries are commonly considered as chemical energy storage [2], together with electrochemical capacitors (ECs) [3], which are normally categorized as capacitive energy storage, they provide major components for energy storage.

1.1 Re-chargeable batteries

Re-chargeable batteries have been developed for over 200 years, although in terms of development rate, re-chargeable batteries are not comparable with IT products, even the fashion show design, but they are competing to be more and more crucial important in human's daily life.

Re-chargeable batteries can be considered as one of the most successful developed techniques in electrochemical field bar none.

A battery normally contains two electrodes and the electrolyte solution. They work together to make ions transfer through the positive and negative electrodes, thus makes the electrodes linked together. Chemical reactions occur in tandem at both electrodes, electrons are involved in the reactions, hence the current is produced which can be used as electrical energy.

Batteries compete with each other using the terminology energy density and power density. Ragone plot is the diagram showing the relationship of both. In terms of electric vehicles (EVs), power density indicates how fast the vehicle can go, while energy density tells how far one can go on a single charge, when using the separated battery as the energy source [3]. Fig. 1.1 shows the competitive relationship within several hot batteries and capacitors.



Fig. 1.1 Ragone plot, for a comparison of electrochemical capacitors, and various batteries

In rechargeable battery family, nickel–cadmium, nickel–metal hydride and lithium-ion (Li-ion) [4] are three main members, of which the most popular one should be Li-ion battery, which is tightly being researched, conquer not only on the portable devices, also on EVs.

Standards must be reached for practical applications, that is, a high performance battery must store more energy per unit volume and weight, and it must be capable of undergoing many thousands of charge-discharge cycles [2], even more importantly, it should be highly safe when practically being used. However, during applications, especially on EVs underline the limitations of rechargeable batteries on those aspects.

1.2 Electrochemical Capacitors (ECs)

Benefiting from the physical storage mechanism, ECs owns the much longer cycling life comparing to the batteries. Apart from this, ECs possess fast charging/discharge rate---can be charged within seconds, high reliability, and wide operating temperatures, which assist it roaring to be another important energy recovery system nowadays. Illustrated by Fig. 1.1, we can see

clearly that ECs seize higher power density then batteries; however, they sacrifice the energy density, which is centrally under criticism. Table 1.1 shows several important factors comparing Li-ion with ECs energy storage system [5].

Charactistic	Li-ion batteries	ECs
Charge time	3~5 mins	~1 sec
Discharge time	3~5 mins	~1 sec
Cycle life	<5000 @1C rate	>500,000
Energy density (Wh/kg)	70-100	5
Power density (kW/kg)	0.5~1	5~10
Cost/Wh	\$1~2	\$10~20
Cost/kW	\$75~150	\$25~50

Table 1.1 Comparison of several important factors of the Li-ion Batteries and ECs [5].

While energy storage of the capacitors can be derived with formulae 1-1,

$$E = \frac{1}{2}CV^2 \tag{1-1}$$

Where C is the capacitance (in farads), V (in volts) indicates the applied potential difference to which the capacitor is charged, and E is the energy (in joules).

Generally, ECs include two storage types, electrochemical double layer capacitors (EDLCs) together with pseudocapacitors. Firstly, EDLCs, the most common devices at present, serves large surface area to attract the charge carriers [3]. Secondly, pseudo-capacitors or redox supercapacitors [6], uses fast and reversible surface or near-surface reactions for charge storage. Transition metal oxides which are widely, deeply under research, are included into ECs.

1.2.1 EDLCs

Up to today, a number of companies around the world currently manufacture EDLCs as a commercial energy storage product for applications in power quality, electric vehicles, etc., see Fig.1. 2. Name EDLCs comes from its working principle, they stores electrical energy using the electric double layer that is created at the interface between the conductive solid material and the electrolyte. Fig. 1.3 shows that they do not contain a dielectric; instead, EDLCs use the electric double layer to function as the dielectric.



Fig. 1.2 EDLCs products, serves as energy backup forvarious practical applications.



Fig. 1.3 Schematic diagram of EDLCs

EDLCs store electrical charge in a similar manner to the conventional capacitors, the amount of electrical charge accumulated by pure electrostatic forces depends on two factors: one is the surface area between the electrode/electrolyte interfaces, while another is the ease of charge

carriers to access the interface [7]. In 1966, The Standard Oil Company, Cleveland, Ohio (SOHIO) patented a device that stored energy in the double layer interface which had shown to the world that the double-layer at the interface behaves like a capacitor of rather high specific capacity.

The specific capacitance can be calculated with equation 1-2, see following:

$$\frac{C}{A} = \frac{\varepsilon}{4\pi\delta} \tag{1-2}$$

Where C is the capacitance (in farads), A is the electrode/electrolyte interface surface area, ε is the relative distance from the electrode surface to the center of the ion layer (usually being of the order of a few angstroms).

Capacitance is proportional to the surface area of the electrodes and inversely proportional to the magnitude of the distance between the two opposite electrodes, the closer the plates are with the premise of no contacting between them, the greater the capacitor's capacitance will be. Therefore, material who exhibit specific surface area (SSA), can attribute to the higher capacitance.

