A novel Ni@Ni(OH)₂ coaxial core-sheath nanowire membrane for electrochemical energy storage electrodes with high volumetric capacity and excellent rate capability

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A B S T R A C T

We report a facile approach to fabricate a novel membrane electrode based on unique Ni@Ni(OH)₂ coaxial core-sheath structures for electrochemical energy storage application in this work. The Ni nanowire membranes, prepared from vacuum filtration of Ni nanowires with unique embossments, can be used as excellent precursors for preparing Ni@Ni(OH)₂ membranes by an electrochemical cyclic voltammetry method. After electrochemical treatment, a layer of amorphous Ni(OH)₂ was obtained on the surface of Ni nanowires. An important property of the as-synthesized Ni@Ni(OH)₂ membranes is that it can be directly utilized for electrochemical energy storage applications without the need for binders or additional conducting additives. The Ni@Ni(OH)₂ electrode demonstrates a high volumetric capacity (111.1 cm⁻³ at 0.12 A cm⁻²), excellent rate capability (83.1 cm⁻³ at 1.92 A cm⁻²), and cycling stability at a high current density (78% capacity retention after 1500 cycles at 1.92 A cm⁻²). This fabrication method is very simple and paves a new route for designing membrane electrodes based on similar structures for high-performance electrochemical energy storage electrodes.

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1. Introduction

Electrochemical energy storage devices can be divided into two types according to the charge/discharge (CD) behaviors. One is the batteries that results in a flat discharge plateau. Another is supercapacitor which exhibits a triangular shape in CD curve. Supercapacitor has drawn increasing attentions due to its numerous intrinsic merits, such as fast CD rate, long cycle lifespan, high power density, lower internal resistance, and fairly high energy density, etc. [1–5]. Generally, supercapacitor is classified into two types, including electric double layer capacitor (EDLC) which stores charges at interface between active material and electrolyte, and pseudocapacitor which stores charges by rapidly reversible redox reactions on the surface of electroactive material [6,7]. However, the energy density of supercapacitor is much lower comparing with batteries, which hinders its further application for high energy storage device.

One of the most important components of an electrochemical energy storage device is the electrode material. A lot of metal oxides and hydroxides including NiO [8,9], Co₃O₄ [10], MnO₂ [11], RuO₂ [12], Ni(OH)₂ [13–15] and Co(OH)₂ [16] have been used for electrochemical energy storage application these years. Among them, Ni(OH)₂ has drawn considerable attention for its high theoretical capacity, low cost, and environmentally benign nature [17]. Recently, it was reported that Ni(OH)₂ and Co₃O₄ in KOH electrolyte is analogous to battery material rather than pseudocapacitive material [18,19]. Ni(OH)₂ as a battery-type faradaic material whose CV is characterized by faradaic redox peaks, often used as the positive electrode to replace the capacitor-type electrode in the EDLC. This hybrid device could improve the operation voltage by making use of different potential windows of two electrodes. In addition, this type of device also offer advantages of both high power density (supercapacitors) and high energy density (batteries). However, the low electrical conductivity and small specific surface greatly limits its actual electrochemical performance for electrochemical energy storage electrode. To solve these problems, various strategies have been proposed. One effective method is to reasonably design and

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engineer the nanostructure of the electrode materials, such as nanoflake, nanotube, nanowire and other nanostructures. Mostly recently, using one-dimensional (1D) or two-dimensional (2D) nanomaterials to assemble into three-dimensional (3D) free-standing membranes and then directly being applied as electrode materials have been studied intensively, for their novel instinct characteristics including staggered network structure, large specific surface area, and excellent mechanical strength. Moreover, unlike traditional technology which involve addition of adhesive and conductive material in certain percentage, this approach can avoid using adhesive or conductive additives which can not only provide direct contact between active material surface and current collector, but also decrease the mass of additives that affect the electrode conductivity, both improving electrochemical performance of electrode materials [20–22].

