

## **Lithium ferrite ( $\alpha$ -LiFe<sub>5</sub>O<sub>8</sub>) Nanorods based Battery-type Asymmetric Supercapacitor with NiO Nanoflakes as the counter electrode**

J. Johnson William, I. Manohara Babu and G. Muralidharan\*

Department of Physics, Gandhigram Rural Institute (Deemed to be University),

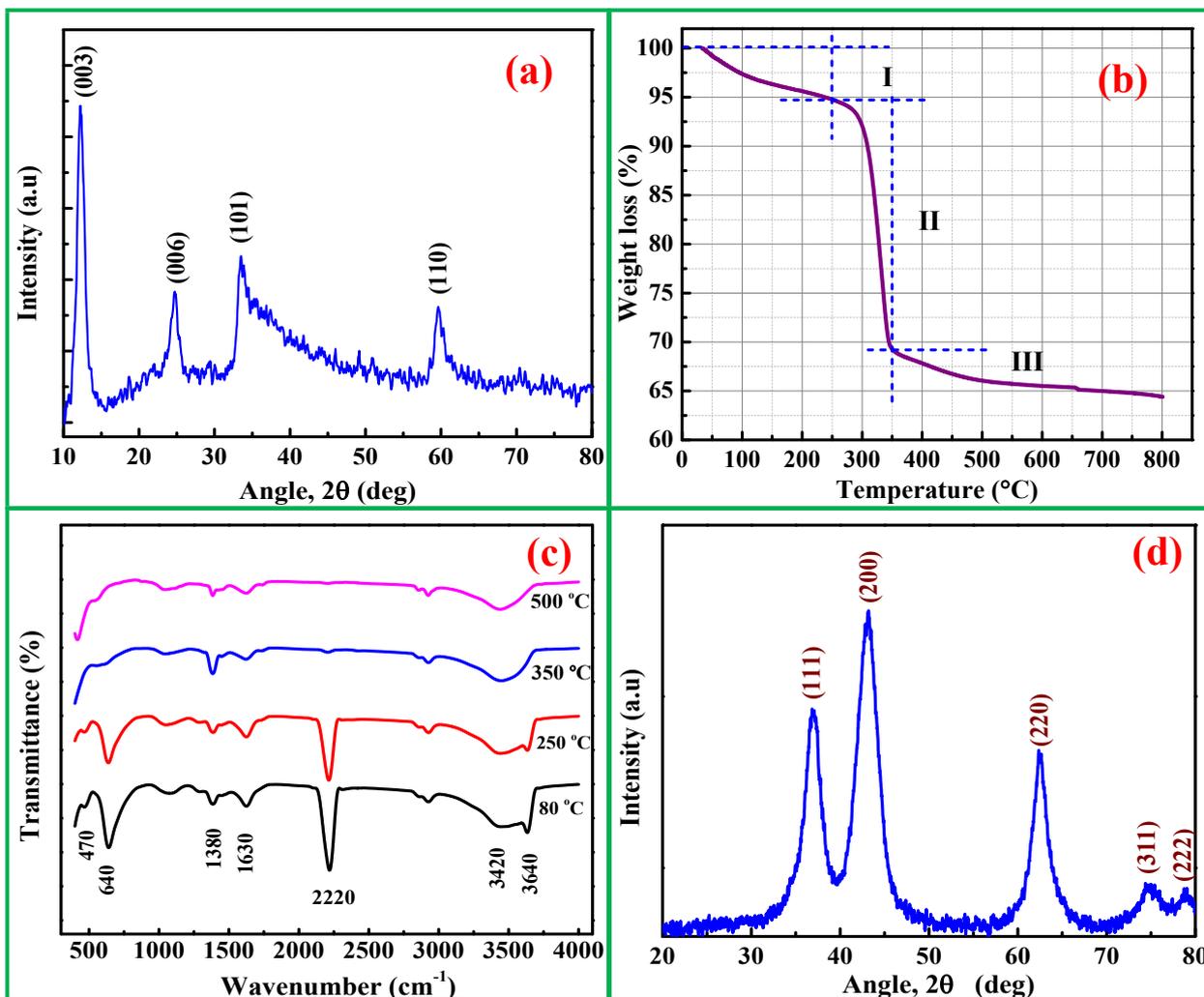
Gandhigram-624302, Tamil Nadu, India

\*e-mail: muraligru@gmail.com; Fax: +91 451 2454466; Tel: +91 451 2452371

---

### **S1. Thermal analysis of NiO**

The XRD pattern of as-prepared nickel hydroxide nanoparticles is shown in figure S1a. The diffraction peaks at 12.2°, 24.8°, 33.2° and 59.4° are indexed with (003), (006), (101) and (110) planes of rhombohedral  $\alpha$ -Ni(OH)<sub>2</sub>·0.75H<sub>2</sub>O (JCPDS: 38-0715). The absence of other peaks indicate the phase purity of the prepared materials. Thermogravimetric analysis is made to identify the phase changes and decomposition details of the  $\alpha$ -Ni(OH)<sub>2</sub>·0.75H<sub>2</sub>O. TG curve in figure S1b provides an information about the thermal decomposition of the nickel hydroxide nanostructures. The experiment was carried out from room temperature (RT) to 800 °C. TG curve reveals three stages of weight loss: RT-250 °C, 250-350 °C and 350-500 °C. Thus, to identify the changes that have caused the weight loss during TG process, the FTIR spectrum were recorded after heat treatment upto 80, 250, 350 and 500 °C. The spectra are displayed in figure S1c. The IR spectrum of sample dried at 80 °C reveals the functional groups present in  $\alpha$ -Ni(OH)<sub>2</sub>·0.75H<sub>2</sub>O (precursor material for NiO) and is as follows. The band centered at: 470 cm<sup>-1</sup> (stretching vibrations of Ni-O), 640 cm<sup>-1</sup> (bending vibrations of Ni-O-H), 1380 cm<sup>-1</sup> (interlayer NO<sub>3</sub><sup>-</sup> molecule), 1624 cm<sup>-1</sup> (O-H bending vibrations of intercalated H<sub>2</sub>O), 2220 cm<sup>-1</sup> (C≡N vibrations of isocyanate ions) and 3640 cm<sup>-1</sup> (O-H bending vibrations of  $\alpha$ -Ni(OH)<sub>2</sub>·0.75H<sub>2</sub>O).

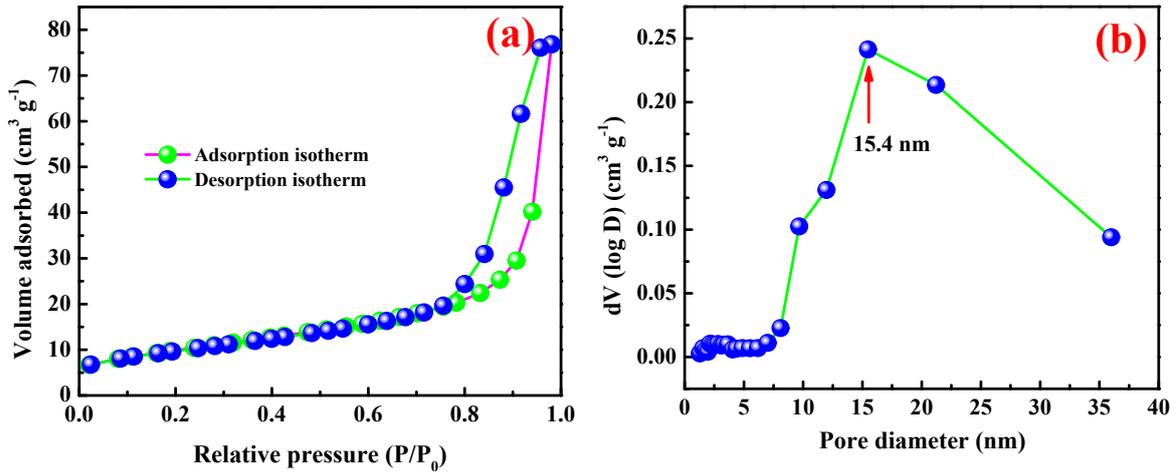


**Figure S1.** (a) XRD pattern of  $\text{Ni(OH)}_2 \cdot 0.75\text{H}_2\text{O}$ , (b) TG curve of  $\alpha\text{-Ni(OH)}_2$ , (c) FTIR spectra of  $\alpha\text{-Ni(OH)}_2$  and NiO and (d) XRD patterns of NiO.

