

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

An investigation of ultrathin nickel-iron layered double hydroxide nanosheets grown on nickel foam for high-performance supercapacitor electrodes





Yi Lu ^{a, b}, Bin Jiang ^b, Liang Fang ^{a, *}, Faling Ling ^a, Fang Wu ^{a, **}, Baoshan Hu ^c, Fanming Meng ^a, Kaiyang Niu ^d, Feng Lin ^e, Haimei Zheng ^{d, f, ***}

^a State Key Laboratory of Mechanical Transmission, College of Physics, Chongqing University, Chongqing, 400044, China
 ^b National Engineering Research Center for Magnesium Alloys, College of Materials Science and Engineering, Chongqing University, Chongqing 400044,

China

^c College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 401331, China

^d Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

^e Department of Chemistry, Virginia Tech University, VA 24061, United States

^f Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, CA 94720, United States

A R T I C L E I N F O

Article history: Received 2 February 2017 Received in revised form 1 April 2017 Accepted 18 April 2017 Available online 19 April 2017

Keywords: NiFe-Layered double hydroxide Nanosheet Electrochemistry Energy storage Supercapacitor

ABSTRACT

Layered double hydroxide materials with sheet-like morphologies (i.e., LDH nanosheets) have been proposed to use in supercapacitors. However, the practical application of LDH nanosheets has been inhibited by the notorious inter-particle aggregation and poor charge transport between active materials and current collectors. In this work, 3D nickel-iron layered double hydroxide (NiFe-LDH) nanosheet films with porous nanostructures were synthesized using a hydrothermal method. The ultrathin nanosheets are homogeneously and vertically aligned on the surface of Ni foam. The pseudocapacitors assembled using NiFe-LDH nanosheets exhibit a superior specific capacitance of 2708 F g⁻¹ at 5 A g⁻¹, higher than the previously reported LDHs. The effect of growth concentration and Ni/Fe mole ratio on the electrochemical properties was also investigated. Asymmetric supercapacitors with the NiFe-LDH nanosheets of 52 Wh kg⁻¹ at an average power density of 800 W kg⁻¹. When two aqueous asymmetric supercapacitors were assembled in series and charged for only 1 min, the stored energy was capable of powering two green light-emitting-diodes for more than 5 min, indicating the great potential of these 3D NiFe-LDH nanosheets for high-performance energy storage.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

With the daunting challenges of global warming and depletion of fossil fuels, a great deal of efforts have been focused on sustainable energy sources, including designing high-performance energy storage systems and developing earth abundant energy resources [1]. Recently, the fabrication of high performance energy

** Corresponding author.

storage devices, such as solar cells, fuel cells, lithium battery and supercapacitor, has become a crucial research field [2]. Owing to their larger capacity in store energy than conventional capacitors, and higher specific power and longer cycle-life than batteries, supercapacitors have drawn great interest [1-3]. Most of the commercial supercapacitors are based on electrical double layer capacitor and mainly consist of carbon-based materials, such as carbon nanotubes [3], graphene [4], and active carbon (AC) [5]. They usually possess good cycle lifetime and high power density, but fail to meet the requirements of high specific capacitance and energy density as peak-power assistance in electric vehicles [6,7]. In contrast, pseudocapacitive materials (e.g., RuO₂, MnO₂, NiO, Co₃O₄, Ni(OH)₂, Co(OH)₂ and their composites), which are dominated by reversible fast surface faradaic redox reactions, can deliver

^{*} Corresponding author. State Key Laboratory of Mechanical Transmission, College of Physics, Chongqing University, Chongqing, 400044, China.

^{***} Corresponding author.

E-mail addresses: Ifang@cqu.edu.cn (L. Fang), fang01234@163.com (F. Wu), hmzheng@lbl.gov (H. Zheng).

much higher specific capacitance than carbon-based materials [8,9]. Among these materials, RuO₂ possesses a specific capacitance as large as 720 F/g, but due to its high cost, the application of this material was limited [8]. Thus, researchers have focused on the development of novel materials for pseudocapacitor applications.

High-performance supercapacitor electrodes should possess characteristics such as high utilization efficiency and high transport rate for both electrolyte ions and electrons [5]. Thus, it is of significance to improve the electron transport in active materials, and the electric contacts between active materials and current collectors by designing nanoscale electrode materials with large surface areas and stable porous nanostructures [10-13]. Layered double hydroxides (LDHs) with a general formula of $[M^{II}_{1-}_{x}M^{III}_{x}(OH)_{2}]^{x+}[A^{n-}_{x/n}\cdot mH_{2}O]^{x-}$ $(M^{II}$ and M^{III} denote the layers of divalent and trivalent metallic ions, respectively; Aⁿ⁻ is an interlayer anion), have attracted increasing attention because of their relatively low cost, high redox activity, large specific surface area, laminated structure and environmentally friendly nature [14]. Specially, LDHs containing transition metals, such as Ni, Co, Mn, Fe, and Al, are deemed as promising candidates [15]. For example, Guo et al. prepared NiMn-LDH nanosheets through a one-step wetmethod and found the specific capacitance of the NiMn-LDH can reach 1511 F g^{-1} at 2.5 Å g^{-1} [16]. Li et al. reported that a novel structure of CoFe-LDH nanoplatelets shell supported on a copper wire produced by an electrosynthesis method delivered a high specific capacitance of 755 mF cm^{-2} at the discharge current density of 2.5 mA cm⁻² [17].