In this study, we report a simple approach to fabricate an additive-free Ni@Ni(OH)₂ film electrode for electrochemical energy storage, through vacuum filtration of Ni nanowires and followed by electrochemical treatment to obtain a layer of active material Ni(OH)₂ on the surface of Ni nanowires. This in situ method could produce an unique core-Ni and sheath-Ni(OH)₂ structure, which ensures strong linking (intimate contact) between conductive material Ni and active material Ni(OH)₂. Ni(OH)₂, as an active material, has a strong interaction with conductive Ni nanowires, which offers an excellent electrical contact and a fast electron transfer channel between Ni and Ni(OH)₂. The membrane electrodes with this unique structure display an excellent electrochemical performance with a volume capacity of 111.1 C cm⁻³ at 0.12 A cm⁻³ and 83.1 C cm⁻³ at 1.92 A cm⁻³. Furthermore, the electrode displays an excellent cycling
stability with 78% capacity retention of initial value after 1500 cycles at 1.92 A cm\(^{-2}\). Our additive-free fabrication method is very simple and paves a new route for designing membrane electrodes based on similar structures for high-performance electrochemical energy storage electrodes.

2. Experimental

2.1. Fabrication of Ni nanowires

All chemicals with analytical grades (AR) were directly used as received. Ultralong Ni nanowires were synthesized through a facile liquid-phase reaction under a magnetic field according to our previous work [23]. Typically, 0.5 g nickel chloride hexahydrate (NiCl\(_2\)-6H\(_2\)O) were added to 100 mL ethylene glycol (EG) to form NiCl\(_2\) solutions of EG. At the same time, 2 g sodium hydroxide (NaOH) were added to 100 mL EG to obtain NaOH solutions of EG. The two solutions were followed by ultrasonic and stirring to ensure complete dissolution. Subsequently, the two solutions were mixed together under stirring for another 5 min to form a homogeneous solution. Afterwards, 20 mL hydrazine hydrate (N\(_2\)H\(_4\)·H\(_2\)O 85 wt%) was added and the mixture was transferred into a flask. Then the flask was placed into water bath with the aid of a magnet, heated to 75 °C, and held for 30 min at atmospheric pressure. The product was washed separately with distilled water and ethanol, each for three times, to remove residual reactants. Finally, it was dried at 60 °C overnight in a vacuum oven.

2.2. Fabrication of Ni@Ni(OH)\(_2\) membrane electrode

The Ni membrane was obtained by re-dispersing the nanowires in a 1 wt% ethanol solution of PVP, vacuum-filtered and dried for 12 h at 60 °C, then pressed at 10 MPa for 5 min. For the convenience of following characterizations, all membranes were cut into 0.5 × 0.5 cm\(^2\). The thickness of the film was 45 μm measured by micrometer screw gauge. To obtain Ni(OH)\(_2\) on the surface of nanowires, all membrane were performed to the cyclic voltammetry (CV) treatments at 5 mV s\(^{-1}\) in the potential window of −1.0–0.1 V in a 6 M KOH aqueous solution [24]. Different thicknesses of Ni(OH)\(_2\) could be obtained by changing the cycle number of CV treatment. The CV cycle number for Ni membrane electrodes were 1, 3, 5 and 10 and labeled as Ni-H1, Ni-H3, Ni-H5 and Ni-H10, respectively. The preparation process can be summarized in Fig. 1.

2.3. Characterization

The crystalline structure of membrane electrodes were recorded by X-ray powder diffraction (XRD) technique on an advanced X-ray diffractometer (D8 Advance, Bruker, Germany) in a

