



Short communication

## Exaggerated capacitance using electrochemically active nickel foam as current collector in electrochemical measurement

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### ABSTRACT

In the past decades, nickel and cobalt oxide/hydroxide materials have been investigated intensively for supercapacitor applications. Some works report very high specific capacitance values, up to  $3152 \text{ F g}^{-1}$ , for these materials. By contrast, some other works report quite modest capacitance values, up to  $380 \text{ F g}^{-1}$  for the same materials prepared using same strategy. It is found that most works reporting very high capacitance value applied nickel foam as current collector. In this paper, surface chemistry and electrochemical properties of nickel foam are investigated by XPS analysis, cyclic voltammetry and galvanostatic charge–discharge measurement. The results show that using nickel foam as current collector can bring about substantial errors to the specific capacitance values of electrode materials, especially when small amount of electrode active material is used in the measurement. It is suggested that an electrochemically inert current collector such as Ti or Pt film should be used for testing electrochemical properties of nickel and cobalt oxide/hydroxide positive electrode materials.

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### 1. Introduction

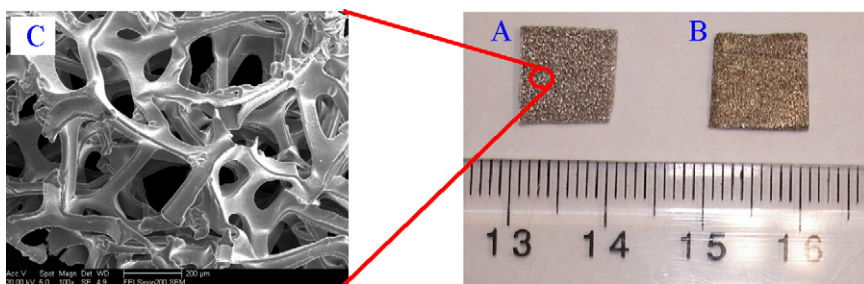
Supercapacitors have attracted considerable attentions over the past decade because of their higher power density and longer cycle life than secondary batteries and their higher energy density compared to conventional electrolytic capacitor [1]. Electrode material with high specific capacitance is highly desired for developing a supercapacitor with high energy density. Amongst the numerous materials studied to date, ruthenium oxide or its hydrate [2] can exhibit a capacitance as high as  $863 \text{ F g}^{-1}$ , which makes it an indispensable material for making a supercapacitor with high energy density. However, large scale commercialization of these materials has been hindered due to their high costs, thus people have resorted to other kind of economical transitional metal oxides/hydroxides, such as nickel and cobalt oxides/hydroxides that also have excellent pseudo-capacitance.

In recent years, some groups [3–8] reported very promising results for nickel and cobalt oxides/hydroxides, the specific capacitances of these materials being even several times higher than ruthenium oxide. For instance, Li group [3] reported that the capaci-

tance of nickel hydroxide electrode deposited directly on a nickel foam can reach up to  $3152 \text{ F g}^{-1}$ , which was claimed by the authors the highest capacitance value for supercapacitor electrode materials reported in the literature. The same group prepared  $\text{Ni}(\text{OH})_2/\text{USY}$  [4] and  $\text{Co}(\text{OH})_2/\text{USY}$  [5,6] composites by chemical precipitation, and the specific capacitances of  $\text{Ni}(\text{OH})_2$  and  $\text{Co}(\text{OH})_2$  in the composites using nickel gauze as current collector were up to 1740 and  $3409 \text{ F g}^{-1}$ , respectively. Hu et al. [7] deposited  $\text{Ni}(\text{OH})_2$  on a nickel foam by chemical deposition and a high capacitance of  $2200 \text{ F g}^{-1}$  was obtained. Lang et al. [8] prepared a  $\text{Ni}(\text{OH})_2$  nanoflake by chemical precipitation and the specific capacitance of the resulting material on nickel gauze was up to  $2055 \text{ F g}^{-1}$ . In contrast, many other works [9–11] applied similar strategies to prepare the same materials, but can only get quite modest capacitances. For example, Srinivasan and Weidner [12] and Hu and Hsu [13] electrodeposited cobalt hydroxide on a gold or graphite substrate, respectively, and the resulting materials possessed specific capacitances of around  $380 \text{ F g}^{-1}$  and  $230 \text{ F g}^{-1}$ . Chang et al. [14] and Wu and Hsieh [15] prepared mesoporous and nanosized  $\text{Ni}(\text{OH})_2$  electrode materials by chemical deposition and their specific capacitances on ITO (tin-doped indium oxide) and stainless steel substrates were no higher than  $108 \text{ F g}^{-1}$ . It means that the materials prepared using the same strategy but a different substrate as the current collector in electrochemical testing possessed significantly different capacitive performances.