In recent years, NiFe-based composites with different morphologies (such as nanoparticles, nanowires, nanorods, nanotubes, and flowerlike) have been introduced as electrode materials in electrochemical energy conversion and storage [1,18]. The analysis of density of states and partial density of states of NiFe-LDH and Ni(OH)₂ showed that NiFe-LDH has a stronger capability for electron transportation and higher activity than Ni(OH)₂ [19]. However, NiFe-LDHs synthesized via co-precipitation and hydrothermal methods are usually powders, and thus polymer binders, e.g., Nafion, are usually required to form compact electrodes, leading to low conductivity with current collectors and poor mechanical stability [20,21]. To overcome these limitations, increasing interest was paid on the growth of hierarchical nanostructured materials directly on the Ni foam, which has large surface area, high porosity and enhanced conductivity to improve supercapacitance performance. Chen et al. fabricated NiCo-LDH nanosheets on Ni foam via a hydrothermal co-deposition process, and the LDH showed very high capacitance (2682 F g-1 at 3 A g-1) [22]. However, to the best of our knowledge, NiFe-LDH grown on Ni foam for supercapacitor has not been reported.

In this work, we propose a one-step hydrothermal method to directly synthesis ultrathin NiFe-LDH nanosheets on 3D Ni foams. The morphologies and electrochemical properties of NiFe-LDHs with different Ni/Fe molar ratios were explored. The assynthesized NiFe-LDH electrode exhibits outstanding performance. We fabricated an aqueous asymmetric supercapacitor using the NiFe-LDH film as the positive electrode and active carbon as the negative electrode. In addition, the asymmetric supercapacitor was used in powering green light-emitting-diode. Our results suggest that the NiFe-LDH nanosheet arrays can act as high-performance electrode materials for supercapacitor applications.

2. Experimental section

2.1. Synthesis of NiFe-LDH nanosheets on Ni foam

All chemical reagents were used as received without further purification. The film electrode material was prepared by a simple one-step process as illustrated in Scheme 1: Firstly, Ni foam $(10 \text{ mm} \times 20 \text{ mm} \times 1.7 \text{ mm}, 380 \text{ g m}^{-2}, 110 \text{ ppi})$ was pretreated successively with 3 M HCl solution, deionized water, and absolute ethanol in an ultrasound bath for 10 min each in order to remove NiO layer and residual organics on the surface. Then, an aqueous solution containing Ni(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, urea, H₂O (36 mL) was stirred thoroughly to form a clear solution. After drving, the Ni foam was immersed in a 50 ml Teflon-lined autoclave containing above homogeneous solution. The autoclave was sealed, maintained at 120 °C for 12 h, and then cooled to room temperature naturally. The final product was thoroughly washed with H₂O and ethanol and vacuum dried at 60 °C for 8 h. For the sake of comparison, nanosheets with different feeding contents of total metal ion (Ni²⁺and Fe³⁺) before reaction and different feeding mole ratio of Ni^{2+}/Fe^{3+} were also synthesized by the same process (see Table S1). The mole ratio of urea/feeding metal ion is 5. The mass of the nanosheets on Ni foam was determined by subtracting the weight before deposition from the weight after deposition. The average loading densities of active materials were about 1 mg cm⁻² for all electrodes.

2.2. Fabrication of asymmetric supercapacitor

To construct an asymmetric supercapacitor, the NiFe-LDH nanosheet arrays on Ni foam were used as the positive electrode and active carbon as the negative electrode (Scheme 1). The negative electrode was prepared by mixing activated carbon, acetylene black, and poly(vinylidene fluoride) with a mass ratio of 8:1:1, which pressed on Ni foam and dried at 80 °C for 12 h. The asymmetric supercapacitor was separated by a separator, and a 1 M KOH aqueous solution was used as the electrolyte.

2.3. Material characterization

The morphological investigations of the samples were received by scanning electron microscopy (SEM, JEOL JSM-7800F), and energy dispersive spectrometer (EDS) attached to the SEM was employed to characterize distribution of elements of samples. Transmission electron microscope (TEM) images were obtained on a HITACHI HT7700 field emission microscope. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance diffractometer using a Cu K α source. The functional groups were analyzed by fourier transform infrared spectroscopy (FT-IR, Nicolet iS50). Kratos Axis Ultra X-ray photoelectron spectroscope (XPS, Al K α source) was used to investigate the surface properties.