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Fig. 3. (a) Photograph of as-prepared Ni@Ni(OH)\(_2\) membrane electrode. (b) SEM image of the Ni-H3 sample. Elemental mapping scan taking from the part b for elements (c) O and (d) Ni, respectively. (e) Cross-sectional SEM image of Ni@Ni(OH)\(_2\) membrane. (f) EDS of Ni@Ni(OH)\(_2\) nanowires.
20° range from 10 to 90° with Cu-Kα radiation at 18 kW. The microstructures and morphologies of various membrane electrodes were observed by a field emission scanning electron microscope (SEM, Ultra Plus, Carl Zeiss, Germany) and transmission electron microscopy (TEM/HRTEM, JEM-2010, JEOL, Japan). Chemical composition and elemental mapping were analyzed by energy dispersive X-ray spectroscopy (EDS, Oxford Instruments INCA PentaFET×3, Model: 7426). X-ray photoelectron spectroscopy (XPS) was acquired using a Japan Kratos Axis UltraDLD spectrometer with a monochromatic Al Kα source (1486.6 eV). Thermogravimetric analyses were recorded from 30 to 900°C by using a thermogravimetric analyzer (TGA, Pyris 1, PerkinElmer, USA) at a heating rate of 10°C/min. A VERTEC 70 (Bruker, Germany) spectrometer was used to record the fourier transform infrared spectroscopy (FTIR) of the sample over the range of 4000–400 cm⁻¹ using KBr as base material.

2.4. Electrochemical tests

All the electrochemical measurements, including CV, galvanostatic CD, and the electrochemical impedance spectroscopy (EIS), were recorded by a three-electrode system using a 6 M KOH as the electrolyte on a CHI760E electrochemical workstation. Various membranes were used as the working electrode with a Pt counter electrode and a Hg/HgO reference electrode. EIS were carried out for the working electrode at open-circuit potential and AC signal amplitude of 5 mV with the frequency range of 0.01 Hz to 100 kHz.

3. Results and discussion

3.1. Composition and morphology characterization

The microstructures of the as-synthesized Ni nanowires were characterized by SEM with different magnifications, as shown in Fig. 2a and b. It can be observed clearly that the straight Ni nanowires have been obtained under the magnetic field. The morphology of the Ni nanowires can be identified as 1D acicular structure with an ultralong length and a diameter of about 300 nm. Moreover, the high magnification SEM image in Fig. 2b displays that the Ni nanowires have a rough surface with a lot of embossments, which can effectively increase the surface area of nanowires, providing more active sites for redox reactions and thus improving their electrochemical performance for electrochemical energy storage application. The crystallographic structures of the as-synthesized Ni nanowires were identified by XRD, as shown in Fig. 2c. The scattering angles (2θ) located at 44.62°, 51.94° and 76.58° match well with Ni crystal planes of (111), (200) and (220), respectively. All diffraction peaks of Ni nanowires are highly consistent with that reported for Ni face-centered cubic (fcc) structure (PDF standard card No. 04-0850). From the XRD patterns, there are no other characteristic peaks of NiO or Ni(OH)₂ detected, indicating the pure Ni nanowires were obtained through this simple liquid-phase method. Fig. 2d shows the TGA curve of Ni nanowires under the air atmosphere at a heating rate of 10 °C/min. According to the TGA curve, the Ni nanowires undergo a significant weight increase from about 300 to 600 °C, corresponding to the

![Fig. 4. XPS spectrums of the Ni-H3 membrane. (a) Survey spectrum. (b) Ni 2p core. (c) O 1s.](image-url)
change from Ni to NiO. No weight decrease detected from the TGA curve, indicating no Ni(OH)$_2$ contained in the sample, which is consistency with the XRD results.

