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## A hybrid nonaqueous electrochemical supercapacitor using nano-sized iron oxyhydroxide and activated carbon

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**Abstract** A beta-iron oxyhydroxide (FeOOH) was synthesized via a hydrolyzing route and investigated as a lithium intercalation host. It delivers a capacity of about 170 mAh/g and exhibits good cycling performance when charged/discharged in the voltage range from 1.6 V to 3.3 V. For the first time we have confirmed that FeOOH is suitable for using it as a negative electrode for hybrid electrochemical supercapacitor assembled with an activated carbon positive electrode in 1.0 M LiPF<sub>6</sub> ethylene carbonate/dimethyl carbonate (EC/DMC, 1:2 in volume) solution. The cell reveals a slightly sloping voltage profile from 0 V to 2.8 V and gives an estimated specific energy of 45 Wh/kg based on the total weight of two electrode materials, approximately two times of carbon/carbon electrochemical double layer capacitors. The hybrid supercapacitor shows a good cycling performance, it remains approximately 96% of initial capacity after 800 cycles at a charge/discharge rate of 4 C. The capacitor also shows a desirable rate capability, even at 10 C discharge rate, it holds 80% of capacity compared with that at 1 C discharge rate.

**Keywords** FeOOH · Supercapacitor · Activated carbon · Nonaqueous electrolyte

### Introduction

Supercapacitors coupled with batteries and fuel cells are considered promising mid- and long-term solutions for low- and zero-emission transport vehicles by providing the power peaks for start–stop, acceleration, and recovering the breaking energy. Nowadays, many researches on the electrochemical capacitors aim to in-

crease both power and energy density, as well as lower fabrication costs while using environment-friendly materials. Compared with the conventional electrochemical double layer capacitors (EDLCs), the hybrid electrochemical supercapacitors (HBES), which rely on two different electrode materials show a higher energy density and a corresponding cycle life. This was recently reported by Telcordia Technologies with a new device named nonaqueous asymmetric hybrid electrochemical supercapacitor in which intercalation compound Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> was used as the negative material and activated carbon (AC) was used as the positive material [1]. For the hybrid electrochemical supercapacitor, one electrode stores charge through a reversible nonfaradaic reaction of anions on the surface of an active carbon or the hole of a nano-pore carbon material, and the other electrode is to utilize a reversible faradic reaction of lithium-ion insertion/extraction in a nano-size lithium-ion intercalated compound. Both increase of the working voltage and high energy density of the intercalated compound electrode material result in a significant increase of the overall energy density of the capacitors. Accordingly, the energy density of the capacitor is critically dependent on the energy density of the carbon positive electrode material and the cell working voltage, and the power density depends on the rate capability of the intercalated compound. In order to achieve high energy density, the negative electrode material must have a low intercalation potential. A number of negative electrode materials for the lithium-ion batteries, e.g., Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and other substitutes such as LiMnPO<sub>4</sub> and WO<sub>2</sub> etc. are the most promising choices for such application. Additionally, in order to demand the requirements of high power of the hybrid capacitors, these negative electrodes are expected to use nano-structured compounds. However, it is difficult to obtain the nano-structured compounds mentioned above as these compounds are most synthesized under high temperature [2, 3]. The active approach is to search a lithium-ion intercalation compound that can be prepared at a milder condition. It has been reported that the beta-FeOOH can be easily prepared by a

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hydrolyzing route under much more milder condition [4–7], and the raw material of intercalation compound based on Fe element is inexpensive and abundant. This material has been investigated as a positive electrode material for lithium-ion batteries. However it shows a very sloping discharge curve from 2.0 V to 1.5 V, and charge curve from 1.5 V to 4.2 V (vs.  $\text{Li}^+/\text{Li}$ ), it is thereby not suitable for use as the positive/negative electrode for lithium-ion batteries. In the present work, we for the first time confirmed that FeOOH is suitable for using it as a negative electrode for HBES. The electrochemical profile of a hybrid electrochemical capacitor based on a FeOOH negative electrode coupled with a commercialized activated carbon in 1 M  $\text{LiPF}_6$  ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:2 in volume) was investigated in this paper.