2.4. Electrochemical measurements

Electrochemical performances of all as-prepared LDH nanosheets electrodes were evaluated using a three-electrode setup. The Ni foam supported NiFe-LDH nanosheets acted as the working electrode (10 mm \times 10 mm \times 1.7 mm), which were soaked in a 1 M KOH solution. A large-area platinum foil and a saturated calomel electrode (SCE) served as the counter electrode and the reference electrode, respectively. The electrochemical properties of asymmetric supercapacitor were investigated under a two-electrode cell configuration in 1 M KOH electrolyte solution. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements were conducted on a CHI760E electrochemical workstation (Chenhua, Shanghai). The specific capacitance, Cs (F g^{-1}), of nanosheets film electrodes were calculated from GCD curves as follows: $C_s = I \times \Delta t / (\Delta V \times m)$, where I (A) is the discharge current, ΔV (V) refers to the potential change during the discharge time Δt (s), and m (g) represents the mass of the active material in the electrode. The C_s of asymmetric



Scheme 1. The formation mechanism of NiFe-LDH films supported on Ni foams and the illustration scheme of the asymmetrical supercapacitor.

supercapacitor was calculated from GCD curves as follows: $C_s = I \times \Delta t / (V \times m')$, where m' (g) is the total mass of the active material in the positive and negative electrodes. The energy density, E (Wh kg⁻¹) and power densities, P (W kg⁻¹) of the film electrodes and the asymmetric supercapacitor were calculated as follows: $E = 0.5 \times C_s \times V^2$, $P = E/\Delta t$.

3. Results and discussion

3.1. Morphological and structural characterization

Morphological and structural characterization of the NiFe-LDH nanosheets which were prepared at the total metal ions of 1 mmol and Ni/Fe mole ratio 1:1 were shown in Fig. 1. It can be observed that the film was supported on the 3D macroporous Ni foam substrate. The structure of Ni foam was well retained after being covered with the film (Fig. 1a). Clearly, the nanosheets were homogeneously deposited on the surface of Ni foam, suggesting

that the urea hydrolysis system was favorable for growing hierarchical NiFe-LDH nanosheets on Ni foam. As shown in Fig. 1b, the film possessed a porous nanostructure composed of nanosheets with thick about 12–15 nm. These nanosheets intersected and aligned vertically on the nickel foam. This vertical array and the porous nanostructure facilitated the charge transport from active materials to current collector, and allowed an easy diffusion of ions to the electrolyte/electrode interface without any blocks of binders. The typical TEM image (Fig. 1c) of the nanosheets obtained after ultrasonic treatment in ethanol shown a transparent feature, indicating its ultrathin nature. EDS mappings displayed the presence of Ni, Fe, C and O unambiguously, which proved that the Ni, Fe, C and O were homogeneous distribution throughout NiFe-LDH/Ni foam.

In the XRD pattern of the nanosheets (Fig. 2a), the bands at $2\theta = 9.7^{\circ}$, 20.0° were corresponding to the (003) and (006), respectively, exhibiting the typical characteristics of LDH materials [21]. The peaks at 44.5°, 51.8°, 76.3° denoted the Ni substrate. In



Fig. 1. SEM images at different magnifications (a and b) and TEM images (c) of the nanosheets supported on Ni foam, EDS mapping (d) of Ni, Fe, C and O element.



Fig. 2. (a) XRD patterns of NiFe-LDH@Ni foam (blue line) and Ni(OH)₂@Ni foam (red line). FT-IR spectrum (b), Ni 2p XPS spectra (c) and Fe 2p XPS spectra (d) of nanosheets supported on Ni foam.

addition, without Fe³⁺ addition, the as-obtained product can be identified as β -Ni(OH)₂ phase (JCPDF 01-1047) by XRD pattern [23]. FT-IR spectra of NiFe-LDH was shown in Fig. 2b. The characteristic bands at 3433, 1620 cm⁻¹ were due to the stretching and bending vibrations of the -OH between LDH layers, and the peak at 1351 cm⁻ ¹ was assigned to the vibration of CO_3^{2-} in the interlayer of LDH [24]. Other absorption bands observed in the range 500–700 cm⁻¹ were mainly corresponding to metal oxygen lattice vibrations, such as M-O, M-O-M and O-M-O. FT-IR spectrum further illustrated that asobtained NiFe-LDH possesses abundant hydrophilic hydroxyl groups, which favored its good wettability to electrolyte. XPS spectra in Fig. S1 showed the presence of Fe, Ni, C and O on the film surface. In Ni 2p XPS spectrum (Fig. 2c), two obvious shakeup satellites (indicated as "Sat") closed to two spin-orbit doublets at 873.5 and 855.7 eV can be identified as Ni 2p_{1/2} and Ni 2p_{3/2} signals of Ni²⁺, respectively [22]. The Fe 2p core-level spectrum of the NiFe-LDH presented Fe $2p_{1/2}$ (725.4 eV) and Fe $2p_{3/2}$ (713.9 eV) spin-orbit peaks (Fig. 2d), indicating the presence of tri-ferrous Fe^{3+} as a component [25].