In TG curve (figure S1b), a minor weight loss of 7 % is noticed in the first stage. This may be due to the partial decomposition of hydroxyl groups ( $3640\text{ cm}^{-1}$ ) and isocyanate ions ( $2220\text{ cm}^{-1}$ ) and it can be clearly seen in IR spectrum of sample annealed at  $250\text{ }^\circ\text{C}$ . In second stage, i.e. from  $250\text{-}350\text{ }^\circ\text{C}$ , a major weight loss of 25.6 % was observed which is mainly attributed to the conversion of  $\alpha\text{-Ni(OH)}_2 \cdot 0.75\text{H}_2\text{O}$  into NiO. The weight loss observed in second stage agrees to a larger extent with the expected loss of 32.8%. A complete transformation of  $\text{Ni(OH)}_2 \cdot 0.75\text{H}_2\text{O}$  to NiO can be confirmed from the FTIR spectra of samples annealed at  $350$  and  $500\text{ }^\circ\text{C}$ . In addition to that, the

isocyanate ions are evaporated in the second weight loss. The third weight loss 5.4 % is observed from 350 to 500 °C and no significant change is observed in FTIR spectrum in figure S1c (500 °C).

## S2. BET measurements of NiO electrodes

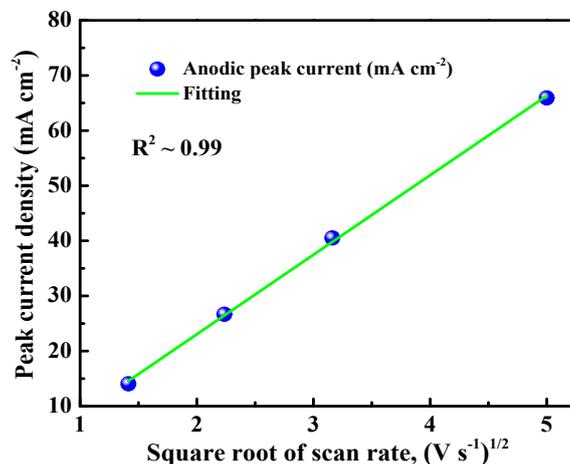


**Figure S2. (a) N<sub>2</sub> adsorption-desorption isotherm curves and (b) Pore size distribution (BJH method) of NiO.**

Moreover, textural properties like pore size and its distributions have been diagnosed with the aid of N<sub>2</sub> adsorption-desorption isotherms (BET studies). The porous structure can offer large specific surface area and good degree of porosity resulting in a better electrochemical performance. Thus, the BET measurements are carried out on NiO nanoflakes to identify the magnitude of specific surface area, pore size and pore volume. N<sub>2</sub> adsorption and desorption isotherms of NiO specimen are displayed in figure 6e. The isotherm curves show a typical H3 Hysteresis loop suggesting the Langmuir type IV isotherm that indicates the presence of mesopores. The specific surface area of NiO is estimated to be a 34.9 m<sup>2</sup> g<sup>-1</sup>. In addition, the pore size distribution within the NiO specimen is estimated using Barrett-Joyner-Halenda (BJH) method (figure 8b). The obtained pore diameter and pore volume are of 15.4 nm and 0.058 cc g<sup>-1</sup> respectively.

According to IUPAC classification of pores, the nature of pores anchored in the NiO specimen are mesopores.

### S3. Diffusion controlled reaction



**Figure S3. Profile of anodic peak current versus square root of scan rate.**

### S4. Electrochemical impedance spectroscopy analysis

Electrochemical impedance spectroscopy is another suitable electrochemical tool to identify the impedance associated with the redox mechanism. The electrochemical impedance characteristics are studied in the frequency range of 10 mHz to 100 kHz at an amplitude of 5 mV. Figure S4a displays the Nyquist plot (fitted to Randle's circuit) of NiO electrode prepared at 350°C. Semicircles in the high frequency regions are attributed to the charge transportation phenomena in NiO electrodes, resulting from the Faradaic reactions (exchange of OH<sup>-</sup> ions or e<sup>-</sup> near the surface of the NiO electrodes). The straight line in low frequency region is recognized as Warburg behaviour, describing the diffusive resistance of electrolyte ions within the pores of NiO electrodes. The Nyquist plot of NiO electrode shows a smaller semicircle part revealing an excellent charge transport kinetics between NiO and NiOOH. Moreover, this minor effect of interfacial impedance is attributed to ideal capacitive behaviour. At high frequency region of the