## Experimental

$\beta$ -FeOOH was prepared by the hydrolysis process [6, 7]. First, 10 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 370-ml  $\text{H}_2\text{O}$ . The 0.1 M solution was subjected to slow hydrolysis at a temperature of  $80^\circ\text{C}$ . During the reaction, a progressive precipitation took place. After 8-h reaction, the precipitate was filtered and washed extensively with purified water and then dried at  $60^\circ\text{C}$  in an oven. The fine powder of the production was obtained. The AC was used as received (provided by the Research Institute of Chemical Defense, Beijing, China).

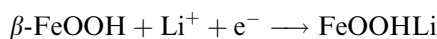
The morphologies of FeOOH powder was characterized using a scanning electron microscopy (SEM, Philips XL-60) and transmission electron microscopy (TEM, JOEL JEM2010). For structure and phase analysis, X-ray diffraction (XRD) was performed using a Bruker D8 X-ray diffractometer with Cu K $\alpha$  radiation.

The FeOOH electrode was prepared by mixing 65% FeOOH, 25% carbon black, and 10% poly (tetrafluoroethylene) (PTFE) dispersed in isopropanol. The slurry was pressed on aluminum mesh current collector and punched to a disc of  $\phi = 12$  mm. The AC electrode was prepared by the same process except that the slurry was made of 85% AC, 10% carbon black, and 5% PTFE dispersed in isopropanol. Then the FeOOH and the AC electrodes were dried in a vacuum oven at  $80^\circ\text{C}$  for 12 h to remove the solvent totally. The electrochemical tests were taken on a coin-type cell (CR2016) assembled with positive electrode/separator/negative electrode in an argon-filled glove box. For the half cell test, the FeOOH electrode or the AC electrode was used as a positive electrode, and metallic lithium as a negative electrode. As to the hybrid supercapacitor, the activated carbon electrode was used as a positive electrode, and the FeOOH as a negative electrode. The electrolyte was a 1 M  $\text{LiPF}_6$  ethylene carbonate (EC)/DMC (1:2 in volume). The typical active material mass load of negative electrode material (FeOOH) is  $5 \text{ mg/cm}^2$  and  $25 \text{ mg/cm}^2$  for the positive electrode material (AC).

## Results and discussion

Figure 1 shows the XRD pattern of FeOOH prepared by the hydrolysis process. XRD intensity investigation reveals that the FeOOH was poorly crystallized. The major diffraction peaks at  $2\theta$  of  $11.8^\circ$ ,  $16.8^\circ$ ,  $26.8^\circ$ ,  $33.9^\circ$ ,  $35.3^\circ$ ,  $39.1^\circ$ ,  $46.6^\circ$ ,  $52.2^\circ$ ,  $56.0^\circ$ , and  $64.7^\circ$  indicated that the prepared material has the signature of  $\beta$ -FeOOH which could be indexed as a tetragonal phase.  $\beta$ -FeOOH can be described as a tunnel-type structure comprising large channels of type  $2 \times 2$ , where lithium can be accommodated during the intercalation process [6, 7]. Scanning electron microscopy observation (Fig. 2) showed a panorama of FeOOH, and the fine particles of FeOOH were all rod-like. It consisted of agglomerated small grains ranging from 200 nm to 300 nm in length, and the entire particles in view were all in the same shape. To get a much more detailed information, a TEM examination was taken and shown in Fig. 3. The grain-like particle was about 40–50 nm thick. Scanning electron microscopy and TEM observation show that FeOOH material prepared by the hydrolysis process was considered to be nano-sized, which demands the requirement of the appreciable performance at high charge/discharge rate for the hybrid electrochemical supercapacitors.