Associated with an ion-permeable layer between two electrodes, EDLCs prevents electrical contact, but still gives the green light to ions; let them transfer through that separator layer. Often targeted as porous carbon or carbon aerogels, activated carbonaceous EDLCs have been extensively studied for their high porosity, large SSA, ease availability. Glassy carbon, amorphous carbon, carbon black, fibers, nanotubes and graphene are allotropic forms of carbonaceous materials [8]. Glassy carbon [10, 11~12] (GC), which has a very low electrical resistivity, is quite able to yield high power density EDLCs. Amorphous carbons can yield high SSA and be utilized as EDLCs, which is abundant solidified deeply beneath the earth's surface as coal, however, as they are more activated, their electrical conductivity may become worse because the cross sections for electron transfer in their bulk [13] structure become narrower. Again EDLC electrodes have been produced from high surface-area carbon black (CB) [14~15], which owns small particle size, hence a lot of binder maybe be needed, which will be the main drawback, namely the conductivity of the electrode may not be guaranteed. Activated carbon fibers (ACFs) [16, 17~18] are commercially available due to their high electrochemical

performance, which is ascribed to their great SSA. Carbon nanotubes (CNTs) [11, 19~20] are also one of the promising carbonaceous materials, together with ACFs, CNTs possess high SSA, but their performance highly depends on the purity and morphology. Oxidization treatment, heat treatment and nitric acid treatment are all being published over the world. Graphene emerges to be an exciting issue even for EDLCs, lately. Using IL-based electrolyte solution [21~23], it was possible to operate grapheme-based EDLCs at 3.5 V demonstrating energy density close to 32 Whk g⁻¹.

As explained above, EDLCs do not use a chemical reaction such as a redox reaction but rather store electricity by means of the physical adsorption of ions to the large specific surface area of activated carbon. Compared to aluminum electrolytic capacitors, EDLCs offer larger capacity, but their larger internal resistance means that their use as ripple absorption for alternating current circuits is not appropriate. For this reason, EDLCs are mainly used like rechargeable batteries, to provide energy backup in direct current circuits.

1.2.2 Evolution of redox supercapacitors

Not involved in the EDLCs, redox reactions actively appear on the surface of pseudo-capacitors, thus another using name should be redox supercapacitor. The components of pseudocapacitors must meet the listed demands: (1) electron conduction, (2) ion conduction, (3) charge storage, and (4) fitting physical structure of the electrode itself [2]. Nanocrystalline such as SnO_2 , RuO_2 , IrO_2 or Fe_3O_4 [24] as well as electronically conducting polymers, have been widely researched in the past decades. In general, these transition metal oxides suffer from poor conductivity [25] compared to EDLCs, in addition, RuO_2 and IrO_2 are limited in commercial application to their high cost, hence, novel materials and structures with proper components to support better conductivity and reasonable cost are impending to be developed.

Grown on stainless steel substrate, amorphous manganese oxide was coated onto crystalline SnO_2 nanowires, and a specific capacitance (based on MnO_2) as high as 637 F g⁻¹ [25] is obtained at a scan rate of 2 mV s⁻¹ in 1 M Na₂SO₄ aqueous solution. With a very simple solution-based preparation method, SnO_2/MnO composite can be the high efficiency electrode material.

$$MnO_2 + M^+ + e^- \leftrightarrow MnOOM \tag{1-3}$$

M can be Li^+ , Na^+ , K^+ , the thin MnO_2 layer coated on SiO_2 provided more chances to absorb M^+ , rendering the system high specific capacitance.

1.2.3 Nickeliferous redox supercapacitors

Porous nickel oxide is always attracting peoples' attention due to its lower cost and easy availability. Lately, A.I. Inamdar [26] etc. published a chemical bath deposition (CBD) method to synthesize porous nickel oxide thin films with high SSA, see Fig. 1.4, which renders Cs (specific capacitance) values to be 104.2 and 51.79 F g^{-1} at 1mA cm⁻² with NaOH and KOH electrolytes, respectively. In this method, NiO were deposited onto the indium doped tin oxide (ITO) coated conducting glass substrates. A certain solution involving nickel nitrate, together with its PH value, is the key point in CBD method.



Fig. 1.4 SEM profile of NiO thin film, showing the porous architecture

The electrical reaction during charge (producing electrons, Ni (II) is oxidized to be Ni (III)) and discharge (extraction of electrons, Ni (III) is reduced to be Ni (II)) is following:

$$NiO + yOH^- \leftrightarrow yNiOOH + e^-$$
 (1-4)

Where y can either be Na^+ or K^+ , the redox reaction depends on the rate of oxidation of H₂, and the Na, K metal ions present in the electrolyte. During the redox reaction, nickel oxide is oxidized to metal nickel hydroxide, i.e. to NaNiOOH or KNiOOH.

Apart from NiO porous thin film, NiO nanorod arrays are another fully developed approach served as supercapacitors. Zhiyi Lu [27] etc. did a series of new trying to fabricate NiO nanorod arrays on Ni foam with simple hydrothermal method, see Fig. 1.5. It finally turns out to perform very well both on specific capacitance (2018 F g⁻¹ at 2.27 A g⁻¹) and power density (1536 F g⁻¹ at 22.7 A g⁻¹), as well as good cycling stability. All these should be ascribed to the well-aligned array structure, good crystallinity, or stable chemical bonding of the NiO nanorods on the Ni foam substrate which enhances the electroconductivity [27].



Fig. 1.5 SEM images of the NiO nanorods on Ni foam annealed at 573 K (left), 623 K (right)

In addition to nickel oxide, nickel hydroxide, due to its high theoretical specific capacitance [29], is a strong candidate for supercapacitors, and even for the batteries application. Nickel hydroxide $(\alpha$ -Ni(OH)₂)films which are directly electrodeposited on nickel foil in Ni(NO₃)₂·6H₂O aqueous solution [28] with a maximum specific capacitance value of 2595 F g⁻¹ are published by Guo-rui Fu etc., where the Ni(OH)₂ films are deposited at -0.90 V versus Ag/AgCl electrode, showing the particle-like morphology with a loosely packed structure, shown in Fig. 1.6.



