

Electrodeposited nickel hydroxide on nickel foam with ultrahigh capacitance

Guang-Wu Yang, Cai-Ling Xu* and Hu-Lin Li*

College of Chemistry and Chemical Engineering, Lanzhou University, 730000 (PR China)

1. Materials Synthesis

$\text{Ni}(\text{NO}_3)_2$ was AnalaR grade and used as received without further purification. Before the electrodeposition, nickel foam (thickness: 1.8 mm, pore density: 110 ppi) was rinsed with acetone and hydrochloric acid to clean and etch the metal surface.

The electrodeposition was conducted by a Chenhua CHI760B model Electrochemical Workstation (Shanghai), with a three-electrode cell consisting of a saturated calomel electrode (SCE) as reference electrode, a 1.0 cm \times 1.0 cm platinum plate as counter electrode and a piece of nickel foam (1 cm² in area) as the working electrode. The electrolyte was a aqueous solution of 0.1 M $\text{Ni}(\text{NO}_3)_2$. The electrodeposition experiments were all carried out at a constant potential of -0.7 V vs. SCE. To deposit a $\text{Ni}(\text{OH})_2$ film of about 0.5 mg, the corresponding deposition charge quantity is approximately 0.8326 C which was estimated by Faraday's law. After deposition, the as prepared $\text{Ni}(\text{OH})_2$ electrode was washed with water several times.

2. Characterization

2.1. Powder X-ray diffraction (XRD)

XRD data were collected using a Rigaku D/MAX 2400 diffractometer (Japan) with Cu $K\alpha$ radiation ($k = 1.5418\text{\AA}$) operating at 40.0 kV, 60.0 mA.

Fig. S1 illustrates the XRD spectra of the $\text{Ni}(\text{OH})_2$ on nickel foam. It can be seen that all the peaks are in good agreement with the patterns of hydrous α - $\text{Ni}(\text{OH})_2$ (JCPDS no. 22-0444)

except some of the characteristic patterns of the Ni substrate. The main peaks for Ni(OH)₂ are labeled with hkl indexes.

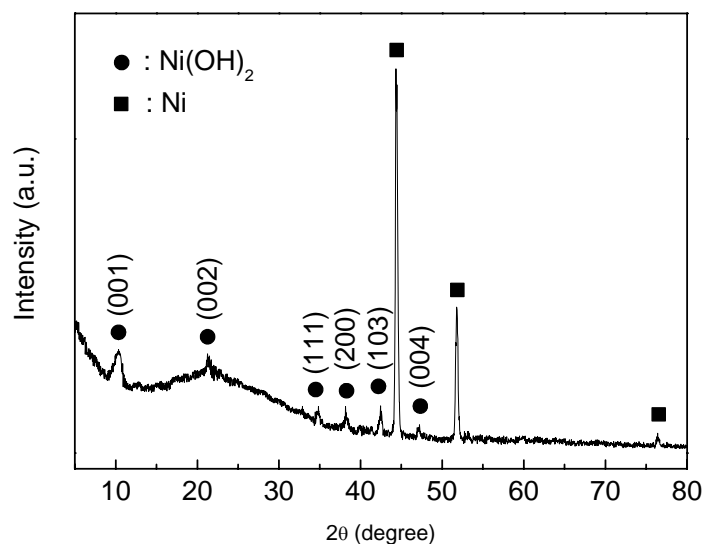


Figure S1. XRD patterns of the Ni(OH)₂ sample.

2.2. Surface morphology

The surface morphology of the Ni(OH)₂ on nickel foam network was examined by field emission scanning electron microscope (FESEM, JEOL JSM-S4800). To confirm the thickness of the coatings electrodeposited on nickel foam surface, we sheared a branch from the Ni(OH)₂-Ni foam and viewed it at the cut.

Fig. S2 clearly shows a Ni(OH)₂ layer coated on the surface of nickel. The coating thickness is approximately 200 nm.