In order to obtain Ni(OH)$_2$, the Ni membrane was subjected to CV sweep at 5 mV s$^{-1}$ in the potential window of $-1.0$–$0.1$ V in a 6 M KOH electrolyte solution. The CV curve with 3CV cycles is shown in Fig. S1. The electrode was directly used for electrochemical test after CV treatments. Fig. 3a shows a photograph of as-synthesized Ni@Ni(OH)$_2$ membrane electrode with a size of $0.5 \times 0.5$ cm$^2$, which is uniform and free-standing. Except for a little smoothening of emboossment caused by the conversion of Ni to Ni(OH)$_2$ on the surface, the morphologies of Ni@Ni(OH)$_2$ nanowires show no significant change compared with those of Ni nanowires (Fig. 2b), as shown in Fig. 3b. The elemental mapping scan taken from Fig. 3b for elements of O and Ni is shown in Fig. 3c and d, respectively. Fig. 3c exhibits the oxygen element distributed evenly on the surface of Ni nanowire, which displays a clear sheath structure, demonstrates the successful transformation of Ni to Ni(OH)$_2$ on the surface. Fig. 3d shows that the Ni element mainly distributed in the core, indicating there is no change in the core of Ni nanowire after 3 cycles of electrochemical treatments. Fig. 3e exhibits the cross-sectional SEM image of Ni@Ni(OH)$_2$ membrane, revealing the uniform porous structure. Furthermore, it can be found that the nanowires are well-linked together and form a uniform 3D network with lots of microspheres. This unique network structure can improve the flexibility and mechanical strength of films. Moreover, this structure can accelerate the diffusion of electrolyte, increase the conductivity of the electrode and improve the active material on the surface of Ni nanowires, all of those features are beneficial for electrochemical energy storage application. Fig. 3f shows the EDS of Ni@Ni(OH)$_2$ nanowires, the result is consistent with the elemental mapping (Fig. 3c and d). The content of O is 3.01 wt% (Table S1). More detail EDS spectral data is shown in Fig. S2, revealing the increasing content of O with the CV cycles increase, which indicating more Ni has converted to Ni(OH)$_2$ on the surface of Ni nanowires. Based on EDS and elemental mapping results, it is suggested that such a Ni@Ni(OH)$_2$ core-sheath structure is obtained by a facile electrochemical treatment.

More detailed surface chemical composition of as-prepared Ni-H$_3$ was studied by XPS measurement. The corresponding results are exhibited in Fig. 4. As shown in Fig. 4a, the Ni-H$_3$ sample mainly consists of C, O, N, and Ni elements, among which C and N are from residues of PVP. The high resolution spectrum of Ni 2p in Fig. 4b shows two major peaks around 855.9 and 873.5 eV with a spin-energy of 17.6 eV, along with two satellite peaks at 861.4 and 879.6 eV, in agreement well with previous reports on amorphous Ni(OH)$_2$ [13]. In addition, the high resolution spectrum of O 1s was shown in Fig. 4c, in which the peak center around binding energy of 531.5 eV is associated to the O1 s of Ni(OH)$_2$, and the formation of amorphous Ni(OH)$_2$ is further confirmed.

In order to confirm the successful conversion of Ni to Ni(OH)$_2$ on the surface of nanowires, XRD, FTIR and TGA were performed. Fig. 5a and b show XRD patterns of Ni and Ni-H$_3$, the scattering angles (2θ) located at 44.62°, 51.94° and 76.58° match well with Ni crystal planes of (111), (200) and (220), respectively. The diffraction peak intensity of Ni-H$_3$ is slightly weaker than that of Ni. This is caused by the transition from Ni to Ni(OH)$_2$, which reduces the crystallinity of Ni nanowires, thereby decreases the intensity of the characteristic peaks of the Ni-H$_3$. No characteristic peaks of Ni(OH)$_2$ could be found from XRD pattern because Ni(OH)$_2$ is present in form of amorphous. To further confirm the XRD results, Ni and Ni-H$_3$ were examined by FTIR spectroscopy ranging from 400 to 4000 cm$^{-1}$. As shown in Fig. 5c, the absorption bands of Ni-H$_3$ are similar to that of Ni except two bands around 605 and 570 cm$^{-1}$, which are ascribed to the $\delta_{\text{OH}}$ and $\nu_{\text{Ni-OH}}$ vibrations, respectively [25,26]. The broad band located at 3435 cm$^{-1}$ can be attributable to the hydrogen-bonded hydroxyl groups O-H vibration. The band at 1637 cm$^{-1}$ is due to the existence of water (bending mode) in the sample. The peak around 1045 cm$^{-1}$ is assigned to C-O-H from reactant of EG. The FTIR results prove that Ni-H$_3$ contains Ni(OH)$_2$.