Fig. 1.6 FESEM images of the Ni(OH)₂: (a) low magnification (b) high magnification[28]

H.L. Wang et al. at Stanford University published another kind of nickel hydroxide grown on lightly oxidized graphene sheets showing the nanoplates morphology [29], exhibit a high specific capacitance of ~ 1335 F g⁻¹ at a charge and discharge current density of 2.8 A g⁻¹, with a little higher cost, and delicate preparation method, but it solves the problem other methods encounter, the slightly oxidized highly conductive grephene sheets offers the fast electron transfer between the active materials, here is the Ni(OH)₂, and the charge collector. Figure 1.7 shows the morphology of the nickel hydroxide nanoplates both on graphene sheets (GS) and lightly oxidized graphite (GO), the latter one exhibits better electrical conducitity.



Fig. 1.7 SEM characterizations of the nanoplates $Ni(OH)_2$ grown on graphene sheets, $a)Ni(OH)_2$ grown on GS; $b) Ni(OH)_2$ grown on GO

Considering all the methods in the processing techniques for nanoporous architecture serving as the electrodes for supercapacitors, it is therefore more meaningful to investigate a new method, a facile one, to fabricate highly stable electrodes, with great capacitive performance. Here, we report an easy achievable synthesis method with few steps including electrodepositon, dealloying and annealing to fabricate high porosity NiO/Ni composite as supercapacitor.

Chapter 2 – Experimental Background

In our work, three detailed parts are utilized in NiO/Ni nanostructure synthesis, electrochemical co-deposition, dealloying and annealing. The first step is to deposit Ni/Cu alloy combining nickel complex ions and copper ions in the same electrolyte. Following is to leach copper, resulting in the nanoporous nickel structure. Porous nickel in our system functions as electrical conductive layer, the active nickel oxide layer surrounding Ni is achieved by annealing in air at certain temperature. The three divided parts work together to provide a facile fabrication method for supercapacitive electrodes.

2.1 Electrochemical deposition of Ni/Cu alloy

In this step, Ni/Cu is co-deposited onto ITO glass, with a three-electrode electrodeposition system controlled by a potentiostat (HEKA, PG 310), see Figure 2.1, in which ITO substrate is placed again the twisted platinum counter electrode, with a saturated calomel reference electrode standing beside the ITO working electrode. In this system, electrolyte includes nickel (II) sulfamate tetrahydrate, copper (II) sulfate pentahydrate and boric acid.



Fig. 2.1 A schematic diagram of electrodeposition system

For the single metal-nickel, its electrodeposition is a process of nickel ions in the electrolyte traveling through the solution and depositing on the cathode (ITO) surface, here nickel sulfamate solution serves as the electrolyte.

Simultaneous electrodeposition of nickel and copper on ITO is not as simple as pure metal deposition system; co-deposition can occur when their deposition potentials reach equal [30] or very close to each other, where deposition potentials indicate smallest potential which can produce electrolytic deposition when applied to an electrolytic cell. In case of single metal depositon, depositon potential φ can be represented with two components: the reversible or equilibrium potential φ_{eq} and polarization η potential [30].

$$\varphi = \varphi_{eq} - \eta \tag{2-1}$$

Where φ_{eq} is closed tied together with the activity of the ions undergoing discharge $a_{M^{n+}}$ and the activity of the metal on deposited on the electrode a_M .

$$\varphi_{eq} = \varphi' + \frac{RT}{nF} \ln \frac{a_M n_+}{a_M}$$
(2-2)

 φ' is the standard electrode potential of the metal, a_M is commonly considered to be 1. But for binary metal co-deposition system, a_M is less than 1. Thus according to equation (2-2), φ_{eq} is supposed to be more positive than when single metal is deposited. This kind of positive shift can be ascribed to the activity difference of the metals in depositing alloys compared with depositing pure metal. Defining the change of the equilibrium potential to be $\Delta\varphi$, named as depolarization, $\Delta\varphi = -\frac{RT}{nF} \ln a_M$, reveals the discipline that with the decrease of a_M , the shift of the equilibrium potential will be bigger [30]. As mentioned, in binary deposition process, $\varphi 1$ should be coincident with $\varphi 2$, $\varphi 1$ and $\varphi 2$ stand for the deposition potential of metal 1 and 2, separately. Based on Equ. (2-1), two kinds of solutions are displayed; either changing φ_{eq} or adjusting η can equalize the potentials. Herein, for Ni/Cu systems, whose standard potentials are considerably different, incorporating Ni ions and Cu ions into complex ones, does make sense to equalize their deposition potentials. The complexion formation can be categorized into three types: (1), complexion the two metal ions with one complexing agent; (2), one metal ion maintains unchanged, while another forms complex ion; (3), complexion two metal ions with two complexing agents, separately. In our work, Ni/Cu frameworks were deposited in a single bath containing the two constituent, of which Nickel (II) sulfamate tetrahydrate is the complex ion, but copper (II) sulfate pentahydrate differs, thus can be explained by method 2.

Apart from incorporation of nickel ions into complex ones, diffusion of metal ions is another concern [31]. When alloy is deposited on ITO substrate, an interface between Ni/Cu and electrolyte will be formed. Fig. 2.2 shows how charge moves on the interface; the exchange of metal ions is just how deposition works. At the equilibrium state, the flux of metal ions diffusing towards the interface equals to the flux of which jumping away, namely, the total flux of ions is zero, indicating that the interface region is neutral. Diffusion of nickel and copper ions has a great impact on the structure, quality and component of the alloy film, nickel complex ions has a large concentration compared with copper sulfate, but the diffusion speed is not superior in terms of big complex ions, leading to the comparable diffusion rate of both ions, which can be proved by the SEM figures taken after removing the copper constituent off the film, in chapter 4.



Fig. 2.2 Illustration of alloy-electrolyte interface

2.2 Dealloying principle

Selective removal of copper from the alloy film is the routine step for rapid and direct fabricating the porous structure [32]. Dealloying procedure is carried out in the same electrolyte with the positive voltage of 0.500 V. Examining the mechanism of dealloying, the standard equilibrium

potentials for the Cu2⁺/Cu and Ni2⁺/Ni couples are 0.34 V (SHE) and -0.257 V (SHE) [33], respectively, hence copper is thermodynamically more stable than nickel at applied dealloying voltage. Nevertheless, the formation of a passive nickel oxide thin film when immersed in sulfamate solutions allows the selective electrochemical etching of copper, the less noble component, producing the porous nickel structure shown in figure 2.3.