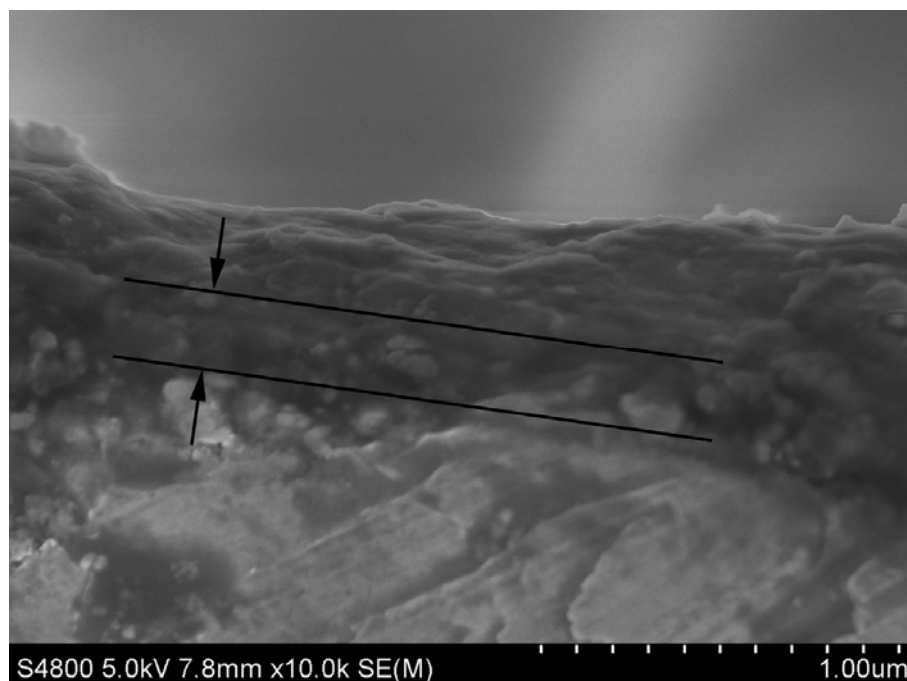


Figure S2. Typical FESEM micrographs of the Ni(OH)₂ coatings electrodeposited on nickel foam.

2.3. Electrochemical properties

Cyclic voltammetric (CV), chronopotentiometric and electrochemical impedance spectroscopic measurements were all performed on CHI760B Electrochemical Workstation, with a three-electrode electrochemical cell, containing 3% KOH aqueous solution as electrolyte.

Their specific capacitance was calculated according to the following equation: ¹

$$C_m = \frac{C}{m} = \frac{I \times \Delta t}{\Delta V \times m}$$

where C_m (F g⁻¹) is the specific capacitance, I (mA) is charge–discharge current, Δt (s) is the discharging time, ΔV (V) represents the potential drop during discharge, and m (mg) is the mass of the active material within the electrode.

Electrochemical capacitor properties of the as-deposited Ni(OH)₂-Ni foam electrode and pristine nickel foam without Ni(OH)₂ deposits were elucidated by CV and chronopotentiometric measurements. Fig. S3 and S4 show the CV and discharge curves of

both electrodes, respectively. As is shown in Fig. S3, no well defined peaks could be observed at bare nickel foam. However, two strong redox reaction peaks appear around at 0.52 and 0.06 V in the same solution at Ni(OH)₂-Ni foam electrode, which are responsible for the pseudo capacitive capacitance and are due to the proton insertion and de-insertion reaction well documented in the course of studies for nickel electrode rechargeable batteries.² Associated with the poor CV property, the pristine nickel foam shows hardly any electrochemical capacity performance.

Electrochemical impedance spectra (EIS) for Ni(OH)₂-Ni foam electrode were carried out at various potentials of interest over the capacitor operating potential range. Fig. S5 presents the complex-plane impedance plots for the Ni(OH)₂-Ni foam electrode. The frequency range studied is 10⁵–10⁻². The Nyquist plots at different potential display obviously different electrochemical properties, suggesting different processes occurring on the electrode. At high frequencies, the presence of semicircle is attributable to the charge-transfer process at the compound-electrolyte interface. The intercept at the real axis (*Z'*) of the plot is the internal resistance, and the internal resistances of these three-electrode systems are all estimated to 2.6–3.0 Ω. The straight line in the low frequency region shows that ionic diffusion appears during charging-discharging process. At low frequencies, a deviation from the straight line along the imaginary axis (*Z''*) is apparent when the potential is -0.05 V, indicating a non-ideally polarizable electrode. While at the potential of 0.45 V, only two circles displayed and the line characteristic disappeared, which is a characteristic of the desorption of adatoms H_{abs}.³ The changes of impedance spectroscopy with the potential illustrate that the proper potential range, in which electrode can generate desirable capacitance, is between -0.05 and 0.45 V. These results are consistent with the potential windows of charge-discharge.

Except the case of Fig. S5(A) and (F), the maximum specific capacitance was calculated from the low frequency data using the equation $Z'' = (2\pi fC)^{-1}$, where *Z''* is the imaginary part

of the impedance, f is the frequency, and C is the capacitance. The specific capacitance at different potentials (0.05, 0.22, 0.35 and 0.40V) calculated from the Z'' value at the lowest frequency ($f = 0.01$ Hz) is 379, 1515, 3055, and 3213 $F\ g^{-1}$, respectively, for the electrode at different applied potentials.

