

Short Communication

Rapid Synthesis of Water-soluble NiCl₂ Nanorods via Recrystallization for Super Capacitors Applications

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Abstract: Highly uniform NiCl₂ nanorods were synthesized successfully via recrystallization and employed as electrode materials for super capacitors applications. The water-soluble Ni/NiCl₂ electrode proves to show typical pseudocapacitive characteristics and delivers a very high specific capacitance of 1182.7 F g⁻¹ at 2 A g⁻¹. The charge storage and conversion process initiates from the chemically combination of Ni²⁺ and OH⁻, and maintains a reversible redox reaction of Ni(II) ↔ Ni(III) on the electrode. It opens a new insight into the fabrication of multifarious water-soluble inorganic salts for super capacitors applications using the ionic electro negativity parameter as the theoretical guideline.

Keywords: nickel chloride, ionic electro negativity, pseudocapacitance, super capacitors, energy storage

1. INTRODUCTION

Electrochemical capacitors (ECs, also called super capacitors) have been widely investigated over the past few decades due to their prominent advantages such as high power density and long lifespan compared with traditional lithium batteries [1-3]. ECs can be classified as electrochemical double layer capacitors (EDLCs) based on ion adsorption at the electrode/electrolyte interface and pseudocapacitors that rely on surface or near-surface fast and reversible redox reactions of the active materials. Pseudocapacitive materials including transition-metal oxides/sulfides, conducting polymers, and their hybrid materials have been extensively explored. So far, many efforts have been focused on rationally designing novel hierarchical structures, hybrid structures, and complex heterostructures of the active materials in order to improve the capacitance [4]. As we know, the pseudocapacitive behavior is primarily associated with the redox reactions of the cations (or changes in the oxidation states of cations) in electrode materials during charge/discharge. On this account, it's of great importance to probe the pseudocapacitance of the water-soluble metal cations in inorganic pseudocapacitor electrodes for further understanding the charge storage mechanism.

Herein, water-soluble NiCl₂ nanorods synthesized via recrystal-

lization were employed as electrode materials for pseudocapacitors and exhibited very high pseudocapacitance.

2. EXPERIMENTAL

In a typical synthesis, 2 g of nickel chloride hexahydrate (NiCl₂·6H₂O) was dissolved in 10 mL of anhydrous ethanol with constant stirring at 50 °C for 30 min, followed by natural cooling to room temperature. The obtained solution was then quickly poured into a 100 mL reactor filled with 40 mL of acetone at a stirring rate of 300 r min⁻¹ for 20 min. Finally, anhydrous NiCl₂ powders were collected after ultrasonication, filtering, drying in an oven at 60 °C for 8 h, and then sintering at 300 °C for 4 h. All chemicals above are of analytical grade and used without further purification.

The as-obtained products were characterized by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM).

Cyclic voltammetry (CV) and galvanostatic charge/discharge technique were conducted in 2 M KOH aqueous solution using a classical three-electrode system on an electrochemical workstation. The Pt wire electrode served as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The Ni/NiCl₂ electrodes were fabricated by pasting the slurry mixture containing 80 wt% of NiCl₂, 10 wt% of carbon black (super P), and 10 wt% of polyvinylidene difluoride (PVDF) onto a Ni foam.

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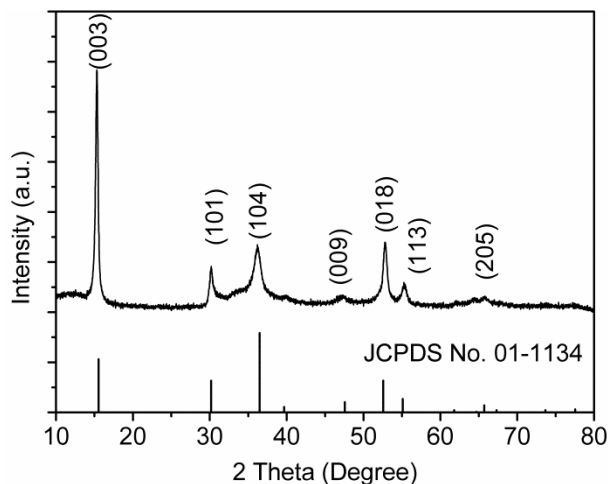


Figure 1. XRD pattern of the as-prepared products.