Fig. 3 showed the images of the nanosheets with different Ni/Fe feeding mole ratios and different feeding contents of total metal ions. Without Fe³⁺, the as-obtained nickel hydroxide (Ni1Fe0) film appeared 45–56 nm thick (Fig. 3a). With the addition of Fe³⁺, the morphologies of the nanosheets changed significantly and the mean thickness decreased to less than 20 nm. The nanosheets were small and disordered at the Ni/Fe ratio of 3:1 (Fig. 3b). As the Ni/Fe mole ratio decreased from 1:1 to 1:3, more Fe³⁺ became embedded into NiFe-LDH nanosheets, and the mean thickness of the NiFe-LDH nanosheets increased to 14 nm, 18 nm, respectively (Figs. 1b and 3c). Additionally, incorporation of Fe improved the size uniformity of nanosheets and the porous structure of film, which suggested that the incorporation of Fe could increase the oriented

growth ability and weaken the self-aggregation of nanosheets. This should attribute to that Fe³⁺ isomorphically replaced some of the Ni²⁺ sites in forming LDHs, inducing excessive positive electric charge on the host sheets [26], which can depress the excessive self-aggregation of double hydroxide layers by electrostatic interaction. Moreover, the thin nanosheets random stack when the feeding contents of total metal ions was 0.5 mmol. As the concentration of feeding contents changed from 1 mmol, 2 mmol to 3 mmol, the mean thickness of the LDH nanosheets increased to 14, 20, and 27 nm, respectively (Figs. 1b and 3e, f). More importantly, the thin nanosheets aggregated with the total metal ions increasing could induce the decrease of active surface areas on the electrode materials, which was adverse for electrochemical reaction.

The possible mechanism to form NiFe-LDH nanosheets by hydrothermal method is illustrated in Scheme 1. At the beginning of the hydrothermal treatment, the Ni foam was immersed in homogeneous solution containing Ni^{2+} , Fe^{3+} , NO_3 and urea in Teflonlined autoclave. With the temperature rise, the urea was hydrolyzed to produce OH^- and CO_3^{2-} ($CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$, $NH_3 \cdot H_2O \rightarrow NH_4^+ + OH^-$, $CO_2 + H_2O \rightarrow CO_3^{2-} + 2H^+$) [27]. Ni^{2+} and Fe³⁺ first reacted with OH⁻ to produce nickel and iron hydroxide monomers, which precipitated and aggregated on the surface of nickel substrate as the aggregation cores [28]. With the hydrothermal treatment time increase, the hydrolysis of urea was accelerated, and more OH ions were released into the solution. The nickel and iron hydroxide particles continued to aggregate and underwent olation reactions with each other. Then they began to crystallize and grow along the c-axis, gradually forming a NiFe-LDH nanosheets layer [21]. Because the aggregation cores might distribute on Ni substrates along different directions, the as-formed NiFe-LDH hybrid nanosheets were intersected, producing films with highly well-define porous structures. The concentration of



Fig. 3. SEM images of the as-obtained nanosheets obtained at different Ni/Fe feeding mole ratios (total metal ions 1 mmol): (a) 1:0, (b) 3:1, (c) 1:3, and different feeding contents of total metal ions (Ni:Fe = 1:1): (d) 0.5 mmol, (e) 2 mmol, (f) 3 mmol.

reactive ions was significant to the nucleation and growth for highquality crystals [29]. Unlike the methods using adscititious alkali to produce OH⁻, the relatively slow liberation of OH⁻ at high temperatures facilitated the relatively slow generation and aggregation of primary particles and relatively fast crystallization for the formation of thinner, larger nanosheets.