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**Fig. 1.** Morphologies of nickel foams: (a) optical image of a fresh nickel foam, (b) optical image of the nickel foam with 2000 times cycle measurement of CV, and (c) FESEM image of the fresh nickel foam.

Because most works reporting very high capacitance values applied nickel foam as current collector [3–8,16–32], it is quite indispensable to evaluate the potential contribution of nickel foam to the specific capacitances of active electrode materials. Herein, we investigate the surface chemical properties and electrochemical properties of nickel foam in KOH electrolyte within positive potential window. Based on XPS analyses, cyclic voltammetry (CV) and galvanostatic charge–discharge measurements, we find that using nickel foam as a current collector can bring about substantial errors to the specific capacitance values of electrode materials. To the best of our knowledge, this is the first report focusing on the potential errors derived from usage of a nickel foam as the current collector in supercapacitor studies.

## 2. Experimental

HCl is purchased from Ajax Finechem. KOH and acetone are purchased from Aldrich. All chemicals are AR grade and used as received. Nickel foam (Heze Tianyu Technology Development Co. Ltd.) was sonicated in 1 M HCl solution for 10 min, then washed with acetone and deionized water, and rinsed with 1 M KOH solution before electrochemical testing. CV and galvanostatic charge–discharges were performed in a three-electrode cell equipped with a piece of nickel foam (1 cm × 1 cm) as working electrode (without any active electrode material loaded on this nickel foam), a platinum counter electrode, and a Ag/AgCl reference electrode (filled with 3 M NaCl) in 1 M KOH aqueous solution. A potential window of 0–0.5 V vs. Ag/AgCl reference electrode was applied to both CV and galvanostatic measurements on Solartron 1480 Maltistat. For comparison purposes, both nickel foam and Ti gauze were used to fabricate working electrodes using mesoporous carbon [33] and mesoporous nickel oxide [34] as active materials that were prepared according to the literatures. The mass ratios for active material, carbon black and PTFE (polytetrafluoroethylene) binder are 85, 10 and 5, respectively. The mass of active material in each electrode is about 2 mg.

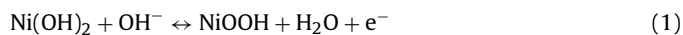
The morphology of nickel foam was observed by both a digital camera (DSC-HX1, Sony) and a field emission scanning electron microscope (Sirion 200, FEI) operated at 20 kV. The X-ray photoelectron spectroscopy (XPS) measurements were performed on ESCALAB220i-XL (VG Scientific, UK) using monochromated Al K $\alpha$  excitation source. The survey and high-resolution spectra were collected with 100 eV and 20 eV pass energy, respectively. The best peak fits were obtained using mixed 30% Gaussian–Lorentzian line shapes at the same full wave at half maximum (FWHM) for all fitted peaks.

## 3. Results and discussion

Fig. 1 shows the surface morphologies of the nickel foams. Before CV, the nickel foam shows typical silvery metallic luster. By contrast, after cycling for 2000 times within positive potential window

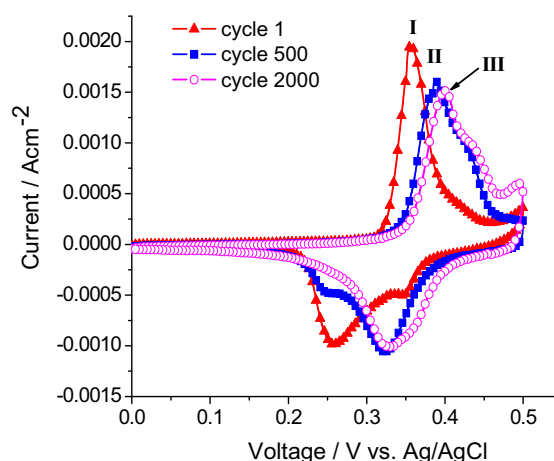
(0–0.5 V vs. Ag/AgCl reference electrode) in KOH electrolyte, the nickel foam presents dark golden color, indicating that some redox reactions may occur on the nickel foam. Scanning electron microscope (SEM) image of the nickel foam with 100 $\times$  magnification (in Fig. 1c) shows that the nickel foam has 3D, porous and cross-linked grid structure. The cell size of the nickel foam is around 100–200  $\mu$ m.