![Fig. 5. (a and b) XRD patterns of Ni and Ni-H$_3$. (c) FTIR spectra of Ni and Ni-H$_3$. (d) TGA curve of Ni-H$_3$.](image-url)
transformed from the surface of Ni nanowires. TGA curve of Ni-H3 is shown in Fig. 5d. Unlike the TGA curve of Ni (Fig. 2d), the Ni-H3 shows a slightly weight loss around 150 °C, corresponding to the decomposition of Ni(OH)2 to NiO (Ni(OH)2 → NiO + H2O). When the temperature reaches up to about 400 °C, Ni(OH)2 decomposes completely. Then, the weight begins to increase with the rising of temperature, indicating the oxidation of Ni nanowires. The TGA results are consistent with the XRD and FTIR results, confirming that the Ni is converted to Ni(OH)2 after electrochemical treatments.

TEM was performed to further confirm and more intuitively understand the core-sheath structure of Ni@Ni(OH)2. Fig. 6a shows the TEM image of a single Ni nanowire, revealing that there are many embossments on the surface of nanowire, which is consistent with the SEM result (Fig. 2b). For better understanding the surface crystal structure of Ni nanowire, Fig. 6b exhibits HRTEM image from border of an embossment, as revealed by red circle from Fig. 6a. Well-ordered crystal fringes can be detected with a crystal spacing of about 0.23 nm, ascribing to the {111} spacing planes of the Ni fcc structure. Fig. 6c shows the TEM image of a Ni-H3 nanowire shows no significant difference compared with Fig. 6a, which is consistent with the SEM image above mentioned. Ni and Ni(OH)2 phase can be identified by lattice spacing from the HRTEM image in Fig. 6d. A layer of amorphous material on the surface without any lattice structure corresponds to amorphous Ni(OH)2 converted from Ni. The core of the sample shows the crystal structure of Ni with a crystal spacing of 0.21 nm and 0.17 nm, corresponding to the spacing of {111} and {200} planes, respectively. The TEM results are in consistence with the XRD, FTIR and TGA results, further demonstrating the Ni core and Ni(OH)2 sheath structure of our as-prepared Ni-H3 electrode.

3.2. Electrochemical performance

Generally, the morphology and structure of electrodes have great influence on electrochemical performance [27]. This distinctive 3D structure nanowires provide large surface area and enable better intercalation of charges into material. As a result, the as-prepared materials should have promising electrochemical properties for electrode application. The electrochemical performance of as-prepared membrane electrode was performed by a three-electrode test system in 6 M KOH electrolyte. In order to obtain active material with different thicknesses on the surface of Ni nanowires and to determine the maximum capacity, the CV cycle number of electrochemical treatments is changed. The electrochemical performance of Ni@Ni(OH)2 membrane electrode with different CV cycle numbers was tested by CV, galvanostatic CD and EIS, as shown in Fig. 7. Fig. 7a shows the CV curves of the Ni@Ni(OH)2 membrane electrode with different CV cycle numbers in the potential range of 0–0.6 V at 20 mV s−1. Unlike the EDLCs with rectangular CV curves, the shapes of CV curves show two strong symmetrical peaks, suggesting that the capacity are mainly
derived from Faradaic redox reaction, which is consistent with battery-type electrode. For Ni(OH)$_2$ electrode material, the charge storage arises from the following redox reaction [28]:

$$\text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{Ni(OH)}_2 + \text{H}_2\text{O} + e^-$$  \hspace{1cm} (1)

Two peaks observed from CV curves are nearly symmetric, revealing the reversibility of as-prepared active material Ni(OH)$_2$. Furthermore, the Ni-H3 membrane electrode which treated by three CV cycles possesses the maximum CV area, indicating it has better electrochemical performance than that of other samples.