3.2. Electrochemical properties of the film electrodes

The electrochemical characteristics of the Ni(OH)₂ and NiFe-LDH electrodes were investigated using CV (Fig. 4a). Considering the capacitance contribution from conductive substrates, the CV curves of nickel foam was also studied, which indicated the capacitance contribution from Ni foam can be negligible [30]. The Ni(OH)₂ film exhibited a pair of well-defined redox couple at 0.3 V vs SCE, which attributed to the transformation between Ni(OH)₂ and NiOOH [31]. This redox couple also occurred on the NiFe-LDH film. More importantly, the LDH electrode showed a larger redox current density than Ni(OH)₂, which due to the abundant active sites provided by the ultrathin LDH nanosheets after the incorporation of Fe³⁺ in the Ni(OH)₂ lattice. Additionally, the comparison of CV curve average areas further indicated that the NiFe-LDH nanosheets film-electrode possessed a significantly higher specific capacitance than unitary nickel hydroxide electrodes [32]. Fig. S2 showed the CV curves of the NiFe-LDH electrode at different scan rates of 1–50 mV s⁻¹. With the increase of scan rate, the anodic and cathodic peaks in the CV curves respectively shifted toward a positive and negative potential, indicating the quasi-reversible feature of the redox couples. This observation was attributed to the Ohmic resistance and increasing polarization of the electrode when the electrolyte ions diffused in the porous electrode during the redox reaction as the increase of scan rates [33]. The GCD of the film-based electrode at different current densities (Fig. 4b), displayed a typical pseudocapacitive behavior. The charge-discharge plateaus further demonstrate the Faradaic characteristic of electroactive materials. The special capacitance values of the Ni1Fe1-LDH electrode calculated from the galvanostatic discharge curves were 2708, 2149, 1874, 1694, 1566 and 1456 F g⁻¹ at current densities of 5, 6, 7, 8, 9, and 10 A g^{-1} , respectively. The Columbic efficiency (~95.8%) is obtained for the Ni1Fe1-LDH electrodes at current density of 5 A/g, which demonstrate their good capacitive properties. The specific capacitance of Ni1Fe1-LDH nanosheet arrays at different current densities was shown in Fig. S3.

Fig. 4c demonstrated the GCD of the hybrid film-electrodes at different feeding metal ion concentrations and different Ni/Fe feeding mole ratios. It is found that Cs increase with more Fe embedded. However, too much iron, such as 1:3 of mole ratios for Ni/Fe, caused a decrease of C_s. In addition, when the feeding content of metal ions increased from 0.5 to 1, 2, 3 mmol, the calculated C_s changed from 1028 to 2708, 2572 and 2487 F g⁻¹, respectively. This C_s variation could be also well reflected by the gradual changes of morphology of hybrid films at various Ni, Fe feeding mole ratios (Figs. 1b and 3). The thinner nanosheets with vertically oriented on the nickel foam and well-defined porous nanostructure seemed to be more effective for contributing pseudocapacitance. The highest C_s (2708 F g⁻¹ at 5 A g⁻¹) was higher than that of most of previously reported nickel-based and cobalt-based oxide/hydroxide composite pseudocapacitive materials (Fig. 4d and Table S2). Besides, EIS measurements were performed to examine the electron transfer and ion diffusion property of the seven electrodes (Fig. 4e). No obvious semicircles were observed for all of the above electrodes in the high frequency region, which attributed to the high charge transfer process. Warburg resistance of Ni1Fe1-LDH electrode was lower than other electrodes, which indicated that the Ni1Fe1-LDH electrode possessed suitable ionic conductivity. Furthermore, the tendencies of Equivalent Series Resistance (Resc) agreed well with the specific capacitances [34,35]. These results clearly demonstrated that Ni1Fe1-LDH based electrodes have much faster electron transfer speed than other electrodes.

The high supercapacitive performance of NiFe-LDH nanosheet arrays can be attributed to the synergistic effects of the nanostructures as follows: (i) The NiFe-LDH film which was composed of much thinner nanosheets and better defined porous nanostructures not only provided numerous electroactive sites for the ions but also promote access for the electrolyte. (ii) The NiFe-LDH phase nanosheets with enlarged interlayer spacing (compared with Ni(OH)₂), which can enhance the ions diffusion within active materials. Thus, the reaction kinetics were accelerated and more charges can be stored to the electrode in unit time [12]. (iii) Incorporation of Fe³⁺ in the Ni(OH)₂ lattice led to a high dispersion of Ni unit, ensuring the Ni species participated in the faradic reaction efficiently, especially improving of the utilization of Ni



Fig. 4. (a) Comparative CV curves of the Ni1Fe1-LDH, Ni $(OH)_2$ and Ni foam at a scan rate of 5 mV s⁻¹. (b) Galvanostatic charge-discharge curves of Ni1Fe1-LDH in different current densities. (c) Galvanostatic charge-discharge curves and (d) Comparison of specific capacitance of different LDH-based electrode materials. (e) Nyquist plots of NiFe-LDH with different Ni/Fe feeding mole ratios and different feeding contents of metal ions.

species. (iv) NiFe-LDH with highly oriented layered single crystal structure was directly grown on Ni foam, resulting in higher conductivity, which can improve the electron carrier mobility.