We first examined the charge/discharge profile of FeOOH in a voltage range between 4.2 V and 1.5 V versus  $\text{Li}^+/\text{Li}$ , the cell was first discharged to 1.5 V, then charged to 4.2 V. Figure 4 presents the typical charge/discharge curves of the Li/FeOOH coin cell at a current density of  $0.5 \text{ mA/cm}^2$ . It delivers a capacity of  $237 \text{ mAh/g}$ , corresponding to a lithium-ion insertion/extraction occurring as follows:



Considering both specific energy and cycling life, the  $\beta$ -FeOOH shows a large capacity in the voltage range

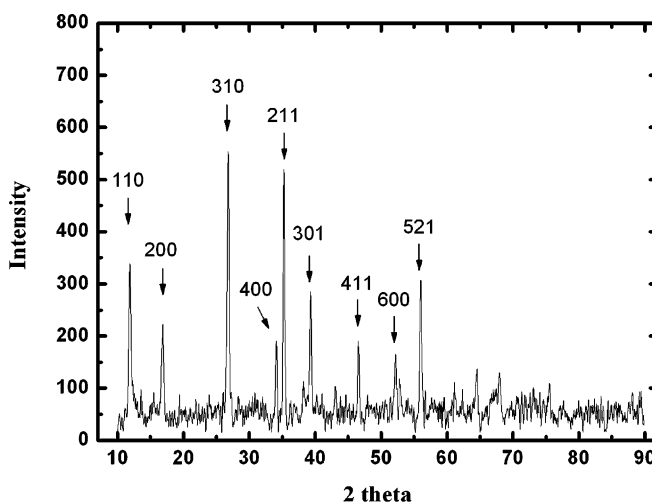
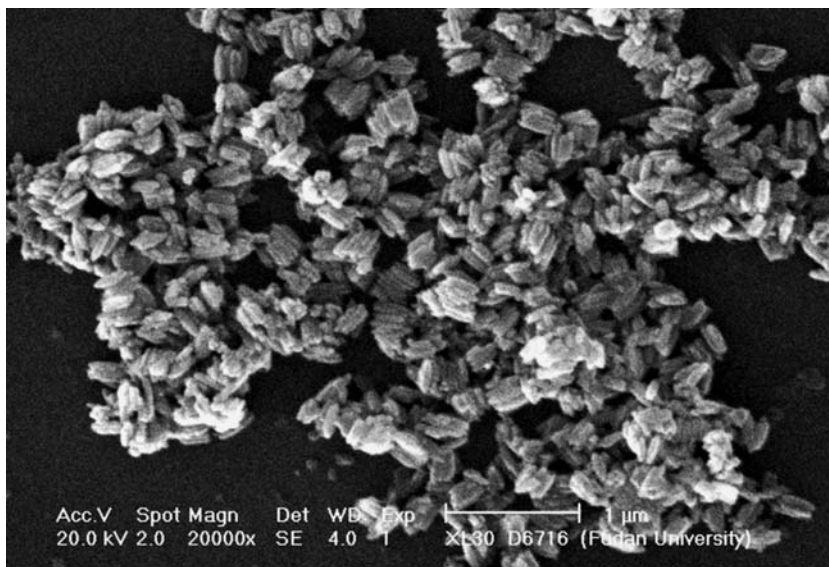
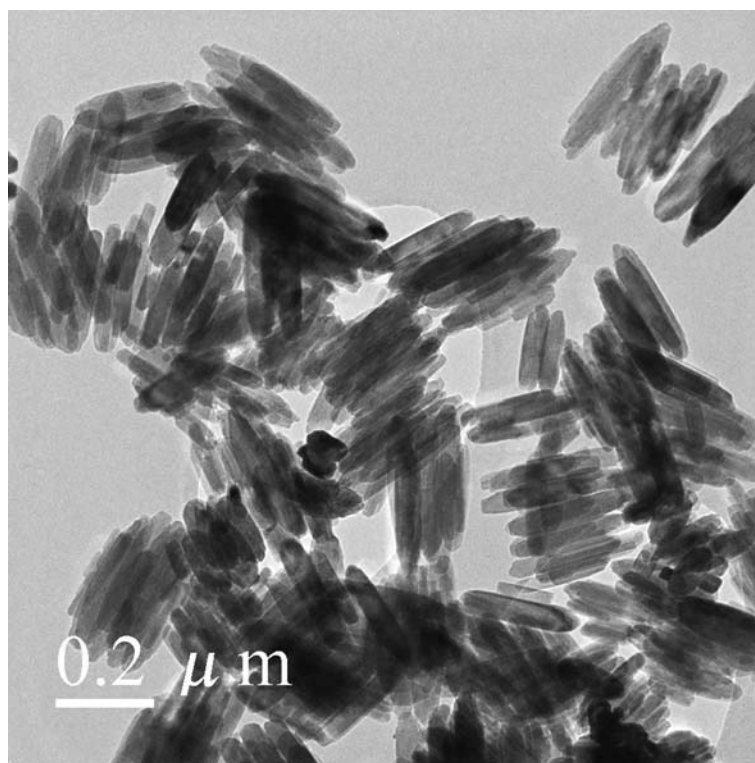


