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Electrochemical Deposition of Porous Co(OH)$_2$ Nanoflake Films on Stainless Steel Mesh for Flexible Supercapacitors

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Flexible porous Co(OH)$_2$ nanoflake films were prepared by galvanostatic electrodeposition on lightweight and inexpensive stainless steel mesh. The as-prepared porous Co(OH)$_2$ nanoflake films were characterized by X-ray diffraction, thermogravimetric analysis, and scanning electron microscopy. Electrochemical tests including cyclic voltammetry, constant current charge–discharge, and electrochemical impedance spectroscopy were also used to investigate the electrochemical performance. The results show that the highest capacitance is 609.4 F g$^{-1}$, the specific capacitance decreases by less than 5% as the mass loading of Co(OH)$_2$ increases by more than 340%, and the specific capacitance only decreases by less than 15% when the current densities increase up to 10 times, indicating the good high-rate performance. The electrochemically active specific surface area of the annealed porous Co(OH)$_2$ nanoflake films remained virtually unchanged after 3000 cycles, showing the stability of the microstructure.

In recent years, the rapid development of portable devices (e.g., mobile phones, computers, and special medical devices) has created an urgent requirement for high-performance supercapacitors, which should have not only a high capacitance, but also good mechanical properties (lightweight and even flexibility).$^{1-3}$ Stainless steel mesh, which is lightweight, inexpensive, and has good mechanical properties, has been used as an electrode substrate for batteries or supercapacitors.$^{4,5}$ From the active materials point of view, considering the low capacitance of carbon (in electrical double-layer capacitors), researchers have paid much more attention to metal oxides/hydroxides (in pseudocapacitors), which show higher specific capacitance, because redox reactions can contribute extra capacitance.$^{6,7}$ Among the metal oxides/hydroxides, RuO$_2$ shows the highest capacitance and ideal capacitor performance, but the high cost is the big hindrance for commercial usage.$^8$ Cobalt hydroxide shows that the highest capacitance is 609.4 F g$^{-1}$, the specific capacitance decreases by less than 5% as the mass loading of Co(OH)$_2$ increases by more than 340%, and the specific capacitance only decreases by less than 15% when the current densities increase up to 10 times, indicating the good high-rate performance. The electrochemically active specific surface area of the annealed porous Co(OH)$_2$ nanoflake films remained virtually unchanged after 3000 cycles, showing the stability of the microstructure.

**Experimental**

The porous Co(OH)$_2$ nanoflake thin films were electrodeposited at room temperature in a two-electrode system onto stainless steel mesh (Metal Mesh Pty Ltd., Australia). Pt foil was used as the counter electrode. The electrolyte was 0.025 M Co(NO$_3$)$_2$ solution, in accordance with our recent investigation.$^{22}$ Typically, the porous Co(OH)$_2$ nanoflake thin films were prepared by using galvanostatic electrochemical deposition at a current density of 1 mA cm$^{-2}$ for 3, 10, and 20 min with Co(OH)$_2$ loading masses of 0.14, 0.39, and 0.62 mg cm$^{-2}$, respectively. The as-obtained porous Co(OH)$_2$ nanoflake films on stainless steel mesh were washed with deionized water three times, allowed to dry in air, and then annealed at 150°C in air for 2 h.

The morphology and microstructure of the as-prepared porous Co(OH)$_2$ nanoflake films were characterized by X-ray diffraction (XRD; GBC MMA 017), scanning electron microscopy (SEM; JEOL JEM-3000), and thermogravimetric analysis (TGA; TA 2000 thermoanalyzer). Electrochemical measurements were tested in a three-electrode electrochemical cell, including charge–discharge (Neware battery test system), and cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) (CHI 660 electrochemistry workstation). The electrochemical cell was composed of as-prepared porous Co(OH)$_2$ nano flakes on stainless steel mesh as the working electrode, a Pt foil sheet (4 cm$^2$) as the counter electrode, a standard calomel electrode (SCE) as the reference electrode, and 1 M KOH solution as the electrolyte.

**Results and Discussion**

Figure 1 shows XRD patterns, TGA results, and SEM images. It can be observed in Fig. 1A that the XRD patterns show broad peaks between 15 and 40°, indicating the amorphous crystal structure of Co(OH)$_2$, regardless of whether the sample was on or off substrate. The TGA curves (shown in Fig. 1B) mainly demonstrated two stages. Below 175°C, the weight loss is due to the evaporation of absorbed water, as the XRD pattern at 150°C of the Co(OH)$_2$ still shows an amorphous crystal structure (Fig. 1A and B). Between 175 and 400°C, weight loss occurs because the Co(OH)$_2$ is decomposing and oxidizing to CoO.$^{24}$ It has also been reported that Co(OH)$_2$ annealed at 150°C in air for 3 h showed a higher surface area and higher capacitance,$^{22}$ so the as-prepared Co(OH)$_2$ samples on stainless steel mesh were all annealed at 150°C for 3 h in air for further characterizations in order to improve the performance. SEM images of the nanoflake electrode are shown in Fig. 1C–E. Figure 1C reveals that the Co(OH)$_2$ is homogeneously coated on the wires of the stainless steel mesh. The inset of Fig. 1C shows a photograph of Co(OH)$_2$-loaded stainless steel mesh between two fingers, showing the good flexibility of the Co(OH)$_2$ on stainless steel mesh electrode. Figure 1D, an enlargement of Fig. 1C, shows that the coating has a porous structure. The higher resolution SEM image in Fig. 1E shows that the Co(OH)$_2$ has a flowerlike porous nanostructure, which is formed by a network of nanoflakes 20–30 nm thick.