To investigate the change of nickel foam during electrochemical process, CV experiments were performed. The CV curves of a nickel foam electrode at different cycles at a scan rate of 1 mV s $^{-1}$  in 1 M KOH are shown in Fig. 2. In the first CV scan (Fig. 2, curve I), an oxidation current peak is found at around 0.36 V, and a main reduction current peaks at 0.26 V with a shoulder peak at 0.34 V. Such peaks could be mainly related to Faradaic reaction of Ni(OH) $_2$ :



The existence of nickel hydroxide or nickel oxide on the surface of nickel foam was evidenced by XPS analysis which will be shown and discussed later. As has been reported [35], nickel hydroxide may generally exist in two different crystallographic forms designated as  $\alpha$ -Ni(OH) $_2$  and  $\beta$ -Ni(OH) $_2$  which are hydrous and anhydrous, respectively. In addition, the oxidation of nickel hydroxide gives two other varieties of oxyhydroxides ( $\beta$  and  $\gamma$ ) [36], which can explain the existence of the two reduction peaks during the backward sweep. The anodic peak at 0.36 V and cathodic peak at 0.26 V are attributed most probably to  $\alpha$ -Ni(OH) $_2$ / $\gamma$ -NiOOH redox couple. The shoulder cathodic peak at 0.34 V could be attributed to phase change from  $\gamma$ -NiOOH or  $\beta$ -NiOOH to  $\beta$ -Ni(OH) $_2$  [37].

After 500 cycles, as shown by Curve II in Fig. 2, the main anodic and cathodic peaks shift to higher potentials 0.39 V and 0.32 V, respectively, which is due to un-stoichiometric property of electrochemically active nickel hydroxide and nickel oxyhydroxide phases



**Fig. 2.** CV curves of nickel foam at 1 mV s $^{-1}$  within a potential window of 0–0.5 V vs. Ag/AgCl in 1 M KOH. I: the first cycle; II: after 500 cycles; III: after 2000 cycles.

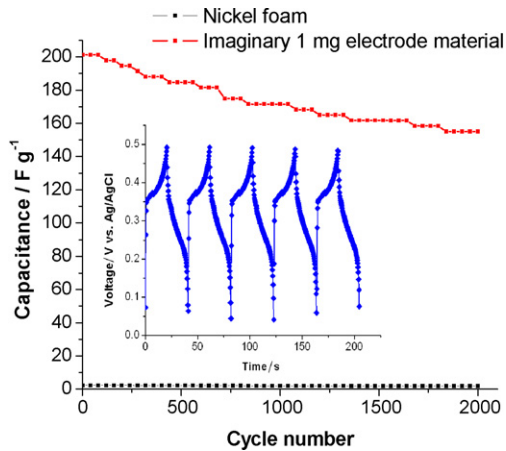


Fig. 3. Cycle life data at a constant current of  $5 \text{ mA cm}^{-2}$  (inset: galvanostatic charge–discharge curves for the first 5 cycles).

[38,39]. The anodic shoulder peak at 0.43 V may be ascribed to the phase transformation from  $\beta\text{-Ni(OH)}_2$  to  $\beta\text{-NiOOH}$  because this transformation is preferred compared with the conversion from  $\alpha\text{-Ni(OH)}_2$  to  $\gamma\text{-NiOOH}$  [40]. It is further noticed in Fig. 2 that there is not much difference between CV at 500th and CV at 2000th cycles, suggesting that the change on the surface of nickel foam occurs mainly in the first 500 cycles. Whereas, it can further be observed that the cathodic peak on curve III becomes much broader than curve II, which may be due to the convolution of two separate peaks at 0.32 V and 0.36 V. After 2000 cycles, it is more clear to observe the anodic peak at 0.43 V and cathodic peak at 0.36 V, which are expected to be due to  $\beta\text{-Ni(OH)}_2/\beta\text{-NiOOH}$  redox couple. The above CV curve evolution does demonstrate that electrochemical reactions occur during this voltage sweep cycling, which leads to the color change for the nickel foam, as shown in Fig. 1(b). These redox reactions occurred on the nickel foam will definitely generate pseudocapacitances, which will inevitably bring about errors to the specific capacitance of active electrode materials when using the nickel foam as current collector. It also should be noted that these anodic/cathodic peaks appear in the first CV test, suggesting that nickel hydroxide or oxide species preexists on treated nickel foam, which coincides with Allen's results [41]. Our results further indicate that these nickel hydroxide or oxide species formed on the nickel surface cannot be effectively removed by a common acid wash using diluted HCl solution.