The cycling stability of NiFe-LDH nanosheet electrode was further measured at 10 A g⁻¹ (Fig. S4). With the increases of cycle number, the specific capacitance decreased gradually and retained about 621 F g⁻¹ after 500 cycles (42.6%). In order to understand the causes to induce the decrease of the specific capacitance and design better electrode materials, Raman spectroscopy and SEM were employed after cycling stability test. As shown in Fig. S5a, the bands at 449 cm⁻¹ and 461cm⁻¹ were attributed to Ni(OH)₂ [36]. The band at 494 cm⁻¹ and 530 cm⁻¹ were assigned to defective or disordered of Ni(OH)₂. However, the stronger intensities of the band in NiFe-LDH compared with that in Ni(OH)₂ reflected the more complex local environments around Ni-O, and suggested that the NiFe-LDH film possessed more structural defects [37]. According to the spectrum of the NiFe-LDH after cycle test, the pair of bands located at 474 and 554 cm⁻¹ were attributed to Ni-O vibrations in NiOOH, which indicated that the conversion of Ni²⁺ to Ni³⁺ is more facile than the reverse process for NiFe-LDHs materials under numbers of fast charge/discharge conditions. The bands of Fe₃O₄, Fe₂O₃ and FeOOH, which should exhibit at 670, 650-740, and 660 cm^{-1} , respectively, were not observed clearly, indicating that Ni was the active site for faradaic adsorption reaction. Thus after numbers of charge/discharge process, the irreversible conversion of Ni²⁺ to Ni³⁺ leads the gradual decrease of Ni²⁺ in the active materials, causing the special capacitance of the pseudocapacitor become lower and lower. In addition, the top of the nanosheets are found to have some collapse after numbers of cycles. As shown in Fig. S5b, the fundamental sheet structure of NiFe-LDH film is essentially retained after cycle test, which further demonstrated the robustness of the electrode (Fig. S5b). However, the top parts of some nanosheets collapsed leads to a reduced specific surface area. which is responsible for the decrease of specific capacitance. Thus, it is significantly to improve the stability and cycle reversibility of NiFe-LDH in KOH electrolyte for better cycling performances.

3.3. Electrochemical properties of NiFe-LDH based asymmetric supercapacitor

To further investigate the potential application of the asfabricated NiFe-LDH in electrochemical energy storage, an aqueous asymmetric supercapacitor cell was assembled and measured, in which NiFe-LDH nanosheet arrays were used as the positive electrode and active carbon (at -1.0-0.0 V) was used as the negative electrode (NiFe-LDH//AC), as illustrated in Scheme 1. The fundamental electrochemical performance of AC was shown in Fig. S6. In order to obtain the maximum performance of the asymmetric supercapacitor cell, the charges of the positive and negative electrodes should be optimized based on the relationship [38] $m^+/m^- = C^-\Delta V^-/C^+\Delta V^+$, where C^+ and C^- represent the specific capacitance values of the positive and negative electrodes, respectively, and ΔV is the potential range. The CV curve exhibited double contribution of electric double-layer capacitance and pseudocapacitance at 0-1.6 V (Fig. 5a). The GCD curves of the asymmetric supercapacitor at various current densities were shown in Fig. 5b. The C_s of NiFe-LDH//AC were calculated to be 141.3, 115.5, 83.0, 59.25, and 47 F g⁻¹ at current densities of 1, 2, 4, 6, and 8 A g⁻¹, respectively. In addition, the Columbic efficiency of the asymmetric supercapacitor is 91.5% at the current density of 1 A/g. The Nyquist impedance spectra of the asymmetric supercapacitor were shown in Fig. S7. The charge-transfer resistance is about 2 Ω , implying that the asymmetric supercapacitor exhibits favorable charge-transfer kinetics and fast electron transport. Based on these $C_{\rm s}$ values, the calculated energy densities of the NiFe-LDH//AC were 50.2, 41.1, 29.5, 21.1 and 16.7 Wh kg⁻¹ at average power densities of 800, 1600, 3200, 4800 and 6468 W kg⁻¹, respectively (Fig. 5c). The obtained highest energy density (50.2 Wh kg⁻¹ at 800 W kg⁻¹) was higher than that of the reported devices in literature, such as Ni(OH)₂//AC (21.8 Wh kg⁻¹ at 660 W kg⁻¹) [39], NiCo-LDH-Zn₂SnO₄//AC (23.7 Wh kg⁻¹ at 284.2 W kg⁻¹) [40], NiAl-LDH/GNS// GNS (31.5 Wh kg⁻¹ at 400 W kg⁻¹) [41], RGO-CoAl-LDH//AC (35.5 Wh kg⁻¹ at 875 W kg⁻¹) [42] and NiCo-LDH-ZTO//AC (23.7 Wh kg⁻¹ at 284.2 W kg⁻¹) [40]. We also used GCD measurement to evaluate the durability of the as-fabricated asymmetric supercapacitor. As shown in Fig. 5d, the as-obtained asymmetric supercapacitor can retain about 65% of its original capacitance after 2000 cycles, which is comparable to that of other asymmetric supercapacitors. Furthermore, two asymmetric supercapacitors in series can easily light two green light-emitting-diodes (LEDs) (3 V, 20 mA) for more than 5 min after charging for a total time of 1 min, as shown in Fig. 5e, which indicated the potential applications in supercapacitor devices.