Fig. 1 X-ray diffraction (XRD) pattern of  $\beta$ -FeOOH

**Fig. 2** Scanning electron microscopy (SEM) image of  $\beta$ -FeOOH



**Fig. 3** Transmission electron microscopy (TEM) image of  $\beta$ -FeOOH



from 1.5 V to 4.2 V, but the results of cycling life test in Fig. 5 reveals that a poor cycling performance was observed. Therefore, it is necessary to choose a proper voltage range of the FeOOH negative electrode. In the current work, FeOOH was used as a negative electrode combined with an AC positive electrode to consist of a hybrid electrochemical supercapacitor. The AC positive was normally operated from 3.3 V [open-circuit-voltage (OCV)] to 4.6 V (vs.  $\text{Li}^+/\text{Li}$ ) which is safe limitation potential of the organic electrolyte against the electrochemical oxidization. The HBES is normally charged/

discharged from 0 V to a high voltage, suggesting that the charge cut-off voltage of FeOOH negative electrode should be lower than the discharge cut-off voltage of AC positive electrode. Accordingly, the charge cut-off voltage of FeOOH negative electrode was limited to 3.3 V (vs.  $\text{Li}^+/\text{Li}$ ). In corresponding to it, the discharge cut-off voltage was set on 1.6 V (vs.  $\text{Li}^+/\text{Li}$ ). The charge/discharge curves of  $\beta$ -FeOOH in the voltage range between 1.6 V and 3.3 V are also given in Fig. 4. The cell shows a discharge plateau at around 2 V (vs  $\text{Li}^+/\text{Li}$ ) with a capacity of over 200 mAh/g. The results of cycling test

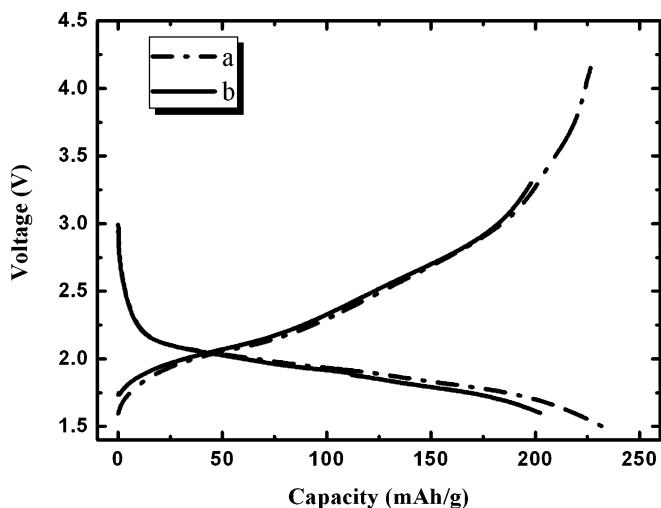


Fig. 4 First charge and discharge curves of Li/ $\beta$ -FeOOH cell. The current density is  $0.5 \text{ mA/cm}^2$  (a 1.5–4.2 V; b 1.6–3.3 V)