Fig. 2.3 Rough model of porous structure comprised of nickel

Leaching out copper [34] results in a continuous porous structure composed almost entirely of nickel, noticed that with sufficient dealloying time and higher enough voltage within bounds, copper can be removed. Because of the interlace-growth of the Ni/Cu alloy, after removing the copper with positive voltage, the whole structure turns to be full of hollow pores, which is very efficient for the intercalation of hydroxyl ions, leading to the higher performance as a capacitor. In another word, due to the braided framework of the alloy---nickel and copper share every region closely, after removing off the copper, high porosity structure will be formed, providing more paths for the hydroxyl ions, hence enhancing the capacitance performance.

As a conclusion, dealloying procedure is based on the finely co-deposition, they work together to produce the framework, they are both very facile and cost effective methods, moreover, fabricating samples in large size is also viable, determining its promising future for industrial application.

2.3 Annealing process

Clearly, for generating NiO/Ni composite, annealing is absolutely necessary. Treated in air, certain amount of nickel can form oxide, to participate the redox reaction with OH⁻, to

accomplish the charge and discharge processes; this is what we called redox supercapacitor. Herein, annealing can be simply represented by the chemical reaction.

As is known to everyone, chemical reaction is closely related to the reagents, reaction time, and temperature. The more Ni contact the oxygen in air, the higher reaction rate will be; also according to the Arrhenius equation: $K = Ae^{-\frac{E_a}{RT}}$ (Where K indicates the chemical reaction rate, E_a is the activation energy, T stands for the temperature, while R is gas constant.) the higher reaction temperature, the fast the oxidation rate will be.

Therefore annealing temperature is one of the most important parameters to be considered. In our work, we did a series of tests to examine the optimal annealing temperature at the duration of 3 hours---300 °C is the best trying we did so far. After annealing, nickel oxides load surrounding metal nickel, due to the contact of oxygen with nickel only occurs at the naked part. The composite structure was easily yielded without delicate instrument, or complex method.

In our system, NiO reacts with hydroxyl ions, while metal nickel beneath NiO is in charge of electron collector and transporter with its excellent conductivity. In Fig. 2.4, the pathway of electrons and OH⁻ ions inside the framework is schematically illustrated, showing NiO and Ni cooperate their work in good order.



Fig. 2.4 Exhibition of intercalation of hydroxyl ions into NiO/Ni framework during charge/discharge

In summary, followed by dealloying process, co-deposition of nickel and copper contributes a lot to the final structure; the morphology of the films is based on the original Ni and Cu distribution of the deposited film. In electrochemical deposition step, -0.800 V was applied, negative to the equilibrium potential of nickel. While for dealloying, the more active component nickel is passivated, thus is kinetically rather than thermodynamically stable than copper [33]. Apply voltage of +0.5 V will only make copper be removed from alloy film, yielding porous structure, enlarging the specific surface area. Annealing is necessary to fabricate the thin active material layer comprised of nickel oxide. The characterization of NiO/Ni composite, when serves as the electrode, is notably affected by the structure; only robust, high specific surface area, high ordered structure can provide supercapacitor with high power/energy density, good cycling stability, and fast charge/discharge rate. These experimental procedures present several advantages: fine structure for electrode application, relatively high cost effective, ease for use in large size parts, high controllability and reliability, template free, and furthermore, it is a room-temperature technology.

Chapter 3 – Experimental

3.1 Preparation of the porous Ni framework

The ITO substrates (CSG PVTech Co., Ltd., $2\text{cm} \times 2 \text{ cm}$) were cleaned by ultra-sonication in acetone, ethanol and D.I. water for 15 min in each solvent. A three-electrode electrodeposition system controlled by a potentiostat (HEKA, PG 310) was used: a saturated calomel reference electrode, a platinum ring as the counter electrode and an ITO substrate as the working electrode. Both electrodeposition and dealloying processes were carried out at room temperature in the aqueous electrolyte: 0.5 M nickel (II) sulfamate tetrahydrate (Aldrich, 98%), 0.005 M copper (II) sulfate pentahydrate (Riedal-Dehaën, ACS reagent), and 0.6 M boric acid (Riedal-Dehaën, ACS reagent). Electrodeposition was carried out by applying a voltage of -0.800 V for 6000 sec, while the dealloying process was carried out by applying a voltage of 0.500 V for 20 min in same chemical bath to selectively etch away the Cu component in the Cu/Ni film. The samples were then annealed in Furnace with three different temperatures: 300 °C, 350 °C, 400 °C for 3 hours.

3.2 Synthesis of NiO/Ni hybrid film

The porous Ni film was fabricated on cleaned ITO by simple electrochemical deposition and dealloying process. At the beginning of the electrodeposition step, the rate of copper deposition was fast leading to the copper islands surrounded by nickel. As the film growth, the core/shell structure of Cu/Ni was finally deposited on ITO substrate. The porous Ni film can then be obtained by the selective etching of the Cu component in sulfamate solution. Futhermore, the deposition thickness can be controlled by the deposition time, also the porosity of the Ni film can be tuned by adjusting the applied voltage. Herein, all our samples, 6000 sec deposition duration of the film was used. The porous Ni film was subsequently annealed in air with three different temperatures.