To evaluate how large error will be brought about to the specific capacitances of active electrode materials when using a nickel foam as the current collector, galvanostatic charge–discharge measurements were conducted. As can be seen from Fig. 3, the specific gravimetric capacitance of a pure nickel foam is not high, about

$2 \text{ F g}^{-1}$ , which is mainly from surface faradic reaction as demonstrated by CV tests. However, in some studies, the active material used is very small, sometimes, no more than 1 mg [7,42,43]. If we omit this additional capacitance derived from the nickel foam, the specific capacitance of the active electrode material may be substantially overestimated. For instance, providing the nickel foam contains 1 mg active material in experiment, the specific capacitance of the active material can be overestimated by  $200 \text{ F g}^{-1}$  due to the contribution from nickel foam, as is shown in Fig. 3. Furthermore, it is noteworthy that the specific capacitance of the nickel foam decreases very slightly with increasing cycling times, which is due to the gradual transformation from  $\alpha\text{-Ni(OH)}_2/\gamma\text{-NiOOH}$  redox couple to  $\beta\text{-Ni(OH)}_2/\beta\text{-NiOOH}$  redox couple, as demonstrated in Fig. 2. It has been reported that the gradual transformation from  $\alpha\text{-Ni(OH)}_2/\gamma\text{-NiOOH}$  to  $\beta\text{-Ni(OH)}_2/\beta\text{-NiOOH}$  redox couple can lead to capacitance decay because the oxidation state of nickel in  $\beta\text{-NiOOH}$  is lower than that of  $\gamma\text{-NiOOH}$  ( $\beta\text{-NiOOH} \sim 3$ ;  $\gamma\text{-NiOOH} \sim 3.5$ ) [44].

More realistically, the specific capacitances of mesoporous carbon and mesoporous nickel oxide were determined using both nickel foam and Ti gauze as current collector. As shown in Fig. 4(a), mesoporous carbon on nickel foam can discharge much longer than that on Ti gauze. The calculated specific capacitances for mesoporous carbon are  $22 \text{ F g}^{-1}$  and  $190 \text{ F g}^{-1}$  on Ti gauze and nickel foam, respectively. Similar results were also obtained for mesoporous nickel oxide, as illustrated in Fig. 4(b), the calculated specific capacitances for nickel oxide are  $129 \text{ F g}^{-1}$  and  $494 \text{ F g}^{-1}$  on Ti gauze and nickel foam, respectively. These results once again demonstrate that using nickel foam as current collect can substantially overestimate the specific capacitance of active material, especially when small amount of active material is applied in the electrochemical testing.

To confirm the electrochemical reactions occurring on the surface of nickel foam during charge–discharge cycles, it is necessary to clarify the changes in surface chemistry of nickel foam before and after cycling. As reflected by the XPS spectra in Fig. 5, the Ni (2p) of fresh nickel foam can be deconvoluted into three peaks at 852.7, 854.1 and 855.9 eV, corresponding to nickel metal,  $\text{Ni}^{2+}$  in NiO and  $\text{Ni(OH)}_2$ , respectively [45]. The O (1s) spectrum of fresh nickel foam consists of three peaks at 529.7, 530.5 and 531.6 eV, attributed to chemisorbed molecular oxygen and  $\text{O}^{2-}$  in NiO and  $\text{Ni(OH)}_2$ , respectively [46,47]. This demonstrates that some surface atoms on the nickel foam chemically react with  $\text{O}_2$  and water in the atmosphere to form NiO and  $\text{Ni(OH)}_2$  species, which accounts for pseudocapacitive behavior of the nickel foam indicated by cyclic voltammetry and galvanostatic testing. However, this NiO and  $\text{Ni(OH)}_2$  layer is not compact and thick enough to shield the nickel metal, which still can be detected by X-ray in XPS measurement.

After the nickel foam was cycled for 2000 times in 1 M KOH solution within 0.0–0.5 V range, the peak at 852.7 eV disappeared, indicating that all the surface nickel metal atoms were oxidized

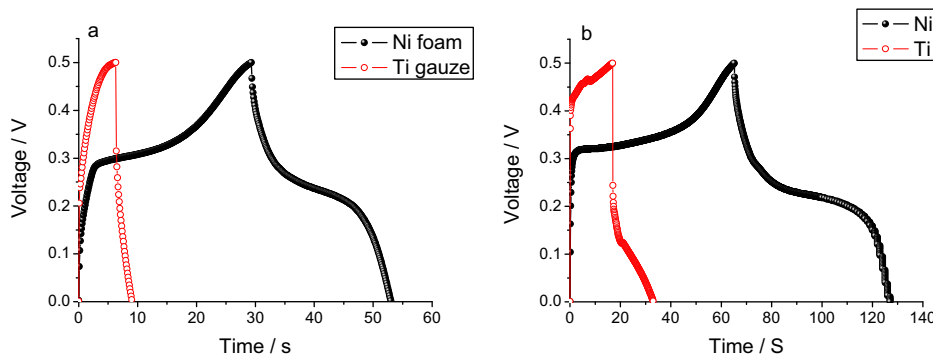


Fig. 4. Galvanostatic charge–discharge curves at  $4 \text{ A g}^{-1}$  for mesoporous carbon (a) and mesoporous nickel oxide (b) using nickel foam and Ti gauze as current collector.