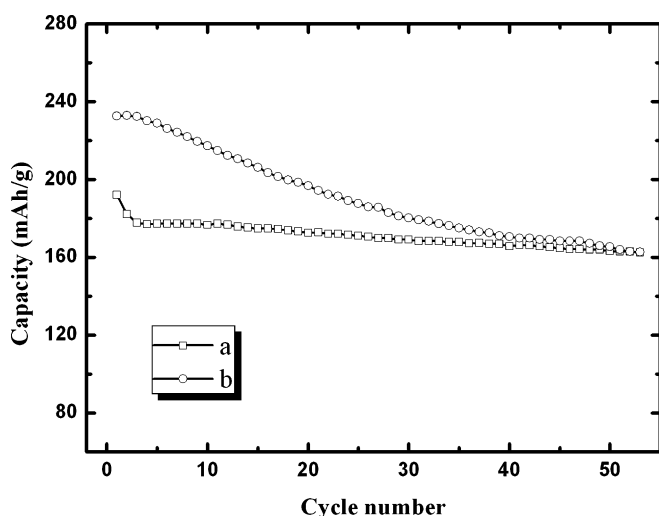


Fig. 5 Cycle performance of Li/ $\beta$ -FeOOH cell. The current density is  $0.5 \text{ mA/cm}^2$  (a 1.6–3.3 V; b 1.5–4.2 V)

at the voltage range between 1.6 V and 3.3 V are also given in Fig. 5, the cell maintains a stable capacity at about 170 mAh/g after 50 cycles of testing, indicating that  $\beta$ -FeOOH has much improved the cycling performance compared with that cycled between 1.5 V and 4.2 V.

In the HBES described in the present work, the AC was used as a positive electrode. The charge/discharge process is associated with the adsorption/desorption reaction of  $\text{PF}_6^-$  on the surface of the AC. Considering the decomposition potential of the electrolyte, the potential range was normally set from 3.3 V to 4.6 V (vs.  $\text{Li}^+/\text{Li}$ ). The typical charge/discharge curves of AC in 1 M  $\text{LiPF}_6$  (EC/DMC, 1:2 in volume) solution are given in Fig. 6. It delivered a capacity of about 35 mAh/g.

The asymmetric hybrid cell was fabricated utilizing FeOOH as the negative electrode material and active

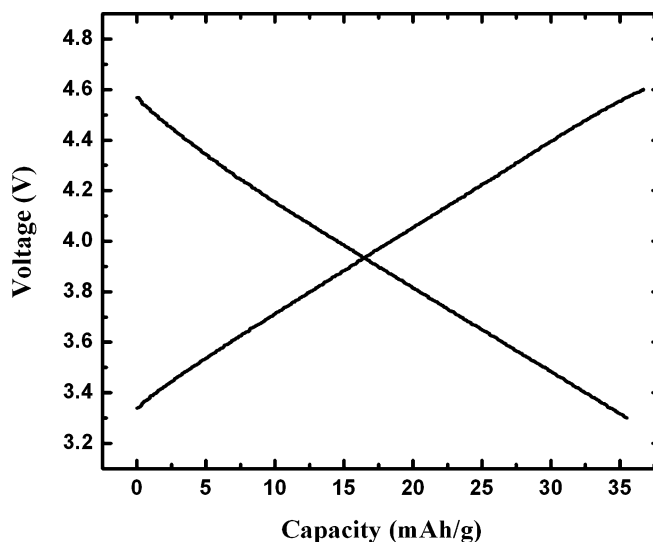


Fig. 6 Typical charge and discharge curve of Li/activated carbon (AC) between 3.3 V and 4.6 V. The current density is  $0.5 \text{ mA/cm}^2$

