



Hydroxyl compensation effects on the cycle stability of Nickel–Cobalt layered double hydroxides synthesized via solvothermal method



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ABSTRACT

Ni-Co layered double hydroxides (LDHs), as typical battery-type materials with high specific capacity and good rate property, have suffered poor cycle stability. In this work, we develop an in-situ synthesis method, which employs Ni foam as the substrate for crystal growth, simply by compensating a certain amount of hydroxyl in precursors before solvothermal reactions. Results prove that the sample prepared with hydroxyl compensation still exhibits relatively high specific capacity, about 170.6 mAh g^{-1} at 10 A g^{-1} and good capacity retention, about 63.2% when the current density is increased to 40 A g^{-1} . Especially, the cycle stability of the electrodes have been improved greatly, with about 99% capacity retention after cycling 3000 times. The improved cycle stability are competitive or superior to those of many other systems with more complicated modifications. Material characterizations indicate that the greatly enhanced cycle stability can be attributed to the strengthened connections between nanosheets and substrates and the inner structure stability of matrix, boned by sufficient hydroxyl.

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1. Introduction

During recent years, plenty of attentions have been concentrated on electrochemical energy storage system (ESS) in the form of batteries, electrochemical capacitors, as they can be widely utilized in portable electronics, vehicles (EVs), hybrid EVs (HEVs) and smart micro-grid [1–4]. The research efforts mainly focus on developing electrode materials with high energy density and fast charge capability [5]. Except for traditional lithium ions battery electrodes, many types of metal oxides and hydroxides are also reported as the ESS electrode materials, such as V_2O_5 , MnO_2 , RuO_2 , Co_3O_4 , $\text{Ni}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, et al. and their binary types [6–16].

Recently, metallic layered double hydroxides (LDHs) with general formula of $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}[\text{A}^{n-}_{x/n}\text{mH}_2\text{O}]^{x-}$ (M^{2+} and M^{3+} , the bivalent and trivalent metal cations, respectively; A^{n-} , the charge-balancing anion of valence; $x = \text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$) have attracted increasing interests in the application of ESS area [17–19]. Specially, Ni-Co LDH has been regarded as a promising candidate with high specific capacity, due to the synergistic effects of two elements and multi-valence state of Co ions [20–22]. However, as typical battery-type materials, Ni-Co LDHs, along with

other transition metal based LDHs or hydroxides, have suffered poor rate capability and cycle stability, because the diffusion-controlled process can limit its kinetics especially at high rates and phase change process may cause structure instability, leading to capacity fading [5,23]. Accordingly, many efforts have been devoted to improve its performance, including compositing with carbon materials to improve its conductivity, anchoring active materials on conductive substrates or designing nano-sized architecture to activate more surface reaction sites [20, 24–26,35]. But, special strategies on increasing cycle life and investigating detailed mechanism are seldom reported.

In this report, we focus on a facile and effective method to prepare high-performance Ni-Co LDH electrodes, which directly employs Ni foams as the substrate to allow the vertical growth of Ni-Co LDH nanoplatelets arrays (NPA). Ni foam is cost-effective, light and highly conductive. Especially, its unique 3D open-porous structure, not only facilitates the sufficient immersion of electrolytes, but also provides a large specific surface area for the growth of NPAs. Besides, the rough surface of Ni foam provides sufficient condensation nucleus sites, beneficial for the vertical growth of Ni-Co LDH nanosheets on the substrate, which also provides a visual way to investigate the capacity fading mechanism. Therefore, Ni foam is selected as the substrate. Considering hydroxyl, which plays key roles in the nucleation rate and crystal growth of Ni-Co LDHs, is slowly released during solvothermal reaction, we

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attempted to compensate the supply of hydroxyl to control the growth of crystals and research whether it has relationship with cycle stability of electrodes. Specially, we simply added a certain amount of hydroxyl into precursors before solvothermal reactions, and the sample added a certain amount of proton was also prepared for comparison.

2. Experimental Section

2.1. Preparation of Ni foam-based Ni-Co LDH electrodes

All the chemicals are of analytical grade and were used without further purification. The electrode material was prepared by a simple solvothermal process as follows: Typically, nickel foam (10 mm × 20 mm × 0.1 mm, 320 g m⁻²) was pretreated with acetone, 1 M HCl solution, deionized water, and absolute ethanol, each for 15 min, to ensure a clean surface. The cleaned nickel foam was then immersed in a 80 ml Teflon autoclave with a homogeneous solution of Ni(NO₃)₂·6H₂O (0.21 mmol), CoCl₂·H₂O (0.14 mmol), CTAB (0.25 g), H₂O (3.0 g), and methanol (12 g), followed by heating the autoclave in an oven at 180 °C for 24 h. 1 M HCl and 1 M NaOH solutions were also prepared for hydroxyl compensations. The samples added 30 μL HCl and untreated show pH values of about 4.4 and 5.5, while the samples added 30, 60 and 150 μL NaOH solutions present pH values of about 6.1, 6.7 and 9.2. We name all the samples as P1, P2, P3, P4, and P5, respectively. The Ni foam, covered with nanoplatelets, was washed with deionized water and ethanol to remove surface ions and molecules using an ultrasonic bath cleaner for about 20 min, and then dried at 80 °C for 12 h to remove the adsorbed solvents. The mass density of active materials for P1-P4 was about 1.33, 1.46, 1.55, 1.62 mg cm⁻², respectively