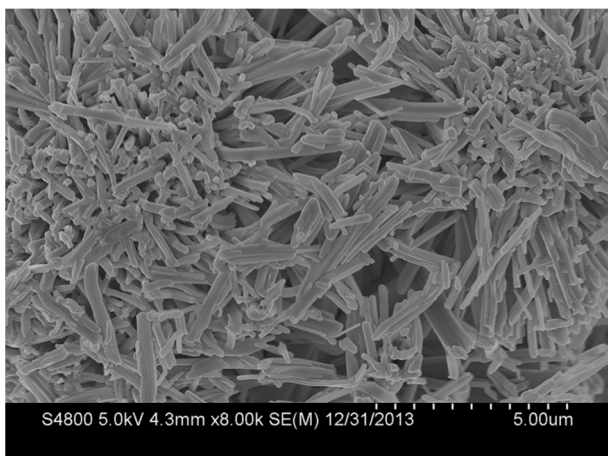


Figure 2. SEM image of the as-prepared products.

3. RESULTS AND DISCUSSION

Fig. 1 shows a typical XRD pattern of the as-obtained NiCl_2 products. All characteristic diffraction peaks can be readily assigned to pure rhombohedral phase of NiCl_2 (JCPDS No. 01-1134). The SEM image shown in Fig. 2 reveals the NiCl_2 products exhibiting rod-like morphology with an average diameter of approximately 250 nm.

The electrochemical properties were investigated by CV as shown in Fig. 3. A distinct pair of redox peaks is observed during the anodic and cathodic sweeps, showing a typical pseudocapacitive characteristic. Compared with the negligible current signal from the CV curve of the pure Ni foam electrode, the current response for the Ni/NiCl_2 electrode is sharply promoted, suggesting that the NiCl_2 active materials are contributing to the remarkable pseudocapacitance.

However, inorganic salts such as transition-metal chlorides, to our knowledge, are easily dissolved in aqueous solution, resulting in the absence of electrochemical activity [5]. Especially for NiCl_2 , facile water intercalation into the van der Waals gaps occurs

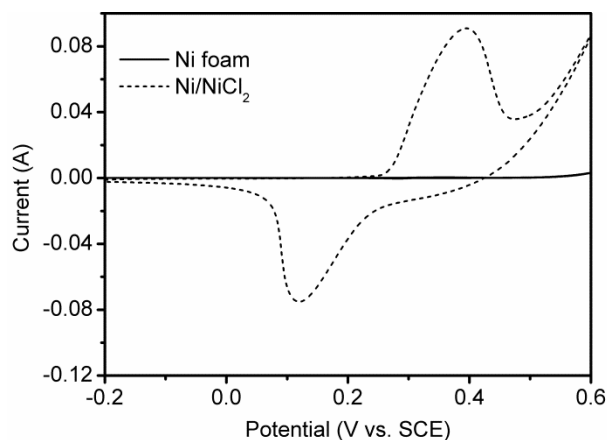


Figure 3. CV curves of Ni foam with and without loading of NiCl_2 at a scan rate of 5 mV s^{-1} .

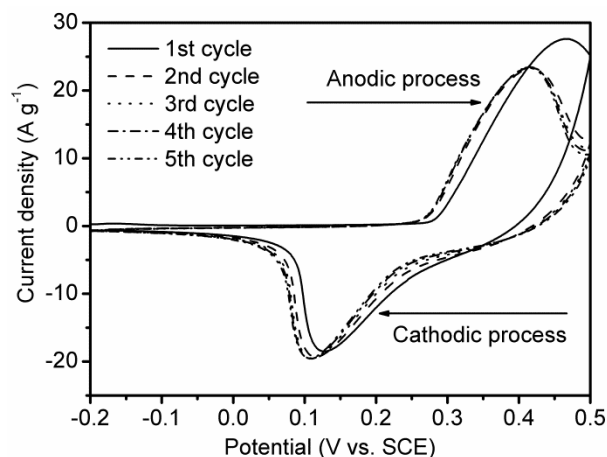


Figure 4. CV curves of the Ni/NiCl_2 electrode for the initial 5 cycles at 5 mV s^{-1} .

through the prismatic ($hk0$) edges, which makes NiCl_2 crystals self-dissolved to some extent [6]. To explore the evolution of the present pseudocapacitance, the electrochemical reaction processes on the Ni/NiCl_2 electrodes were detected by CV response for the initial five cycles at a scan rate of 5 mV s^{-1} , as shown in Fig. 4. Except for the first anodic peak that appears at 0.465 V, the following anodic peaks occur at about 0.415 V, indicating an oxidation process from Ni(II) to Ni(III) [7]. Conversely, the cathodic peaks at around 0.110 V are related to the reduction process from Ni(III) to Ni(II) . It's noted that the anodic peak potential of the first cycle is higher than those of the following cycles. It may be attributed to the serious polarization of the electrode owing to the poor conductivity of NiCl_2 that cannot be converted into Ni(OH)_2 completely in the first cycle.