The same situation can be found in galvanostatic CD measurement at 0.24 A cm$^{-2}$ in Fig. 7b. The Ni-H3 sample possesses the longest discharge time, suggesting the highest electrochemical capacity, which matches well with the CV curves. Furthermore, the coulombic efficiency of Ni-H3 is 95.3%, which is the highest value compared with other samples (83.6%, 72.8% and 78.6% for Ni-H1, Ni-H5 and Ni-H10, respectively). Fig. 7c exhibits the volumetric capacity with respect to CV cycle number calculated from galvanostatic CD curve, according to the follow equation:

$$C = \frac{I \times \Delta t}{\Delta V}$$  \hspace{1cm} (2)

where $C$ is volumetric capacity (C cm$^{-3}$), $I$ is the discharge current density (A), $\Delta t$ is the discharge time (s), and $\Delta V$ is the volume of the electrode (cm$^3$) [20]. The volume of an electrode is calculated to be $1.125 \times 10^{-2}$ cm$^3$. From Fig. 7c it can be found that Ni-H3 has the biggest volumetric capacity of 104.3 C cm$^{-3}$, while the value of Ni-H1, Ni-H5, and Ni-H10 is 70.1, 71.1 and 52.6 C cm$^{-3}$, respectively. One reason for the higher performance of Ni-H3 sample should be attributed to the rough surfaces which offer more surface area between active material Ni(OH)$_2$ and electrolyte, ensuring paths for ions diffusion. The other reason is the suitable thickness of active material Ni(OH)$_2$, too thick or too thin is not beneficial to better electrochemical performance for electrochemical energy storage. Fig. 7d shows the EIS of the samples with different CV cycle numbers. The results show that the solution resistance ($R_s$) value is around 1.9 $\Omega$ for all samples. As we know, the solution resistance is the combination of intrinsic resistance of the Ni@Ni(OH)$_2$ electrode, diffusive as well as contact resistance at the interface of Ni/Ni(OH)$_2$ current collector, and electronic resistances. The low values of our membrane electrodes reveal excellent conductivity of all membrane electrodes. A charge transfer resistance of 4 $\Omega$ is obtained in high frequency region, suggesting a small resistance of as-synthesized electrode as well as the rapid charge transfer between electrode and electrolyte.

Based on the analysis results above-mentioned, Ni-H3 sample possesses the best electrochemical performance compared to other samples. Thus, more detailed electrochemical characterizations have been performed to study this sample. Fig. 8a presents typical CV curves of the Ni-H3 sample at various scan rates ranging from 2 to 50 mV s$^{-1}$ in the potential window of 0.0–0.6 V. Two redox peaks are mainly due to Faradaic redox reaction. With the increase of scan rate, the oxidation and the reduction peaks shift positively and negatively, respectively. This is owing to the internal resistance of electrochemical electrodes. With the scan rate increase, the diffusion resistance in Ni@Ni(OH)$_2$ increase, leading to shift of redox peaks [29–31]. However, two redox peaks of CV curves with nearly symmetrical behaviors are observed throughout the scan rate range of 2–50 mV s$^{-1}$, indicating excellent electron conductivity and reversibility of redox reactions at the surface of membrane electrode.