carbon as the positive electrode material. The active weight ratio of AC/FeOOH is 5:1. The balancing ratio was calculated using 35 mAh/g specific capacity of the AC and 170 mAh/g specific capacity of FeOOH. Figure 7 gives the charge/discharge curves of an asymmetric hybrid versus a carbon-carbon EDLC. For the AC/AC EDLCs, during charge process, the potential of AC positive electrode increases linearly from 3.3 V (OCV) to 4.6 V. Simultaneously, the potential of AC negative electrode decreases from 3.3 V to 2.0 V, it yields a cell charge cut-off-voltage of 2.6 V. For the asymmetric hybrid cell (Curve a in Fig. 7), the negative electrode undergoes a lithium-ion insertion/extraction at 2.0 V (vs.  $\text{Li}^+/\text{Li}$ ) plateau. Simultaneously, the AC positive electrode proceeds a

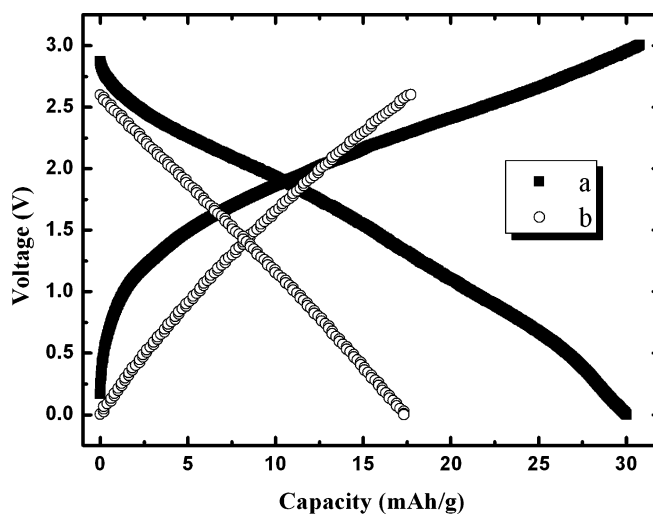


Fig. 7 Charge and discharge curves of a  $\beta$ -FeOOH/AC hybrid electrochemical supercapacitor and b AC/AC electrochemical double layer capacitor. The current density is  $0.5 \text{ mA/cm}^2$

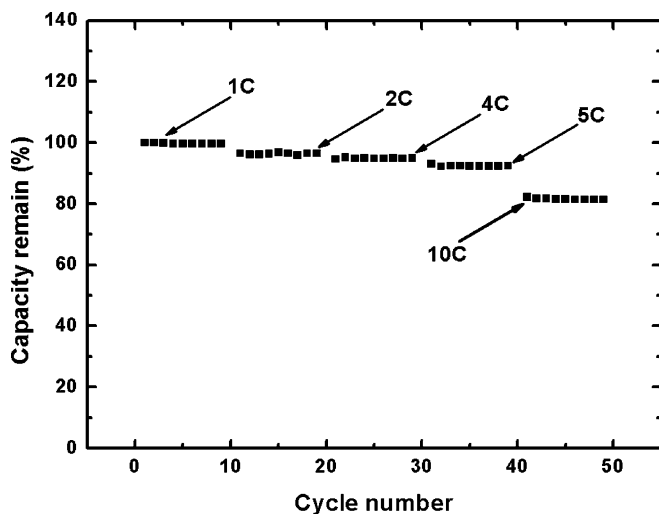


Fig. 8 Rate capability of a  $\beta$ -FeOOH /AC hybrid electrochemical supercapacitor. The current rate is from 1 C to 10 C. The voltage range is 0–3.0 V

