## **Supporting Information**

# Asymmetric hybrid energy storage of battery-type nickel hydroxide and supercapacitor-type electrochemically reduced graphene oxide: Effect of redox additives

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## 1. Calculation

1.1 Optimization of the mass ratio between positive and negative electrodes

The equation below (s1) is applied to evaluate the optimized masses of positive and negative electrodes;

$$\frac{m_+}{m_-} = \frac{C_{s-}\Delta V_-}{C_{s+}\Delta V_+} \tag{51}$$

where m is the mass of active material,  $C_s$  is the specific capacitance, and  $\Delta V$  is the cut off potential range for positive(+) and negative(–) electrodes<sup>1, 2</sup>. According to the CV test at 5 mV s<sup>-1</sup>, the mass ratio between  $\alpha$ -Ni(OH)<sub>2</sub> and ERGO in 4mM K<sub>3</sub>[Fe(CN)]<sub>6</sub> in 1M KOH is 0.34.

$$\frac{m_+}{m_-} = \frac{(538.21)(0.90)}{(1475.32)(0.95)} = 0.34$$

In this experiment, the active material is 3 mg which are from 0.76 mg of  $Ni(OH)_2$  on positive electrode and 2.24 mg of ERGO on negative electrode.

### 1.3 The cell capacitance of the supercapacitors

The cell capacitance ( $C_{cell, cv}$ ) of the supercapacitor can be calculated from the CV technique by the following equation (s2);

$$C_{cell,cv} = \frac{Q}{\Delta V_{cv} \times m}$$
(s2)

where Q is an average charge in the discharge process (Coulomb) of the CV curve,  $\Delta V_{cv}$  is a working potential window (V) and m is a total mass of active material used in both positive and negative electrodes.

The cell capacitance ( $C_{cell, GCD}$ ) of the supercapacitor can also be evaluated from the galvanostatic charge discharge (GCD) technique by the following equation (s3);

$$C_{cell,GCD} = \frac{I_{GCD} \times \Delta t_{GCD}}{\Delta V_{GCD} \times m}$$
(s3)

where  $I_{GCD}$  is the applied constant current (A),  $\Delta t_{GCD}$  is the discharge time (s) and  $\Delta V_{GCD}$  is the working potential window (V) of the cell excluding the IR drop.

#### 1.4 b values

The voltammetric response at various scan rates from 10 to 100 mV s<sup>-1</sup> was calculated by following the equation (s4) below;

where *i* is a current, *v* is a scan rate. *a* and *b* are adjustable parameters for which *b* is determined from the slope of the linear plot of log i versus log v. In general, *b* is equal to 1 involving non-diffusion controlled capacitive effect while *b* is equal to 0.5 indicating the ideal diffusion-controlled redox intercalation process (battery-type behaviour).

## 1.5 The capacitive contribution fraction

The capacitive contribution fraction of the capacitive effects at different scan rates can be calculated according to the equation (s5) as follow;

$$i(V) = k_1 v + k_2 v^{0.5} \tag{55}$$

where  $k_1$  and  $k_2$  are alterable parameters that can be determined from the slope and y-axis intercept of this straight line, and v is a scan rate.

#### 1.5 Specific energy and specific power of the supercapacitor cells

Specific energy ( $E_{cell}$ ) and specific power ( $P_{av}$ ) are calculated from the following equations (s6-s7);

$$E_{cell} = \frac{i}{m} \int_{0}^{t_a} V dt \tag{s6}$$

$$P_{av} = \frac{Ecell}{t} \tag{(s7)}$$

where *i* is an applied current (A), *m* is the total mass of active materials, *V* is the working  $\int_{0}^{t_{a}} V dt$  voltage, *t* is the discharging time (s) and  $\int_{0}^{0}$  is the area under the GCD discharge curve.

For the maximum power density of the as-fabricated device, it can be calculated by following the equation below;

$$P_{max} = \frac{V_0^2}{4R_{cell}} \tag{(s8)}$$

where  $V_0$  is an initial voltage of the cell,  $R_{cell}$  is the cell's resistance determined from the GCD.

#### 2. XPS spectra of Ni(OH)<sub>2</sub>/CFP

To further characterization, X-ray Photoelectron Spectroscopy (XPS) is used to investigate chemical composition of Ni(OH)<sub>2</sub> on CFP. In Fig. S1(a), wide-scan XPS spectra of Ni(OH)<sub>2</sub>/CFP compose of C<sub>1s</sub>, Ni<sub>2p</sub> and O<sub>1s</sub> core level peaks. In addition, sulfur peaks are observed on its the surfaces because of the adhesive used in the production of CFP. For the C<sub>1s</sub> region (Fig. S1(b)), the peaks at 284.6, 285.0, 285.7, 286.7, 288.8 and 289.6 eV are due to the C-C, C=C, C-OH/ C-O-C, O=C-OH and CF<sub>2</sub>, respectively. Those are from the treated CFP. While Ni<sub>2p</sub> spectrum reports a deconvolution of Ni<sub>2p3/2</sub> core level peaks at 855.6 eV and 857.3

eV with their satellite peaks at 861.24 and 863.25 eV, respectively. Ni  $_{2p1/2}$  peaks are at 872.77 eV and 874.52 eV with their satellite peaks at 878.11 and 880.10 eV, respectively (Fig. S1(c)). This shows the characteristics of  $\alpha$ -Ni(OH) $_2$ <sup>3</sup> and  $\gamma$ -NiOOH<sup>4</sup>. For O1s region, the peak at 530.7 eV is assigned to a C-O-Ni bond. Whilst, the peak at 531.8 eV is due to C=O groups or shoulder peak of O1s in Ni(OH) $_2$ . Also, the peak of C-OH and C-O-C groups is at 532.8 eV (Fig. S1(d)).