3.3 Electrochemical Measurement

The electrochemical measurements were carried out using three-electrode configuration with electrochemical workstation (Princeton Applied Research PAR V3 instrument). The sample film $(2 \text{ cm} \times 2 \text{ cm})$ on ITO, a platinum foil $(2 \text{ cm} \times 2 \text{ cm})$ and saturated calomel electrode (Sigma-Aldrich) were connected as the working and counter electrode and reference electrode

respectively, and 1 M aqueous potassium hydroxide solution was used as electrolyte, well displayed by Fig. 3.1. The cyclic voltammetry (CV) was measured at a scanning rate of 5 mV s⁻¹ between 0 V to 0.5 V at 25 $^{\circ}$ C. The galvanostatic charge/discharge cycling was tested with current density 1 Ag⁻¹ for 500 cycles. The specific capacitance of sample is calculated by following equation:

$$C = \frac{It}{MV}$$
(3-1)

Where C (F g⁻¹) is the specific capacitance of the active materials and, I (mA) indicates the discharge current, Δt (s) is the discharge time and M (mg) is the mass of the active materials, ΔV (V) the potential windows.



Fig. 3.1 Interpretations of the instrument for a series of electrochemical performance measurement, including cyclic voltammetry (CV), constant current discharge, cyclic chronopotentiometric charge/discharge, cycling stability.

Chapter 4 – Results and Discussion

Two characterization methods: X-ray diffraction (XRD) and scanning electron microscopy (SEM) have been used for characterizing the physicochemical properties of NiO/Ni electrode. Furthermore, in order to investigate the capacitive behaviors including specific capacitiance of prepared samples, lifetime and other various electrical parameters, the galvanostatic charge-discharge electrochemical analyses are carried out.

4.1 XRD characterization

The extent of oxidation of the film could therefore be calculated from the ratio of Ni/NiO characteristic peak areas. Fig. 4.2 shows the magnified peak areas from the rectangular dashed box in Fig. 4.1.



Fig. 4.1 XRD powder diffraction patterns of the synthesized NiO/Ni film obtained after annealed for 3 hours, at 300 °C, 350 °C, 400 °C, separately







Fig. 4.2 Magnified XRD powder diffraction patterns of Ni porous framework after annealed at a) 400 °C; b) 350 °C; c) 300 °C. The overlapped peaks are divided into two separated peaks representing NiO (left) and Ni (right), respectively [35]

After heating, the NiO characteristic peak turns gradually to be sharper and higher with the higher temperature; while in contrast, Ni peak becomes broader gradually, suggesting that higher temperature did a favor to the oxidization of the Ni film, which can be proved by the calculated molar ratio of the film, derived from the peak's area ratio of Ni/NiO by the following equation:

$$\mathbf{r} = \mathbf{f} \mathbf{I}_{NiO} / \mathbf{I}_{Ni} \tag{4-1}$$

Where f [35, 36] is correlation factor, f = 0.79, I_{NiO} is the peak's area of NiO while I_{Ni} is the peak's area of Ni, and r stands for the molar ratio of the composite film.

- a), sample was annealed at 400 $^{\circ}$ C, NiO area = 42.963, Ni area =13.019, r=2.607
- b), sample was annealed at 350 $^{\circ}$ C, NiO area = 23.079, Ni area = 36.128, r=0.5046
- c), sample was annealed at 300 $^{\circ}$ C, NiO area = 9.038, Ni area = 24.893, r=0.2868

According to the calculated molar ratio, sample a annealed at 300 °C displays the lowest nickel oxides content, a further investigation of the capacitive performance of the various electrodes annealed at different conditions should be carried out to examine the optimal nickel content.

4.2 SEM measurement

To further confirm the results by XRD, the morphology diagrams characterized by SEM, are exhibited, shown in Fig. 4.3, from which we can figure out the sharp edge of the porous structure in pristine sample turns to be dull, after annealing at 300 °C, there is no big change in pore size and the porosity. However, the 350 °C annealed film suffered from the larger pore size, approximately 400 nm, leading to the lower porosity. Things turn worse when the film was treated at 400 °C; the pore fell in, which made the pore turn small again, but not only the structure was inflicted, the porosity, directly related to the capacitance, turned out to be much lesser. In conclusion, with increasing annealing temperature, the less surface area of NiO will be generated, namely, the accessibility of the electrolyte will be lower down, leading to the decreasing of SC.



Fig. 4.3 SEM characterizations with two different magnifications of the porous frameworks, 1) fresh prepare; 2) 300 °C; 3) 350 °C; 4) 400 °C. Samples 2, 3, 4 all have been annealed for 3 hours

4.3 Electrochemical properties testing

In order to investigate the capacitive performance of prepared samples, including specific capacitance, lifetime and other various electrical parameters, the galvanostatic charge-discharge electrochemical analyses of the supercapacitor were performed at various current densities.

To investigate the Faradaic pseudocapacitive behaviors, (1 M KOH was used in all measurements) three different annealed temperature Ni/NiO electrode were characterized by using cyclic voltammetry (CV) with scan range of 0 to 0.5 V (vs. SCE) at a scan rate 5mV s⁻¹ shown in Fig. 4.4. The observed redox peak in CV curve is corresponding to electrochemical redox reaction given in below [37]:

$$NiO + OH^- \leftrightarrow NiOOH + e^-$$
 (4 - 2)

The charge/discharge mechanism in alkaline aqueous solution is based on the redox reaction occurs between the interface of electrode/electrolyte. In redox reaction, the insertion and extraction of the hydroxyl ion change the oxidation state between Ni²⁺ and Ni³⁺, therefore the capacitive performance depends on two aspects: hydroxyl ion diffusion rate in the host material and charge storage capability in the host material through redox reactions.

Analyzed from Fig. 4.4, it is notably that the peak shapes of electrodes annealed at 300 $^{\circ}$ C greatly differs from other two curves, the enclosed CV area of 300 $^{\circ}$ C annealed NiO/Ni is larger than those annealed at 350 $^{\circ}$ C and 450 $^{\circ}$ C, demonstrating it possesses the best capacitive property over others.