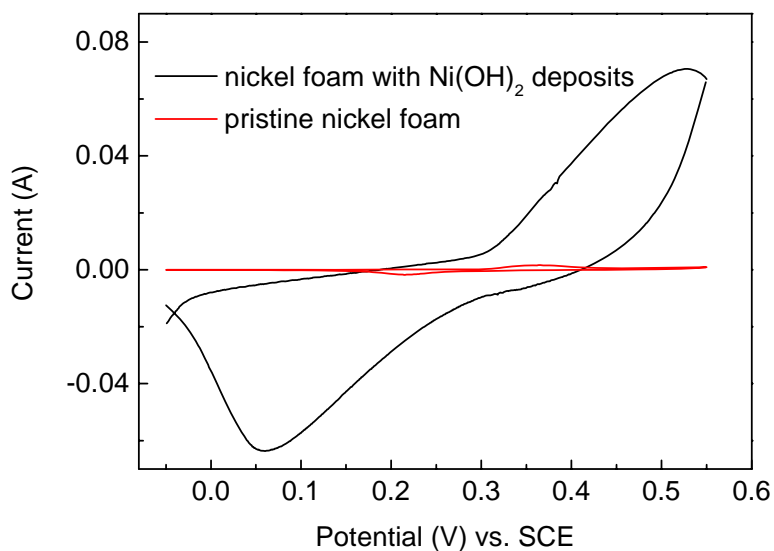


Figure S3. CV responses exhibited by the as-deposited Ni(OH)₂-Ni foam electrode and pristine nickel foam without Ni(OH)₂ deposits in 3% KOH solution at a scan rate of 20 mV s⁻¹ within a potential window of -0.05 to 0.55 V vs. SCE.

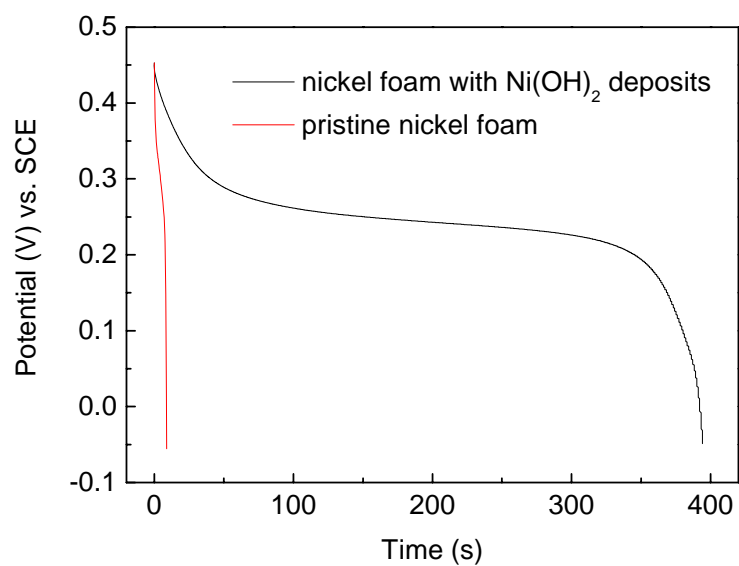
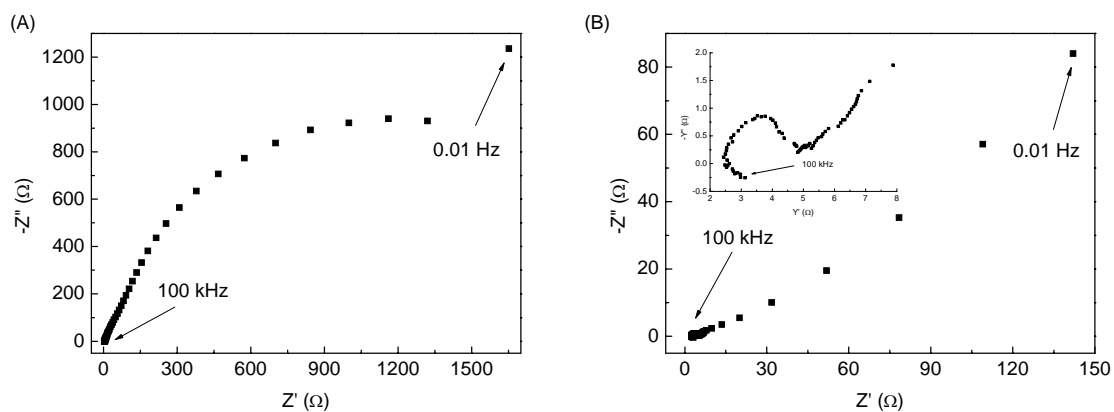


Figure S4. Chronopotentiometric responses exhibited by Ni(OH)₂-Ni foam electrode and pristine nickel foam without Ni(OH)₂ deposits in 3% KOH solution in the potential range from -0.05 to 0.45V at a discharge current density of 4 A g⁻¹.