2.2. Characterization

The crystalline structure was characterized by X-ray diffraction patterns (XRD, D/max-V2500, Rigaku) from 8° to 60° at 8° min⁻¹, using Cu Kα radiation (λ=1.5406 Å) as source. Field-emission scanning electron microscope (SEM, LEO-1530, Zeiss) and transmission electron microscopy (TEM, TECNAI G²20, FEI) were used to investigate the morphology and crystal structure of the as-prepared samples. Nitrogen adsorption and desorption experiments of Ni foam-based samples were carried out by a specific surface area analyzer (Autosorb-iQ2-MP, Quantachrome Instruments). The surface area was calculated using the Brunauer-Emmett-Teller (BET) equation based on the mass of active materials for accuracy. Pore-size distributions were calculated by the Barrett-Joyner-Halenda (BJH) method.

All the samples were investigated under a 3-electrode cell configuration at 25 °C, which is appropriate for assessing the capacity rather than energy and power density output of one electrode in real application [27]. The nickel foam supporting Ni-Co LDH NPAs was acted directly as the working electrode, which was soaked in a 1 M KOH solution and degassed in a vacuum for 5 h before tests. Platinum foil and Hg/HgO (1 M KOH) were used as the counter and reference electrodes, respectively. The cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) measurements were conducted on an electrochemical workstation (IM6, Zahner), while galvanostatic charge-discharge tests were carried on a supercapacitor test instrument (BT2000, Arbin). The specific capacity of each sample was calculated from galvanostatic charge-discharge curves as follows:

$$C_s = I \times \Delta t / m = I \Delta t / 3.6m \quad (1)$$

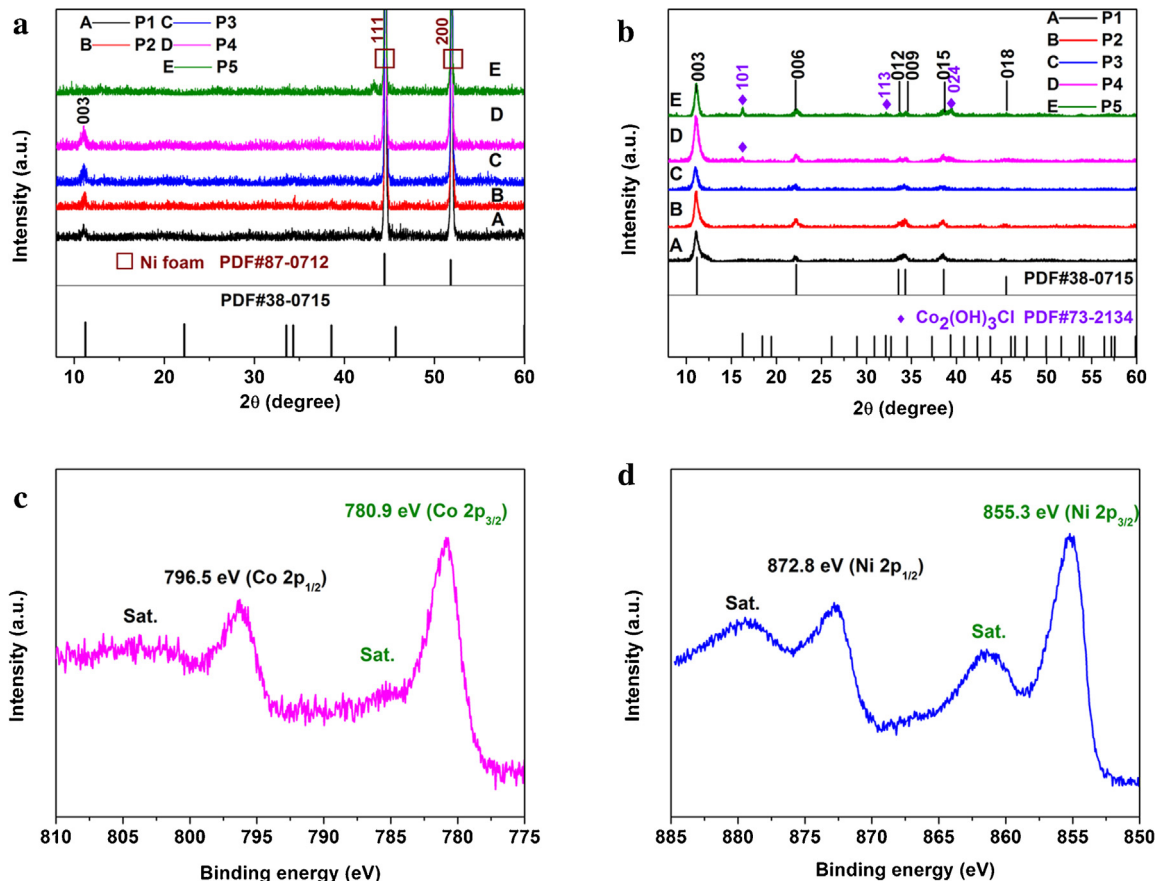


Fig. 1. XRD patterns of the samples (a: Ni Co-LDH NPAs supported on Ni foam, b: relative powders), and XPS spectra of P4 powders (c).

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