Fig. 4.4 Cyclic voltammometric (CV) curves of NiO/Ni composite films annealed at different temperatures for 3 hours, the scan rate is 5 mV s^{-1}

To compare the reaction kinetic of pseudocapacitor prepared by different annealing temperature, the galvanostatic discharge curve was measured with current density of 1mA g⁻¹. Figure 4.5 shows the discharge curve of 300 °C, 350 °C and 400 °C, and the 300°C annealing sample has longer discharge time. The capacitance of 300 °C annealed NiO/Ni electrode was calculated from discharge curve with equation (3-1). The energy storage performance of electrode annealed at 300 °C significantly better than samples with higher annealing temperature. It can be explained by the ohmic resistivity which is related to the NiO amount in the sample film. The calculated the NiO to Ni molar ratio of 300 °C, 350 °C and 400 °C annealed porous Ni film from XRD peaks at 43.6 and 44.8 are 0.2868, 0.5046 and 2.607 respectively. As we observed, the amount of NiO increases as the annealing temperature. As more NiO generated on electrode surface layer, which could isolate the porous metal core network and increase the resistivity of electrode, resulting in the weak capacitive behavior. The consistent results have been reported by Qi Lu's work [38].



Fig. 4.5 Constant current discharge curves of the as-prepared NiO/Ni composites at different annealing temperature, the current density is set as 1 Ag^{-1}

The specific capacitance of the Ni/NiO electrode using different current densities has been conducted from 1 A g^{-1} and 16 A g^{-1} as shown in Figure 4.6. As current density 1 A g^{-1} increases to 16 A g^{-1} , the SC decreases to 88.3%, leading to a conclusion that the NiO/Ni electrode, even at the high current density (16 A g^{-1}), can maintain the good capacitive behavior, revealing that the NiO/Ni electrode can be applied with various current in practical use, when shifted at high current densities to provide high specific power density, it can live up to the use demanding. Surprising enhancement of SC behavior is mainly due to its nanoporous structure; after annealing, NiO loaded on the outside surface of Ni and conductive metal nickel are good contacted, transferring electrons very effectively, again the high specific surface of nickel oxide makes electrode exposing itself fully to electrolytes.



Fig. 4.6 Constant current discharge curves of NiO/Ni framework at different current density, scanning from 1 A g^{-1} to 16 A g^{-1}

According to Equation (4-2), Fig. 4.7 displays the several cycles representative voltage profiles of the NiO/Ni nanoporous electrodes from galvanostatic charge/discharge measurements performed at a constant current density (2 A g^{-1}) indicating reversible process of insertion and extraction of OH⁻ anions. In terms of each cycle, the left (upward) part is related to the oxidizing section turning NiO to NiOOH, while the right (downward) part refers to the reduction of NiOOH. The peak remains in good shape during repeated charge/discharge process cycle, demonstrating the high reversibility and good stability of NiO/Ni electrode, however, to further examine its periodical cycling stability, thousands of cycling are needed to be carried out, by reason that it is only a segment of total cycling performance, shown in Fig. 4.8.



Fig. 4.7 Cyclic chronopotentiometric profile with a charge/discharge current density of 2 A g^{-1} for the Ni/NiO electrode, in terms of each cycle, the left (upward) part is charging section turing NiO to NiOOH, while the right (downward) part refers to the reduction of NiOOH

The cycling stability test was shown in Figure 4.8, indicating that during the first 100 cycles, specific capacitance (SC) was increased from ca. 780 F g⁻¹ to maximum 930 F g⁻¹ on account of activation process of the NiO electroactive material. After activation of NiO, SC was kept almost constant and no significant change occurred during the subsequent 500 continuous cycles. Noticing the SC behavior starts to fade when cycled 600 times, the reasons for the advance SC drop maybe be ascribed to operating errors that the prepared electrode was tested before; moreover, during the test, which last for few days, the potassium electrolyte was more or less vaporized, leading to the uncompleted cover for our electrode, unfortunately no replenishment was implemented. But on the other hand, the SC degradation will happen sooner or later, due to the fact that through numerous tiny shrinks and expansions during extraction and insertion of hydroxyl ions when being reduced and oxidized, separately, the structure will fade anyway. The

even weeny fading of the unique nanoporous structure of the electrode inspires us to improve it in structure strengthening studies, to enhance the cycling life of our products.



Fig. 4.8 Cycle performance of NiO/Ni electrode (annealed at 300 °C), the current density was held constant at 1 Ag⁻¹. However, the imperfect results cannot fully represent the cycling life of our sample, due to the reason that the prepared electrode was tested before; moreover, during the test, which last for few days, the potassium electrolyte was more or less vaporized leading to the incomplete cover of our electrode.

4.4 Discussion

Combined all these virtues together, NiO/Ni framework can be utilized as the electrode for long lifetime, high cost-effective and high power density supercapacitors. Causes for high pseudocapacitor performance are analyzed, summarized as follows.

1. The good performance of NiO/Ni electrode annealed at 300 $^{\circ}$ C is contributed by the uniform porous architecture. The high porosity provides more chances for hydroxyl ions' insertion and extraction, namely, more efficient diffusion paths for the OH⁻ ions are established, resulting a high capacitance behavior.

The high porosity leads to the small pore size, apparently, without affecting the intercalation of the OH⁻ ions. According to the SEM profiles, the pore size of NiO/Ni composite after annealing for 3 hours is ca.150 nm, which is larger enough for OH⁻ electrolyte diffusion.

