Electrodeposited nickel hydroxide on nickel foam with ultrahigh capacitance[†]

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Electrodeposited Ni(OH)₂ on nickel foam with porous and 3D nanostructures has ultrahigh capacitance in the potential range -0.05-0.45 V, and a maximum specific capacitance as high as 3152 F g⁻¹ can be achieved in 3% KOH solution at a charge/discharge current density of 4 A g⁻¹.

Electrochemical capacitors (ECs), also called supercapacitors or ultracapacitors, have raised considerable attention over the past decade because of their higher power density and longer cycle life than secondary batteries and their higher energy density compared to conventional electrical double-layer capacitors.¹⁻⁴ To develop an advanced EC device, an active electrode material with high capacity performance is indispensable.⁵ Amongst the numerous materials studied to date, various forms of ruthenium oxides have been extensively studied as active electrode materials for supercapacitors as they exhibit a capacitance as high as 863 F g^{-1} in aqueous acidic electrolytes.⁶ However, the expensive nature of ruthenium has limited it from commercialization. Hence, much effort has been aimed at searching for alternative inexpensive electrode materials with good capacitive characteristics, such as NiO,⁷ CoO_x,⁸ MnO₂,⁹ and so forth. Ni(OH)₂, known as a promising electrode material for applications in energy/power storage devices, especially ECs, is attractive in view of its low cost, its well-defined electrochemical redox activity and the possibility of enhanced performance through different preparative methods.10-14

It is well accepted that the overall performance of an electrode material depends not only on the microstructure but also the conductivity of the electrode.^{15–17} Nickel foam, as a commercial material with high electronic conductivity and a desirable 3D structure can be the electrode substrate material of choice. It would not only reduce the diffusion resistance of electrolytes but also enhance the facility of ion transportation and maintain the very smooth electron pathways in the very rapid charge/discharge reactions.

In this Communication, α -Ni(OH)₂ coatings are directly electrodeposited on nickel foam. A maximum specific capacitance of 3152 F g⁻¹, was obtained (see ESI for details[†]). To the best of our knowledge, our value is the highest reported for ECs (the highest value for specific capacitance reported is 3108 F g⁻¹ for a Co(OH)₂/zeolite nanocomposite).¹⁸

The field emission scanning electron microscopy (FESEM) images in Fig. 1 show that foamed nickel has a 3D, cross-linked



Fig. 1 FESEM photographs of nickel foam: (A) an overview and (B) the surface of a branch.

grid structure, with considerable and uniform wrinkles on its surface, which would provide a high porosity and a high specific surface area. Fig. 2 displays a Ni(OH)₂ thin film electrodeposited onto the nickel surface. The thickness of the coating is approximately 200 nm (Fig. S2†). Comparing Fig. 1B with Fig. 2B, one can see that the electrodeposition of Ni(OH)₂ results in a significant morphology change in the nickel foam surface. In Fig. 2B, Ni(OH)₂ coatings are stacked by very small grains (about 10 nm in diameter), forming a 3D and porous superstructure.

Associated with the favorable morphology change, the electrochemical capacity performance of $Ni(OH)_2$ is markedly improved. Fig. 3A shows the CV curves obtained for our $Ni(OH)_2$ in 3% KOH solutions. It is clear that the peak

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S4800 10.0kV 9.8mm x100k SE(U) 500nm Fig. 2 FESEM photographs of the Ni(OH)₂ sample deposited on the

surface of a nickel foam branch (A) and an enlarged view (B).

shapes, especially that of the anodic peak, are different from those of the bulk Ni(OH)₂. For bulk Ni(OH)₂, the peaks are sharper, indicating a dominance of charge transfer control. While for nano-sized Ni(OH)₂ the peaks have a diffusion tail, suggesting a mass transfer dominance in the redox mechanism. The difference in peak shapes could be attributed solely to particle size. Apart from inter-grain conduction, loosely packed nano-sized Ni(OH)₂ grains increase the shift of conduction and valence band leading to a greater charge separation.¹⁹

The specific capacitance values of the Ni(OH)₂–Ni foam electrode are calculated to be 3152, 1848, 1000 and 280 F g⁻¹ corresponding to the charge/discharge current densities of 4, 8, 12 and 16 A g⁻¹, respectively (Fig. 3B). The maximum specific capacitance value is supported by EIS (see ESI for details[†]). The surprising enhancement of the specific capacitance is mainly attributable to the effective utilization of Ni(OH)₂. Different from the previously reported Ni(OH)₂ materials, which were packed tightly in bulk, our Ni(OH)₂ grains are loosely dispersed on nickel foam, making every Ni(OH)₂ "island" contact with the conductive Ni substrate and exposing itself to electrolytes. Besides, the 3D structure of nickel foam together with the porous Ni(OH)₂ superarchitecture not only facilitate the penetration of electrolytes into the whole



Fig. 3 The electrochemical properties of the as-prepared Ni(OH)₂–Ni foam electrode: (A) CV curves at different scan rates within a potential window of -0.05 to 0.55 V vs. SCE; (B) discharge curves in the potential range from -0.05 to 0.45 V at different discharge current densities; (C) cycle life data at a discharge current density of 4 A g⁻¹.

hydroxide matrix, but also shortens the proton diffusion distance, providing an important morphological foundation for a ultrahigh specific capacitance.

From Fig. 3C, we notice that the repetitive charge/discharge induces degradation of the porous structure, resulting in a noticeable discharge specific capacitance loss (about 48% after

300 cycles). The flaking off of $Ni(OH)_2$ grains from nickel substrate may be unavoidable due to their loose packing. Despite the relatively poor electrochemical stability, the attractive specific capacitance exhibited by this electrode material inspires us to improve it in latter studies.

In summary, an advanced electrode material with ultrahigh capacitance is simply designed and tailored by the electrodeposition method. Loosely packed nanometre scale Ni(OH)₂ grains spread on nickel foam maintain a much greater surface area for reaction and result in the effective utilization of the electrode material. Its intriguing architectures consisting of mesopores and 3D networks definitely enhance the capacity performance due to the facile electrolyte penetration and fast proton exchange. This simple approach will have potential applications in fabricating a wide range of EC materials.

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