Fig. 5. (a) CV curves of the NiFe-LDH//AC asymmetric supercapacitor at different scan rates. (b) Galvanostatic charge-discharge curves of NiFe-LDH//AC asymmetric supercapacitor at different current densities. (c) Ragone plots of NiFe-LDH//AC device in this work, in comparison with the reported supercapacitor. (d) Cycling performance of the NiFe-LDH//AC asymmetric supercapacitor at a current densities. (e) Photographs of two green LEDs powered by two asymmetric supercapacitor cells in series.

4. Conclusion

Ultrathin NiFe-LDH nanosheet arrays with different Ni/Fe molar ratio and different feeding contents of metal ions have been successfully fabricated using a facile one-step hydrothermal method on three-dimensional Ni foam. Benefiting from the highly oriented layered single crystal structure and ultrathin nature of nanosheets as well as the well-define porous nanostructure, the NiFe-LDH nanosheets film electrodes exhibited ultrahigh specific capacitance (2708 F g⁻¹ at 5 A g⁻¹). The specific capacitance was obviously higher than that of most of the previously reported electrodes based on LDHs. In addition, the as-obtained NiFe-LDH//AC asymmetric supercapacitor presented high energy density (50.2 Wh kg-¹) at the power density of 800 W kg⁻¹, significantly exceeded most of the previously reported nickel oxide/hydroxide-based asymmetric supercapacitors. The present work suggests that the asprepared NiFe-LDH nanosheets are promising electrode materials to fabricate high performance supercapacitors.

Acknowledgment

This work was supported by SKLMT-KFKT-201419 and SKLM-ZZKT-2015 Z16, National High Technology Research and Development Program of China "863 Plan"(2015AA034801), NSFC (No.11374359,11304405,11544010 and 11547305), the Nature Science Foundation of Chongqing (cstc2013jcyjA50031, cstc2015jcyjA50035 and cstc2015jcyjA1660), the Fundamental Research Funds for the Central Universities (CDJZR14135502, CDJZR14300050, 106112016 CDJZR288805 and 106112015CDJXY300002) and the Sharing Fund of Large-scale Equipment of Chongqing University (Grant Nos. 201606150016, 201606150017 and 201606150056).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.jallcom.2017.04.197.

References

- [1] Y. Feng, H. Zhang, Y. Zhang, X. Li, Y. Wang, ACS Appl. Mater. Interfaces 7 (2015) 9203–9210.
- [2] S. Sahoo, K.K. Naik, D.J. Late, C.S. Rout, J. Alloys. Compd. 695 (2017) 154.
- [3] F. Su, X. Lv, M. Miao, Small 11 (2015) 854–861.
- [4] Y. Song, J. Yang, K. Wang, S. Haller, Y. Wang, C. Wang, Y. Xia, Carbon 96 (2016) 955–964.
- [5] W. Hu, R. Chen, W. Xie, L. Zou, N. Qin, D. Bao, ACS Appl. Mater. Interfaces 6 (2014) 19318–19326.
- [6] P.C. Chen, G. Shen, Y. Shi, H. Chen, C. Zhou, ACS Nano 4 (2010) 4403–4411.
- [7] J. Huang, B.G. Sumpter, V. Meunier, Angew. Chem. Int. Ed. 47 (2008) 520–524.