2. The metallic conductivity of Ni framework

The high conductivity of the Ni metal framework facilities the charge and discharge rates of the hydroxide ion and electron [38] charge storage and delivery reduce the resistance of the film. After annealing in air for 3 hours, the limited Ni was converted to NiO. When the temperature was control at 300 °C, the calculated molar ratio of NiO/Ni was 0.2868, besides, the electroactive material---NiO loaded on the top of Ni, thus the conductive network of the film will be maintained, in accord with which, the charge transfer speed didn't decrease. The current density, closely related to the specific power density, was guaranteed under the condition of annealing in air for 3 hours at 300 °C. Either increasing the anneal temperature, or raising the heat treatment time, will affect the composite's conductivity in some degree, therefore, its charge collecting ability will be discounted.

Chapter 5 – Future Innovations

Future generations of ECs are expected to gradually achieve high energy density as the Li ion batteries, maintaining their high power density [3]. In our work, we used -0.800 V to co-deposit the thin film, the pore size after dealloying is deterministic, and only 300 °C annealing temperature was accepted to fabricate the NiO/Ni electrode. Therefore, the pore size stays unchanged; tuning the porosity of the framework will definitely cause some variances to the capacitive behavior. In addition, for active material, we have a lot of candidates, herein NiO is conveniently generated after annealing. Cobalt hydroxide together with manganese dioxide, etc. can be utilized as the active materials in other peoples' work [39, 40], thus the synergistic effect of new active materials with nanoporous Ni framework can be investigated to improve the SC behavior. Moreover, even fancier, the flexible, printable, wearable and portable can be embodied into our future innovations. However, it is too long way to go, since the little expansion caused by the extraction and insertion of hydroxyl ions will murder the NiO/Ni electrodes at certain degree, no mention making it flexible. As known to all, metals such as nickel don't exhibit good ductility as polymer, while a great majority of easy accessible polymers do not possess the electric conductivity as metals. A new idea, involving synthesis the metal/polymer composite materials as the electrode for capacitance application, will be worth a try.

5.1 Tuning the pore size

Adjusting the applied voltage pore size tuned to fit the size of hydroxyl ions of the electrolyte with angstrom accuracy will increase the service coefficient of the surface area. In our work, electrodes annealed at 300 °C exhibit over 100 nm pore size, much bigger than hydroxyl ion radius which is less than 1 nm, hence a great step can be done to reduce the pore size. C.K. Tsang et al. [41] fabricated the periodical multilayers of Ni/Cu alloy by tuning the applied voltage, proving that working potential has a significant impact on the Ni content of the alloy film. At potentials negative to the equilibrium potential for nickel (-0.257 V (SHE)), copper deposition is diffusion-limited [33], therefore the deposition rate is independent of applied voltage, but for nickel, the deposition rate increases with increasing potential negatively. As a result, the applied potential will only affect the nickel deposition under -0.257 V (SHE), the

bigger the difference between the applied voltage and the equilibrium potential of nickel, the higher the deposition rate of nickel will be. After dealloying, as mentioned, only Cu will be removed, hence the Ni content of the thin film reflects the pore size after annealing, directly.

Future work should involve negatively turning the current applied voltage -0.800 V to -1.000 V, or even more, to investigate how the pore size will affect the capacitance, that is, the energy density.

Yet, a balance must be made, since higher specific surface area means higher capacitance, but lower electrode conductivity, therefore the capability to collect the electrons will fade in some degree, reducing the current density output, which will affect the power density of the capacitance. Competing with the energy density, we can tolerate a little decrease of the power density of electrochemical ultracapacitors, at least at present, the energy density remains to be the main issue, in order to put into more practical applications to support electrical motor, even heavier machine, as the power storage tool.

5.2 Coating different active material on porous Ni

Apart from tuning the pore radius to examine if higher specific energy density can be achieved, the altered active layer of capacitors herein, we annealed the as-deposited Ni film to achieve one layer of NiO, which acts as the electroactive material in this system. However, as mentioned, other active materials, often metal oxide or hydroxide, can be examined to enhance the energy storage performance of conventional NiO/Ni electrodes.

Cobalt hydroxide, one commonly used active material for electrochemical capacitance, can incorporate with Ni framework, to serve as electrode. C.M. Wu et al. [42] reported electrochemical deposition of cobalt hydroxide on an electrochemically derived nano-porous Ni framework, with super-pseudocapacitive performance---the sample with 50 mC cm⁻² deposition amount of Co(OH)₂ displays capacitance of 2650 F g⁻¹, at the CV scan rate of 5 mV s⁻¹ [42]. Moreover the whole procedure is entirely electrodeposition, and annealing is not necessary anymore, thus the advantages of the method: easy controllability, high reliability, high cost effective are maintained. Co(CH₃COO)₂ aqueous solution is utilized as the electrolyte at 25 °C, with the applied potential -0.75 V. Surface architecture remains to be almost identical before

depositing $Co(OH)_2$ onto Ni nanoporous structure, proved by SEM figures in Wu's work, which guarantees the high electrolyte accessibility, and free transference of hydroxyl ions and electrons.

With the evidence that other metal oxides can be electrochemically deposited onto the dealloyed nanoporous Ni substrate, other metals which can participate in the chemical reaction with certain electrolyte ions during charge/discharge can be examined too.

The possible redox reactions during charge/discharge in aqueous electrolyte should be like following [43]: (Assume that M is bivalent before galvanizing)

$$M^{2+} + H_2 0 + 2e^- \leftrightarrow M(0H)_2 + H_2$$
 (5-1)

$$M(OH)_2 + OH^- \leftrightarrow MOOH + H_2O + e^- \tag{5-2}$$

There are other possible redox reactions, dwelling on them is not necessary here.

Therefore choosing the proper metallic substance to be deposited onto as-prepared nanoporous nickel will be standardized, namely, metal should better be multivalent and allow redox reaction during charging. Thinking widely, ferrous hydroxide can be put into the deposition list too, for it can be oxidized to ferric (III) during charge and give out electrons. Further, manganese oxide can be considered as well, which can be viable to support capacitive behavior.