Further evaluation the electrochemical performance of Ni-H3 membrane electrode were investigated by galvanostatic CD tests. As exhibited in Fig. 8b, the galvanostatic CD curves of Ni-H3 electrode at current densities ranging from 0.12 to 1.92 A cm$^{-2}$. On
each curve, there is a pair of voltage plateaus whose potential matches well with the peak on CV curves, corresponding to the reversible oxidation/reduction reaction between Ni(II) and Ni(III) consistent with a battery-type electrode. The volumetric capacity of Ni-H3 electrode is calculated from galvanostatic CD curve according to Eq. (2) as showed in Fig. 8c. The volumetric capacity of the as-prepare Ni-H3 electrode material is 111.1, 104.3, 100.0, 94.3 and 83.1 cm$^{-3}$ at current densities of 0.12, 0.24, 0.48, 0.96 and 1.92 A cm$^{-3}$, respectively. With the increase of current density, the volumetric capacity decreases. This is accounting for the limited diffusion of ions near the surface of active material at high current density, hindering the utilization of the active material. At low current density, the time is enough for OH$^-$ ions to diffuse into electrode. When the scan rate increases, the time for OH$^-$ ions to diffuse is limited so that some active materials on the surface become unavailable for charge storage. With a 16-fold increase of current density, the volumetric capacity of Ni-H3 electrode material can still retain 75%, which is comparable to those of other reports [32–34]. The high rate capability of electrode material is beneficial for its practical application. For a more comprehensive understanding of the electrochemical performance of as-prepared material, the specific capacity is calculated according to mass loading of active Ni(OH)$_2$ (the mass differences were measured by microbalance before and after electrochemical treatment), the result is shown in Fig. S3. The mass of the Ni-H3 electrode before and after electrochemical treatment is 2.21 and 2.25 mg, respectively. So we can calculate the Ni(OH)$_2$ mass of an electrode is 0.109 mg. The Ni(OH)$_2$ mass loading for Ni-H3 sample is approximately 96.9 mg cm$^{-2}$. The specific capacity value is calculated to be 1148.0 C g$^{-1}$ at 1.24 A g$^{-1}$ and retains about 861.0 C g$^{-1}$ at 19.84 A g$^{-1}$.

Long time cycling stability is also crucial to evaluate the electrochemical performance of electrochemical energy storage electrode. So cycling tests (Fig. 8d) of Ni-H3 electrode material at

Fig. 8. (a) CV curves of Ni-H3 at different scan rates ranging from 2 to 50 mV s$^{-1}$; (b) Galvanostatic CD of the sample ranging from 0.12 to 1.92 A cm$^{-3}$; (c) Volume capacity change over current density; (d) Cycle life curve tested at 1.92 A cm$^{-3}$; (e) Nyquist plots of membrane electrode before and after cycling; (f) Ragone plot of Ni-H3.
Table 1
Comparison of the electrochemical performance with other metal oxide/hydroxide.

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Capacity (C)</th>
<th>Volumetric Capacity (C)</th>
<th>Rate Retention (%)</th>
<th>Cycle Performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni@NiO NWs</td>
<td>265 C g⁻¹</td>
<td>19.2 C cm⁻³</td>
<td>96.1%</td>
<td>89% at 7.04 Ag⁻¹</td>
<td>[37]</td>
</tr>
<tr>
<td>(0.44 A g⁻¹)</td>
<td>(0.032 A cm⁻³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Al LDHs/CNTs</td>
<td>750 C g⁻¹</td>
<td>/</td>
<td>70.3%</td>
<td>73% at 6 Ag⁻¹</td>
<td>[38]</td>
</tr>
<tr>
<td>(1 A g⁻¹)</td>
<td>/</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(OH)₂–ZnO</td>
<td>720 C g⁻¹</td>
<td>/</td>
<td>48.24%</td>
<td>/</td>
<td>[39]</td>
</tr>
<tr>
<td>(15.7 A g⁻¹)</td>
<td>/</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Ni(OH)₂-Co(OH)₂ composite</td>
<td>1012 C g⁻¹</td>
<td>/</td>
<td>73.3%</td>
<td>84.7% at 5 A g⁻¹</td>
<td>[40]</td>
</tr>
<tr>
<td>(2 A g⁻¹)</td>
<td>/</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Co binary hydroxide</td>
<td>412 C g⁻¹</td>
<td>/</td>
<td>81.8%</td>
<td>97.3% at 15 A g⁻¹</td>
<td>[41]</td>
</tr>
<tr>
<td>(3 A g⁻¹)</td>
<td>/</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ni(OH)₂/NiOOH composite</td>
<td>738 C g⁻¹</td>
<td>/</td>
<td>81%</td>
<td>1000 cycles</td>
<td>[42]</td>
</tr>
<tr>
<td>(4 A g⁻¹)</td>
<td>/</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Carbon–MnO₂</td>
<td>104 C g⁻¹</td>
<td>124.8 C cm⁻³</td>
<td>68%</td>
<td>1000 cycles</td>
<td>[43]</td>
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<tr>
<td>(0.1 A g⁻¹)</td>
<td>(0.1 A g⁻¹)</td>
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<td></td>
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<tr>
<td>OMC/WO₃ nano-composite</td>
<td>1575 C g⁻¹</td>
<td>116 C cm⁻³</td>
<td>77%</td>
<td>/</td>
<td>[44]</td>
</tr>
<tr>
<td>(0.25 A cm⁻²)</td>
<td>(0.25 A cm⁻²)</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Ni@Ni(OH)₂ NWs membrane</td>
<td>1348 C g⁻¹</td>
<td>111.1 C cm⁻³</td>
<td>75%</td>
<td>78% at 19.84 A g⁻¹</td>
<td>This work</td>
</tr>
<tr>
<td>(1.24 A g⁻¹)</td>
<td>(0.12 A cm⁻²)</td>
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</table>