When the Ni/NiCl_2 electrode was immersed in 2 M KOH aqueous electrolyte, Ni(OH)_2 could be formed by the chemical combination of Ni^{2+} and OH^- because of the strong chemical affinity under alkaline conditions. Therefore, the free Ni^{2+} in the electrolyte

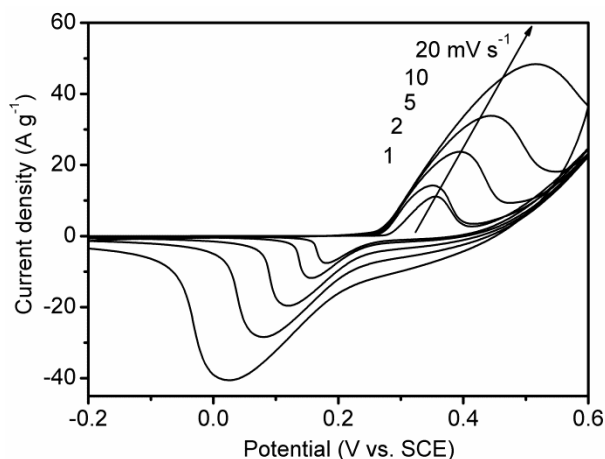


Figure 5. CV curves of the Ni/NiCl₂ electrode at different scan rates in 2 M KOH aqueous solution.

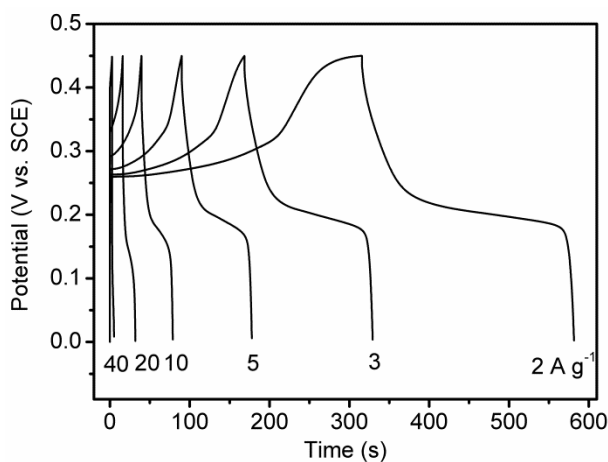


Figure 6. Galvanostatic charge/discharge curves of the Ni/NiCl₂ electrode at different current densities.

can be fixed on the electrode. After the initial chemical reaction, the electrochemical activity was activated. The charge storage and conversion process on the Ni/NiCl₂ electrode can be described as below [8, 9]:

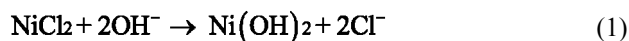


Fig. 5 shows CV curves of the Ni/NiCl₂ electrode at different scan rates in 2 M KOH solution. The shape of the curves is maintained with the scan rates increasing from 1 mV s⁻¹ to 20 mV s⁻¹, revealing the excellent rate performance of the electrode. As the scan rate increases, the peak potentials shift to more anodic and cathodic directions, respectively, and it's related to the internal resistance of the Ni/NiCl₂ electrode [10]. From the discharge curves shown in Fig. 6, the specific capacitances of the Ni/NiCl₂ electrode are calculated to be 1182.7, 1071.3, 976.7, 871.1, and

706.7 F g⁻¹ at 2, 3, 5, 10, and 20 A g⁻¹, respectively. All of the as-obtained electrochemical properties demonstrate that the water-soluble NiCl₂ nanorods can be potential electrode materials for super capacitors applications. However, much work still needs to be done to further enhance the cycling ability and the specific capacitance. Furthermore, the ionic electro negativity can be acted as a theoretical guideline to identify the metal cations effect in the improvement of the pseudocapacitive system [11]. The cation whose electro negativity is in the range of 1.25~1.40 with a +2 state oxidation can hold electrons during Faradic reactions and can be selected as potential electrode materials for pseudocapacitors. Therefore, the water-soluble Ni/NiCl₂ electrode system can be extended to a variety of inorganic salts for potential applications in super capacitors.

4. CONCLUSIONS

NiCl₂ nanorods in uniform size were prepared successfully. The simple recrystallization method manipulated at room temperature under facile conditions allows for rapid and large-scale synthesis. The water-soluble NiCl₂ nanorods were employed as electrode materials for pseudocapacitors and exhibited excellent electrochemical performance. The water-soluble Ni/NiCl₂ electrode system can be extended to a variety of inorganic salts based on the guideline of ionic electro negativity.

5. ACKNOWLEDGEMENTS

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