In conclusion, annealing to generate Ni oxide is not the only way to fabricate thin electroactive layer surrounding Ni, electrodeposition of other active materials can be feasible as well, to examine the possibility of enhancing the capacitive performance.

5.3 Multifunctional NiO/Ni ECs

Flexible, printable, wearable [3] and portable NiO/Ni ECs will find substantive applications if they can be developed. Imagine that if we can wear remarkable coat accessorized with small electrocapacitors, then we will never feel too cold or too hot with the help of a small button. Maybe a thermal electronics (TE) should be involved to collaborate with our ECs. In case of too hot, we can first apply the TE to transform heat into electricity; the produced electricity can be stored by NiO/Ni ECs. Because of Ni/NiO electrode is well sealed, no leak of nickel, thus no risk of allergies. The flexible and portable ECs predict a lot of promising applications, apart from attaching them on the suits, they can also be utilized as the electricity collector on motors when they are stalling, and compensator for any voltage fluctuations when they are in operation; accessorized sunglasses in burning summer; even used on the body-building apparatus, to store the physical energy by sticking the flexible ECs on the working out machine, to make every use of the waste energy. Still we can assemble ECs onto robot, to make those mechanical person more multifunctional.

In addition, in order to lower down the cost, printable redox capacitors will be more suitable for industrial mass fabrication for reduced manufacturing procedure and lower cost. Moreover, to conquer Li-ion batteries for energy supply in terms of cellphone, computer and household appliances, supercapacitors must be practically portable, with rather small weight compared with current ECs products.

Achieving all these characteristics, in terms of nickel oxide as the electrical active material, NiO can never work alone. Metal (oxide) is not comparable in ductility with polymers; therefore synthesis metal/polymer composite may give the way out. Polymers own good ductility, good flexible, rather small density, which meets the demands of portable, wearable and flexible, while for nanoporous Ni framework, it possesses good electrical ductility. The synergy of polymer and metal will make these properties easily achievable. However, how to make them work together, remains to be the question, embedding metal into the polymers seems ridiculous, but maybe we can get the help from nature, to make it happen. All needed is innovative idea, and the willpower.

Chapter 6 – Conclusions

A facile synthetic approach for generating Ni/NiO composite film with superstructures with high porosity and high capacitance has been described. The approach involves electrodeposition of Ni/Cu alloy onto ITO substrate at room temperature by applying a voltage of -0.800 V for 60 min in an aqueous electrolyte containing nickel complex ions, also copper ions. Dealloying by applying 0.500 V to selectively etch away the Cu component from the composite film will form super porous architecture of Ni thin films. Again, in order to form the thin active NiO layer on porous Ni, annealing in air is necessary. The CV characterization shows the sample annealed at 300 °C for 3 hours displays the capacitive behavior, while higher temperature treatment will more or less destroy the nanoporous framework, leading to the undersized area under CV curves. Furthermore, electrochemical data demonstrated that the porous structure of NiO/Ni could deliver 930 F g⁻¹ at a current density of 1 A g⁻¹ and the SC was kept almost constant and no significant change occurred until 600 cycles, which indicates the simultaneous provision of high energy density and rather good electrochemical. Moreover, the preparation described here was carried out without any elaborate instrument, and complex method, which is a convenient and cost-effective way for large batch production of NiO/Ni superstructure to provide good electrochemical performance. Yet, the cycling stability still needs to be improved, by making the framework more robust during periodic charge/discharge, etc. which is the future work.

Appendix

Derivation of depolarization

Simultaneous electrodeposition of nickel and copper on ITO is not as simple as pure metal deposition system; in terms of binary systems, co-deposition would occur when their deposition potentials reach equal [30] or very close to each other, where deposition potentials indicate smallest potential which can produce electrolytic deposition when applied to an electrolytic cell. For one component system, deposition potential can be represented with two components: the reversible or equilibrium potential φ_{eq} and polarization η potential [30].

$$\varphi = \varphi_{eq} - \eta \tag{A-1}$$

Where φ is single metal deposition potential; φ_{eq} is closed tied together with the activity of the ions undergoing discharge $a_{M^{n+}}$ and the activity of the metal on deposited on the electrode a_{M} .

$$\varphi_{eq} = \varphi' + \frac{RT}{nF} \ln \frac{a_M n}{a_M}$$
(A-2)

Where φ' is the standard electrode potential of the metal, a_M is commonly considered to be 1 when depositing single metal. Then equation (A-2) will be like following:

$$\varphi_{eq} = \varphi' + \frac{RT}{nF} \ln a_{M^{n+}} \tag{A-3}$$

However, in binary deposition process, a_M is less than 1, therefore, according to equation (A-2), φ_{eq} is supposed to be more positive than when single metal is deposited. This kind of positive shift can be ascribed to the activity difference of the metals in depositing alloys compared with depositing pure metal. Defining the shift of the equilibrium potential to be $\Delta \varphi$ as depolarization, which can be derived with the help of $\Delta \overline{G}$, partial Gibbs free energy of the metal in the alloy,

$$\Delta \bar{G} = RT \ln a_M \tag{A-4}$$

Equ. (A-4) shows the directly relationship between the activity degree of metal and $\Delta \bar{G}$. Apart from that, partial Gibbs free energy is also involved in the noted thermodynamic formula (A-5):

$$\Delta \varphi = -\frac{\Delta \bar{G}}{nF} \tag{A-5}$$

Consolidating equation (A-4) and (A-5), a solution about potential shift will be obtained,

$$\Delta \varphi = -\frac{RT}{nF} \ln a_M \tag{A-6}$$

Equ. (A-6) shows that with the decrease of activity of metal, depolarization $\Delta \varphi$ will increase, and composition of the alloy [30], namely, the metal content in the alloy will affect a_M . Only figuring out depolarization caused by alloy deposition, can we do more calculations about how to balance the depositon potential of two metals.

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