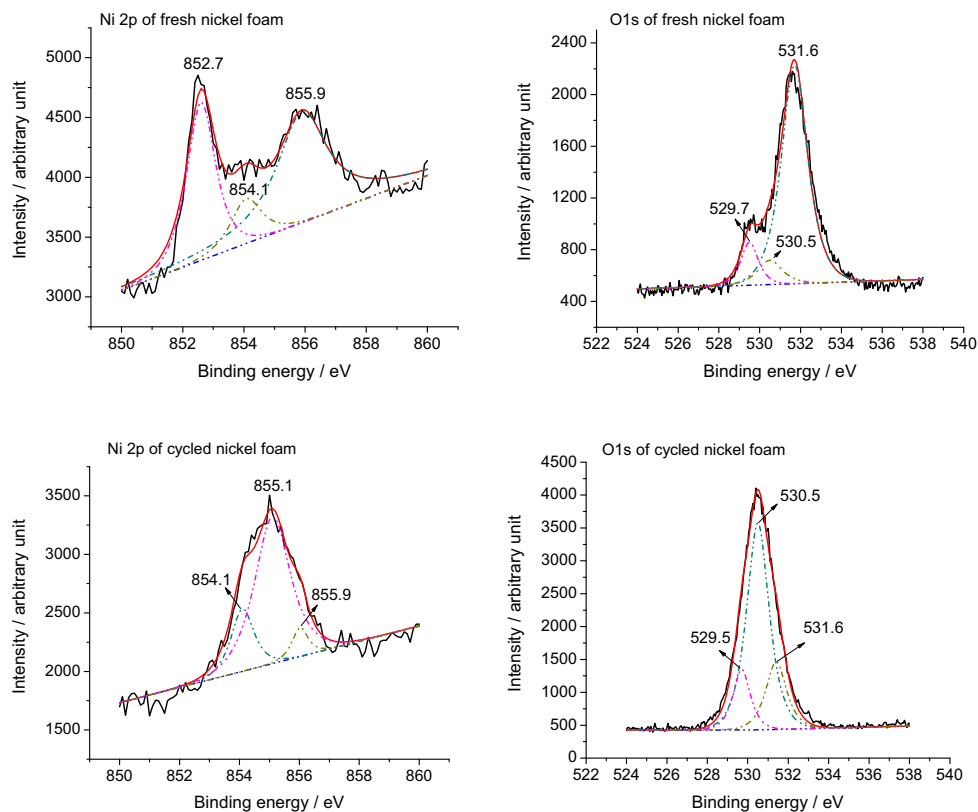


Fig. 5. Experimental XPS results and the corresponding Ni2p and O1s deconvolution of fresh nickel foam and nickel foam after 2000 cycles.

to other nickel species during cycling [40]. There is a new peak emerging at 855.1 eV, corresponding to the formation of  $\text{Ni}^{3+}$  in  $\text{NiOOH}$  during cycling. The largest O (1s) peak at 530.5 (OH species) demonstrates that  $\text{NiOOH}$  and  $\text{Ni}(\text{OH})_2$  are major species on nickel foam after 2000 cycles. This nickel species evolution reflected by XPS coincides with what is described by reaction (1).

#### 4. Conclusions

Cyclic voltammetry and galvanostatic charge–discharge cycling measurements clearly show that the pretreated clean nickel foam itself does have capacitive properties in KOH electrolyte within positive potential window, which can bring about substantial errors to specific capacitance value especially when a small amount of active electrode material is used. XPS analyses further confirm that electrochemically active nickel hydroxide/oxide preexists on the nickel foam, which contributes to the pseudocapacitance of nickel foam. Although nickel foam from different sources [48] may have different properties in some aspects, nickel oxide or hydroxide are easily formed on the surface of fresh nickel metal in the atmosphere at room temperature. Moreover, nickel metal can be in situ electrochemically oxidized to electro-active nickel species in KOH solution at positive potentials [38]. So it is obviously not suitable to use nickel foam as a current collector specifically but not exclusively in KOH electrolyte within positive potential window. At this testing condition, it is suggested that an electrochemically inert current collector such as Ti or Pt foil should be used for supercapacitor studies.

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