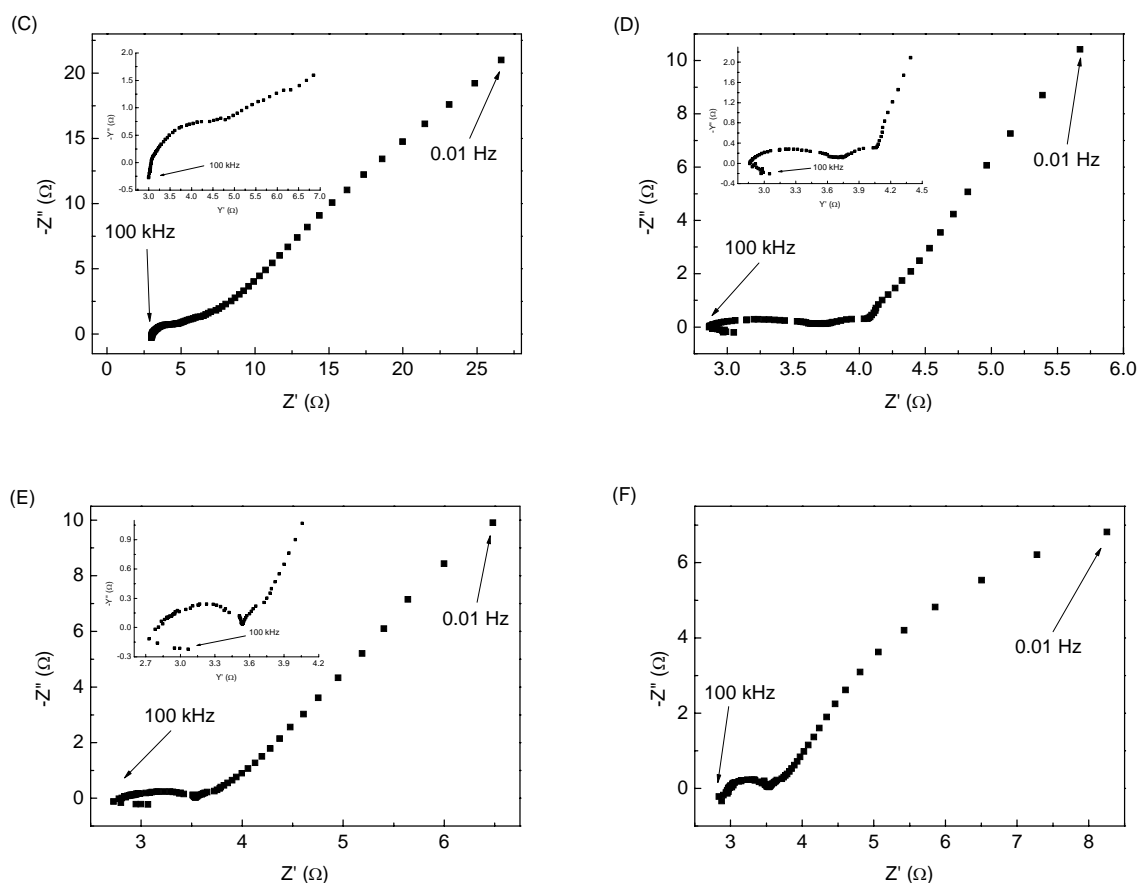


Figure S5. Nyquist plots for the Ni(OH)₂-Ni foam electrode in 3% KOH solution at different potentials: (A) -0.05V, (B) 0.05V, (C) 0.22V, (D) 0.35V, (E) 0.4V, (F) 0.45V.

Reference

- 1 Y. G. Wang, H. Q. Li and Y. Y. Xia, *Adv. Mater.* 2006, **18**, 2019.
- 2 M. Jayalakshmi, M. Mohan Rao, and K.-B. Kim, *Int. J. Electrochem. Sci.* 2006, **1**, 326.
- 3 B. E. Conway, *Electrochemical Supercapacitors, Scientific Fundamentals and Technological applications*, Kluwer Academic/Plenum Press, New York, 1999, ch. 17, pp. 555.