Figure 2 displays the electrochemical test results. Cyclic voltam-
mograms of electrodeposited porous Co(OH)$_2$ nanoflake thin films, collected after annealing at 150°C for 3 h in air, at scan rates of 5, 10, 20, and 50 mV s$^{-1}$ are shown in Fig. 2a. Quasi-reversible redox peaks are observed in the voltage ranges from −0.05 to 0 and 0.05–0.15 V, which may be briefly described by Eq. 1.

$$\text{Co(OH)$_2$} + \text{OH}^- \leftrightarrow \text{CoO(OH)} + \text{H}_2\text{O} + e^- \quad [1]$$

The quasi-reversible redox reaction shows that the porous Co(OH)$_2$ nanoflake thin films can be used as electrode materials in redox supercapacitors. As the scan rate increases, the overall shape of the CV curves is still maintained, indicating good high-rate performance. The specific capacitances calculated from the CV curves are 609.9, 563.5, 507.5, and 427.4 F g$^{-1}$ for scan rates of 5, 10, 20, and 50 mV s$^{-1}$, respectively. Different charge–discharge current densities, which are used in investigating the capacitance behavior of porous Co(OH)$_2$ nanoflake thin films, can be used as electrode materials in redox supercapacitors. As the scan rate increases, the overall shape of the CV curves is still maintained, indicating good high-rate performance. The specific capacitances calculated from the CV curves are 609.9, 563.5, 507.5, and 427.4 F g$^{-1}$ for scan rates of 5, 10, 20, and 50 mV s$^{-1}$, respectively. 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trolyte, and thus increased electrochemical activity. The inset of Fig. 3a is an enlargement of the high-frequency range. The intercepts on the real axis \( Z' \) could be considered as the combination resistance including the ionic resistance of electrolyte, intrinsic resistance of active materials, and contact resistance at the active material/current collector interface.\(^{28,29}\) The combination resistance (\( \sim 4.5 \, \Omega \, \text{cm}^2 \)) is higher than the results previously reported (0.1 \( \Omega \, \text{cm}^2 \)).\(^{22}\) This may be due to the contact resistance of the stainless steel wires which form the stainless steel mesh. This might also be the reason why our capacitance is lower than the results reported previously, though the crystal structure is different.\(^{20,22}\) The semicircle in the high-frequency range is associated with the surface properties of the porous electrode and corresponds to the charge-transfer resistance. The charge-transfer resistances of porous Co(OH)\(_2\) nanoflake film are 1.8, 0.5, and 0.2 \( \Omega \, \text{cm}^2 \) at bias potentials of 0.06, 0.2, and 0.4 V (vs SCE), respectively. Admittance plots shown in Fig. 3b display the knee frequency, which is a very important parameter related to the high-rate performance of supercapacitors. The knee frequency varies from 0.12 to 1.5 kHz when the bias potential is varied from 0.06 to 0.4 V. The frequency for a phase angle of −45°, also representing the power performance of the electrode, is around 0.2–0.8 Hz when the bias potential is varied from 0.2 to 0.8 V, as shown in Fig. 3c. The above analyses reveal the good performance of annealed porous Co(OH)\(_2\) nanoflake films on stainless steel mesh as a flexible electrode for supercapacitors.

The electrochemically active specific surface area \([S_d (\text{m}^2 \cdot \text{g}^{-1})]\) could be calculated from the equation \( S_d = C_d / \varepsilon \), where \( C_d \) is the constant double-layer capacitance, with a value around 20 \( \mu \text{F} \, \text{cm}^{-2} \), and \( C_d (\text{F} \, \text{g}^{-1}) \) is the tested specific capacitance of the double layer.\(^{30,31}\) Because there is no electrochemical reaction at −0.2 V vs SCE, \( C_d \) could be calculated from the equation \( C_d = -1/2\pi f f' Z'' \), where \( m \) (g) is the mass of the active materials, \( f \) (Hz) is the frequency in the low-frequency range, and \( Z'' (\Omega \, \text{cm}^2) \) is the imaginary impedance.\(^{23}\) The electrochemically active specific surface areas are 62.7 and 59.2 \( \text{m}^2 \cdot \text{g}^{-1} \) before cycling and after 3000 cycles, respectively, indicating that the microstructure of Co(OH)\(_2\) could be maintained beyond 3000 cycles, which may be the reason for the long cycle life. Further work using this kind of flexible electrode and solid-state electrolyte to assemble totally flexible supercapacitors is ongoing.

Conclusions

Flexible porous Co(OH)\(_2\) nanoflake films on stainless steel mesh were synthesized by simple galvanostatic electrochemical deposition at a current density of 1 mA \( \text{cm}^{-2} \) in 0.025 M Co(NO\(_3\))\(_2\) electrolyte. The electrochemical measurements demonstrated that the annealed porous Co(OH)\(_2\) nanoflake electrode can be directly used for electrochemical supercapacitors, showing a capacitance as high as 609.9 F \( \text{g}^{-1} \) in 1 M KOH, as calculated from the CV curves at a
scan rate of 5 mV s\(^{-1}\). The electrode also showed long-term electrochemical stability up to 3000 cycles and a good high-rate performance for both thinner and thicker films. EIS made it clear that the electrochemically active specific surface area of the annealed porous Co(OH)\(_2\) nanoflake films remained virtually unchanged after 3000 cycles, showing the stability of the microstructure. The capacitance loss that did occur could be attributed to the transformation from Co(OH)\(_2\) to CoO\(_2\). The flexible porous Co(OH)\(_2\) nanoflake films could be suitable for use as the electrode for the next generation of flexible supercapacitors.

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