* The capacitance is transformed to capacity according to the equation of \( Q = C \times \Delta U \), where \( Q \) is charge storage capacity (C), \( C \) is capacitance (F), \( \Delta U \) is the voltage window (V).

1.92 A cm⁻² were studied, which is the highest current density used for galvanostatic CD tests. From the cycling tests, it can be seen that the capacity decreases gradually before 400 cycles and becomes stable from 400 to 1500 cycles. After 1500 cycles CD at a high current density, the capacity can still retain about 78% of initial value with high coulombic efficiency, this is competitive to those of most works reported [14,35,36], indicating the excellent electrochemical stability of our material. The electrochemical performance of Ni-H3 is also compared with other materials previously reported, as listed in Table 1. As shown in the table, it’s obviously that an outstanding electrochemical performance of our material has been achieved. Fig. 8e shows the Nyquist plots before and after 1500 cycles. The plots show the same \( R_s \) values of 2.2 Ω. The \( R_{CT} \) of the sample increases from about 4 to 49 Ω, which will hinder the transfer of Faradaic reaction electrons and lead to the decrease of the capacity. The collapse of the active material on the surface caused by volume change of active materials during cycling is responsible for the increase of the \( R_{CT} \), which can be confirmed by SEM images (Fig. S4) after 1500 cycles. The volumetric power density and energy density of as-prepared electrode are also crucial parameters to estimate the electrochemical performance of energy storage electrode. According to the Ragone plot at different CD currents density from Fig. 8f, the highest energy density is about 11.1 mWh cm⁻³ when power density is about 42.9 mW cm⁻³, retaining about 8.3 mWh cm⁻³ at a power density of 697.5 mW cm⁻³. The high retention for energy density at high current density is excellent for energy storage and very important for its practical applications.

4. Conclusions

In conclusion, Ni@Ni(OH)₂ membrane electrodes with novel core-sheath structures have been facilely fabricated by vacuum filtration of Ni nanowires with unique embossments and the following electrochemical treatments. A layer of amorphous Ni(OH)₂ was obtained on the surface of Ni nanowires after treatments. The as-synthesized Ni@Ni(OH)₂ membranes can be directly applied as an electrochemical energy storage electrode without addition of adhesive or conducting additive. This facile approach not only simplified fabrication process for electrode, but also reduced the volume and mass of the electrode, which could increase the electrical conductivity for Faradaic reactions. Benefit from the unique structures, the electrode based on Ni@Ni(OH)₂ membrane exhibited a high volumetric capacity (111.1 C cm⁻³ at 0.12 A cm⁻²) with an excellent rate capability and cycle stability at a high current density. These remarkable characteristics make it a promising material for high performance electrochemical energy storage application.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2015.09.087.

References