- [8] K. Krishnamoorthy, G.K. Veerasubramani, S. Radhakrishnan, S.J. Kim, Chem. Eng. J. 251 (2014) 116–122.
- [9] Y. Wei, X. Zhang, X. Wu, D. Tang, K. Cai, Q. Zhang, RSC Adv. 6 (2016) 39317–39322.
- [10] H. Chen, L. Hu, Y. Yan, R. Che, M. Chen, L. Wu, Adv. Energy Mater 3 (2013) 1636–1646.
- [11] Z.S. Wu, D.W. Wang, W. Ren, J. Zhao, G. Zhou, F. Li, H.M. Cheng, Adv. Func. Mater 20 (2010) 3595–3602.
- [12] C. Yuan, J. Li, L. Hou, X. Zhang, L. Shen, X.W.D. Lou, Adv. Func. Mater 22 (2012) 4592–4597.
- [13] G. Zhang, L. Zheng, M. Zhang, S. Guo, Z.H. Liu, Z. Yang, Z. Wang, Energy Fuels 26 (2011) 618–623.
- [14] Y. Lu, B. Jiang, L. Fang, F.L. Ling, J.M. Gao, X.H. Zhang, Chemosphere 152 (2016) 415-422.
- [15] Q. Wang, D. O'Hare, Chem. Rev. 112 (2012) 4124-4155.
- [16] X.L. Guo, X.Y. Liu, X.D. Hao, S.J. Zhu, F. Dong, Z.Q. Wen, Y.X. Zhang, Electrochim. Acta 194 (2016) 179–186.
- [17] Z. Li, M. Shao, L. Zhou, R. Zhang, C. Zhang, J. Han, X. Duan, Nano Energy 20 (2016) 294–304.
- [18] T. Xiao, Y. Tang, Z. Jia, D. Li, X. Hu, B. Li, L. Luo, Nanotechnology 20 (2009) 475603.
- [19] Y. Dong, P. Zhang, Y. Kou, Z. Yang, Y. Li, X. Sun, Catal. Lett. 145 (2015) 1541–1548.
- [20] X. Deng, J. Li, S. Zhu, F. He, C. He, E. Liu, N. Zhao, J. Alloys Compd. 693 (2017) 16–24.
- [21] F. Wang, Q. Zhou, G. Li, Q. Wang, J. Alloys. Compd. 700 (2017) 185.
- [22] H. Chen, L. Hu, M. Chen, Y. Yan, L. Wu, Adv. Func. Mater 24 (2014) 934–942.
 [23] J.W. Lang, L.B. Kong, M. Liu, Y.C. Luo, L. Kang, J. Solid State Electr. 14 (2010) 1533–1539.
- [24] Y. Dong, Y. Liu, J. Yin, X. Zhao, J. Mater. Chem. C 2 (2014) 10386–10394.
- [25] M. Chen, Y. Wu, Y. Han, X. Lin, J. Sun, W. Zhang, R. Cao, ACS Appl. Mater. Interfaces 7 (2015) 21852–21859.
- [26] R. Ma, J. Liang, X. Liu, T. Sasaki, J. Am. Chem. Soc. 134 (2012) 19915–19921.
 [27] Y. Gu, Z. Lu, Z. Chang, J. Liu, X. Lei, Y. Li, X. Sun, J. Mater. Chem. A 1 (2013) 10655–10661.
- [28] G.J.D.A. Soler-Illia, M. Jobbágy, A.E. Regazzoni, M.A. Blesa, Chem. Mater 11 (1999) 3140-10661.
- [29] B. Mayers, B. Gates, Y. Yin, Y. Xia, Adv. Mater 13 (2001) 1380-1384.
- [30] H.C. Chen, J.J. Jiang, L. Zhang, D.D. Xia, Y.D. Zhao, D.Q. Guo, T. Qi, H.Z. Wan,
- J. Power Sources 254 (2014) 249–257. [31] H. Wang, H.S. Casalongue, Y. Liang, H. Dai, J. Am. Chem. Soc. 132 (2010) 7472–7477
- [32] J. Zhu, S. Chen, H. Zhou, X. Wang, Nano Res. 5 (2012) 11–19.
- [33] L. Zhang, K.N. Hui, K.S. Hui, H. Lee, J. Power Source 318 (2016) 76-85.
- [34] F. Lai, Y.E. Miao, L. Zuo, H. Lu, Y. Huang, T. Liu, Small 12 (2016) 3235-3244.
- [35] H. Wan, J. Liu, Y. Ruan, L. Lv, L. Peng, X. Ji, J. Jiang, ACS Appl. Mater. Interfaces 7 (2015) 15840-15847.
- [36] M.W. Louie, A.T. Bell, J. Am. Chem. Soc. 135 (2013) 12329-12337.
- [37] Z. Lu, W. Xu, W. Zhu, Q. Yang, X. Lei, J. Liu, X. Duan, Chem. Comm. 50 (2014) 6479–6482.
- [38] Z.J. Fan, J. Yan, T. Wei, L.J. Zhi, G.Q. Ning, T.Y. Li, F. Wei, Adv. Func. Mater 21 (2011) 2366–2375.
- [39] Y.Z. Su, K. Xiao, N. Li, Z.Q. Liu, S.Z. Qiao, J. Mater. Chem. A 2 (2014) 13845–13853.
- [40] X. Wang, A. Sumboja, M. Lin, J. Yan, P.S. Lee, Nanoscale 4 (2012) 7266-7272.
- [41] L. Zhang, K.N. Hui, K.S. Hui, X. Chen, R. Chen, H. Lee, Int. J. Hydrogen Energ 41 (2016) 9443–9453.
- [42] W. Zhang, C. Ma, J. Fang, J. Cheng, X. Zhang, S. Dong, L. Zhang, Rsc Adv. 3 (2013) 2483–2490.