Nyquist plot, the EIS spectrum of NiO electrode is intercepted at  $1.8 \Omega$  of the real part corresponding to the solution resistance and the diameter of the semi-circle represents the charge transfer resistance of  $3.2 \Omega$ . From the EIS analysis, NiO electrode demonstrates the low charge transfer resistance ensuring the rapid charge storage. Further, NiO electrode is subjected to 5000 continuous charge discharge cycles at a specific current of  $10 \text{ A g}^{-1}$  to analyze its cyclic stability and its characteristic behaviour is displayed in figure S4c. Initially, from its maximum (1<sup>st</sup> cycle) value, the specific capacity of the NiO electrode was found to be decreased to 81.2 % upto 5000<sup>th</sup> charge discharge cycles.

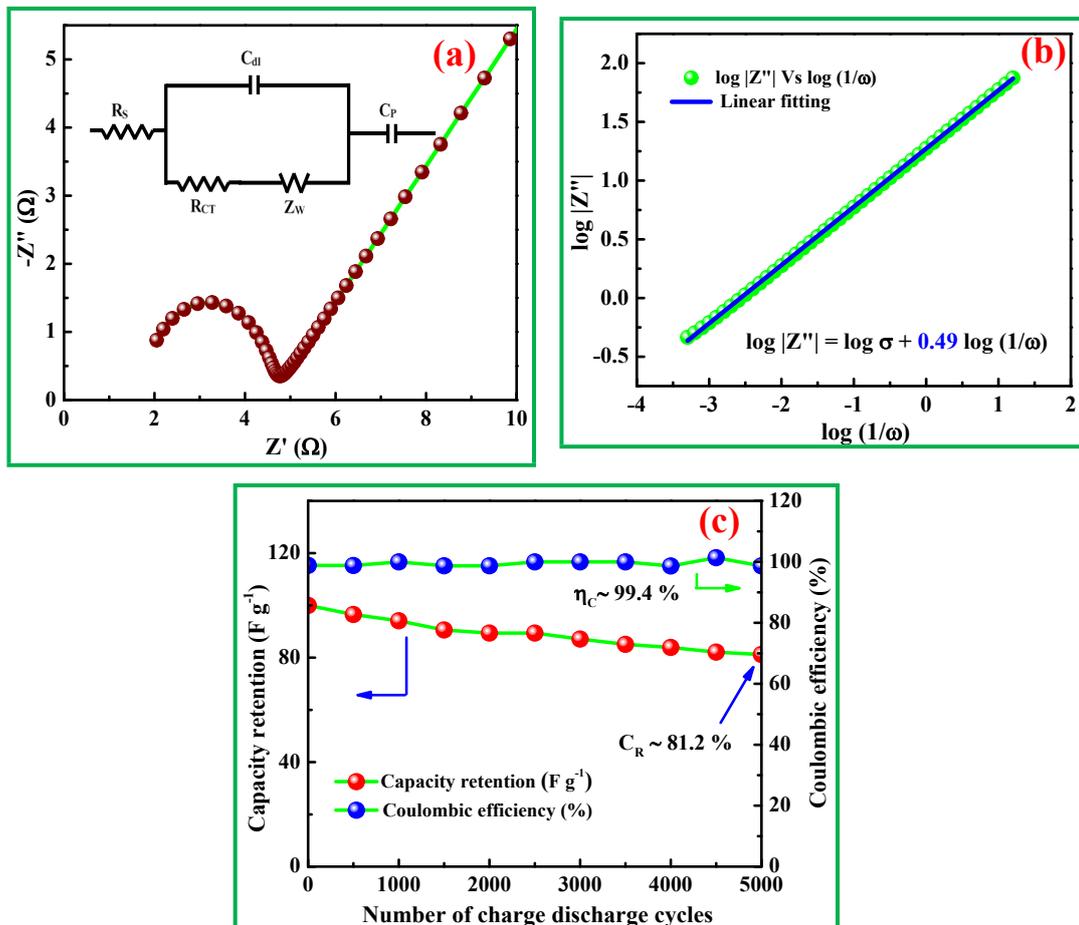


Figure S4. (a) Nyquist plot, (b)  $\log |Z''|$  Vs  $\log 1/\omega$  plot and (c) lifespan test of NiO electrode.