**Fig. S1** (a) The survey XPS spectrum of Ni(OH)<sub>2</sub>/CFP. (b) C 1s spectrum, (c) Ni 2p spectrum and (d) O 1s spectrum of Ni(OH)<sub>2</sub>/CFP.

## 3. FE-SEM and TEM of GO



Fig. S2 (a) FE-SEM and (b) TEM images of GO.



#### 4. The selection of working potential windows

**Fig. S3** (a) CVs of Ni(OH)<sub>2</sub> electrode at 5 mV s<sup>-1</sup> at different potential windows (0.8 to 1.6 V), (b) specific capacitance vs. scan rate of the Ni(OH)<sub>2</sub> electrode at 5-100 mV s<sup>-1</sup> at different potential windows in 1M KOH with 4mM K<sub>3</sub>[Fe(CN)]<sub>6</sub> redox additive, (c) CVs of ERGO electrode at 5 mV s<sup>-1</sup> at different potential windows (0.8 to 1.6 V), and (d) the specific capacitances vs. scan rate of ERGO electrode at 5 to 100 mV s<sup>-1</sup> at different potential windows (0.8 to 1.6 V) in 1M KOH with 4mM K<sub>3</sub>[Fe(CN)]<sub>6</sub> redox additive electrolytes.

#### 5. The electrochemical properties of half-cell electrodes

5.1 Ni(OH)<sub>2</sub>/CFP positive electrode



**Fig. S4** (a) CVs at 5 mV s<sup>-1</sup> and (b) specific capacity vs. scan rate of Ni(OH)<sub>2</sub> electrode at scan rates of 1-25 mV s<sup>-1</sup> in 1M KOH with/without  $K_3$ [Fe(CN)]<sub>6</sub> redox additive. (c) *b*-value vs. potential and (d) bar chart showing the percentage contribution from capacitive and intercalation at the scan rates of 1-25 mV s<sup>-1</sup> in 1M KOH with 4mM  $K_3$ [Fe(CN)]<sub>6</sub> redox additive



**Fig. S5** (c) CVs at 5 mV s<sup>-1</sup> and (d) the specific capacitances vs. the scan rate of ERGO electrode at the scan rates of 5-100 mV s<sup>-1</sup> in 1M KOH with/without  $K_3$ [Fe(CN)]<sub>6</sub> redox additive.

## 6. The electrochemical properties of the cells

## 5.2 ERGO/CFP positive electrode



**Fig. S6** The electrochemical properties of  $Ni(OH)_2//ERGO$  asymmetric energy storage in 1 M KOH: (a) CVs at different scan rates, (b) the plots of normalized power with the frequency, (c) GCD curves and (d) energy density vs. maximum power density of the as-fabricated devices.

Table S1. The charge storage performances of the Ni-based asymmetric supercapacitors.

Materials	Electrolytes	Testing methods	Capacitances	Refs.
β-Ni(OH) <sub>2</sub> -Ni foam//activated carbon	6 М КОН	GCD at 0.13 A g <sup>-1</sup>	106 F g <sup>-1</sup>	5
Ni(OH)2/XC-72/CNT	6 М КОН	GCD at 0.5 A g <sup>-1</sup>	73 F g <sup>-1</sup>	6
NiCo <sub>2</sub> O4-reduced graphite oxide//activated carbon	2 М КОН	GCD at 0.5 A g <sup>-1</sup>	99 F g <sup>-1</sup>	7
Ni-Co oxide// activated polyaniline-derived carbon	2 М КОН	GCD at 0.5 A g <sup>-1</sup>	202 F g <sup>-1</sup>	8
Ni <sub>50</sub> Co <sub>50</sub> -LDH//N-doped graphitic ordered mesoporous carbon	6 M KOH	GCD at 1.25 A g <sup>-1</sup>	108 F g <sup>-1</sup>	9
Ni(OH) <sub>2</sub> -graphene//porous graphene	6 М КОН	CV at 5 mV s <sup>-1</sup>	218 F g <sup>-1</sup>	10
Ni(OH) <sub>2</sub> //ERGO	1 M KOH/ 4mM K <sub>3</sub> [Fe(CN)] <sub>6</sub> in 1M KOH	GCD at 1 A g <sup>-1</sup>	223 F g <sup>-1</sup> / 283 F g <sup>-1</sup>	This work

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