nonfaradic reaction of  $\text{PF}_6^-$  adsorption/desorption. As the discharge end voltage of FeOOH is 1.6 V (vs.  $\text{Li}^+/\text{Li}$ ), the cell charge cut-off-voltage is 3.0 V. As a result, the cell reveals a slightly sloping discharge voltage profile from 0 V to 2.8 V compared with the sharply sloped AC/AC EDLCs (Curve b in Fig. 7). The capacity given in the figure is calculated based on the total weight of the electrode materials, including the positive and negative electrode material. Herein we also estimated the specific energy by the following equation:

$$W = CU^2/2m_{\text{act}}$$

Where  $W$  is the specific energy (Wh/kg) stored in the polarized dielectric material [8],  $C$  the capacity,  $U$  the working voltage and  $m_{\text{act}}$  is the total amount of active materials. The estimated specific energy of the hybrid capacitor is about 45 Wh/kg, approximately two times of AC/AC EDLCs.

Figure 8 gives the rate capability of this asymmetric system. All tests were performed using a coin-type cell. The cell was charged with a current rate of 1 C and discharged at different current densities from 1 C to 10 C. For each current density, nine cycles were tested. Even at a discharge rate of 10 C, it holds 80% of capacity compared with that at 1 C discharge rate. It should be noted that limitation by using a coin-type cell may result in a large ohmic resistance affecting the rate measurements. The cycling life test at charge/discharge rate of 4 C is shown in Fig. 9, FeOOH /C capacitor exhibited a desirable cycle profile, it remained over 96% of initial capacity after 800 cycles.

## Conclusion

In the present work, we prepared a nano-sized iron oxyhydroxide (FeOOH) via a hydrolyzing route under

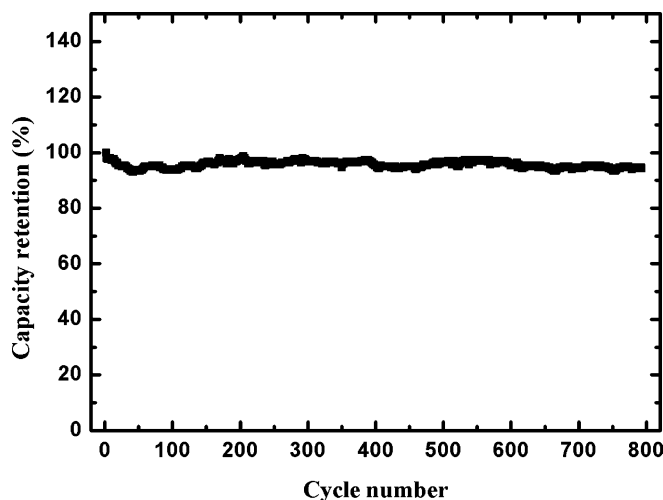


Fig. 9 Cycle life of a  $\beta$ -FeOOH/AC hybrid electrochemical capacitor in the voltage range from 0 V to 3.0 V. The charge and discharge rate is 4 C

mild and facile synthesis condition. It delivers a capacity of about 237 mAh/g in the voltage range from 1.5 V to 4.2 V, and shows a very good cycling performance in the voltage range from 1.6 V to 3.3 V with a capacity of 170 mAh/g. We for the first time applied the nano-structural FeOOH and used it as a negative electrode for an asymmetric HBES combined with an AC positive electrode in 1.0 M  $\text{LiPF}_6$  ethylene carbonate/DMC (1:2 in volume) solution. The FeOOH/AC cell shows a sloping voltage profile from 1.5 V to 2.8 V and delivers a capacity of 30 mAh/g based on the overall active materials, corresponding to the energy density of 45 Wh/kg which is two times of EDLC. This system also shows a good performance of cycle life and rate test. It remains approximately at 96% capacity after 800 cycles. Even at 10 C discharge rate, the capacitor also holds 80% of capacity compared with that of 1 C discharge rate. Despite the undesirable specific power and cycling life in the present stage, which cannot demand the requirement of the practical application level compared with the conventional EDLCs, a high working voltage and energy density, especially with a low cost and nontoxic FeOOH electrode material can be an interesting alternative to the current EDLCs.

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