Variable-temperature preparation and performance of NiCl_2 as a cathode material for thermal batteries

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ABSTRACT Nickel(II) chloride materials were synthesized via a novel two-step variable-temperature method for the use as a cathode material in Li-B/ NiCl_2 cells with the LiCl–LiBr–LiF electrolyte. The influence of temperature on its structure, surface morphology, and electrochemical performance was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and electrochemical measurements of single cells. XRD results showed that after pre-dehydration for 2 h at 270°C followed by sintering for 5 h at 600°C, the crystal water in nickel chloride hexahydrate could be removed effectively. The SEM results showed that particles recombined to form larger coarse particles and presented a layered structure. Discharge tests showed that the 600°C-treated materials demonstrated remarkable specific capacities of 210.42 and 242.84 mA h g^{−1} at constant currents of 0.5 and 2.0 A, respectively. Therefore, the Li-B/ NiCl_2 thermal battery showed excellent discharge performance. The present work demonstrates that NiCl_2 is a promising cathode material for thermal batteries and this two-step variable-temperature method is a simple and useful method for the fabrication of NiCl_2 materials.

Keywords: thermal battery, nickel chloride, variable temperature, electrochemical performance

INTRODUCTION

The thermal battery was invented and developed in the 1940s to provide power for German weapons [1,2]. It was the primary energy storage battery that used molten salts as the electrolyte and internal pyrotechnic sources as the ignition device to bring the battery stack to operating temperature [3,4]. Thermal batteries are an important power source for modern weapons and are widely used in nuclear weapons, guided missiles, and aerospace [5,6]. Over the years, researchers have studied different cathode materials [7–11], including FeS_2 and CoS_2 materials for various applications. They have been extensively studied

and became the primary cathode materials in the thermal battery technology (Li-alloy/ FeS_2 and Li-alloy/ CoS_2 cells) [12–18]. FeS_2 easily decomposes at high temperature in air and usually starts to break down at 540°C, which will affect the discharge performances of the thermal batteries [14,19]. In contrast, CoS_2 would produce impurities during synthesis and storage, which would lead to an increase in resistivity and polarization and decrease in thermal stability, further affecting the electrochemical performance of thermal batteries [20]. Meanwhile, the discharge voltages of the single cells of FeS_2 and CoS_2 sulfide thermal batteries are both below 2.0 V [21,22]. For the above reasons, these materials are not suitable for high power and energy output capability, miniaturization, and micro-mation. Compared with FeS_2 and CoS_2 thermal batteries, nickel(II) chloride (NiCl_2) as a cathode material has many advantages such as power and energy output capability, high open-circuit voltage, and thermal stability. The theoretical electromotive force of a single cell with the Li–Si alloy is 2.64 V, significantly higher than that of FeS_2 and CoS_2 sulfide cells [23–25]. With the Li–B alloy, the working temperature of NiCl_2 thermal battery was 400–750°C, the power density was 1200 W kg^{−1}, and the capacity density was 120 W h kg^{−1}. When the current density was 0.7 and 4 A cm^{−2}, the voltage platform of a single cell was 2.2 and 1.8 V, respectively [19]. Therefore, NiCl_2 is one of the ideal materials to replace sulfide cathode materials [26].

In order to prevent cathode materials from reacting with the molten electrolyte and to increase the discharge capacity, raw nickel chloride materials must be desiccated before use as a thermal battery cathode material. However, the final product, nickel chloride, often includes crystal water, mostly in the form of nickel chloride hexahydrate. Based on the above analysis, nickel chloride hexahydrate must be

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dehydrated before becoming a cathode material. Therefore, in this study, a novel two-step variable temperature solid-state method is used to remove the crystal water from nickel chloride hexahydrate. It includes low-temperature pre-dehydration in air and high-temperature sintering under argon. The influence of temperature on the structure, surface morphology, and electrochemical performances of the material are also discussed in detail.

EXPERIMENTS

Material preparation

The nickel chloride hexahydrate was of analytical grade. In order to obtain the best pre-dehydration temperature of the material, we heated the raw material in a tube furnace for 2 h at a series of temperatures: 270, 310, 350, 400, and 500°C, at the heating rate of 10°C min⁻¹. Subsequently, when the materials cooled to room temperature, they were transferred to an Ar-filled glove-box to prevent hydration and contamination, and ground in an agate mortar. Finally, the pre-dehydration materials were assessed to evaluate the optimized temperature.

The pre-dehydration NiCl₂ samples were then put into a combustion tube in an Ar-filled atmosphere for high-temperature sintering at 400, 500, 600, 700, 800, and 900°C, by heating at the rate of 10°C min⁻¹, and the temperature was kept constant for 5 h. When the materials cooled to room temperature, they were transferred to an Ar-filled glove-box rapidly and ground. Then the high-temperature-sintered materials were characterized and their electrochemical performances were measured.

Material characterization

The X-ray diffraction (XRD) diffraction patterns of the samples were recorded using a Rigaku D/max 2500 Discover diffractometer with Cu-Kα radiation ($\lambda = 0.154178$ nm, 40 kV, and 30 mA) to study the crystallographic structure. The morphology and particle size of the samples were observed using a JEOL JSM-6390 scanning electron microscope (SEM).

Preparation of single cell

The single cell was conventionally prepared by lamination [27]. To obtain the cathode powders, NiCl₂ powders were mixed with the all-Li LiCl-LiBr-LiF electrolyte mixture powders (NiCl₂ content of 80 wt.%), followed by grinding and pressing to make the cathode pellets (diameter 30 mm). The separator was made using a magnesium oxide powder mixture. The Li-B alloy was the anode pellet. The battery was finally built using a reusable test fixture

in which the stack temperature was monitored during activation and discharge.

Electrochemical measurements

The single cells were sandwiched between two temperature-controlled stainless steel cylinders [27], and heated to 500±10°C. Discharge performances were evaluated on an electrochemical test system (LAND, CT2001B-A2). The cells were discharged using the constant current test at 0.5 and 2.0 A, respectively, with sampling intervals of 100 ms to the cutoff voltage of 1.5 V [28].

The single cell discharge test was performed at consecutive current pulses using a current of 2.0 A for 30 s, followed by a current of 4.0 A for 0.1 s. The total internal resistance values of different single cells were calculated from the single cell discharge results using the following equation:

$$R = (V_1 - V_2) / (I_2 - I_1),$$

where, R , V_1 , V_2 , I_1 , and I_2 are the total internal resistance, the working voltage, the pulse voltage, the working current, and the pulse current, respectively.

RESULTS AND DISCUSSION

Structure and surface morphology

The XRD patterns were measured to examine the structural changes of nickel chloride hexahydrate after different low-temperature treatments. As shown in Fig. 1a, all the samples treated below 400°C have similar diffraction peaks, and conform to the JCPDF card #002-0765; there are no new peaks in the diffraction patterns, however, some broad peaks appear at 2θ between 30° and 45°. This indicates that the crystal water was not removed completely. With the increase of temperature to 500°C, in spite of the much higher crystallinity, new diffraction peaks at $2\theta = 32.4^\circ$, 37.3° , and 43.5° appear, which suggests that there are impurity peaks in the diffraction patterns. In order to further explain the phase composition of the impurity peaks, we amplified the diffraction peaks obtained at 500°C as shown in Fig. 1b. It shows that the impurity peaks are nickel oxide, which may be the product of the reaction between nickel chloride and oxygen at high temperature. Nickel oxide impurities would reduce the active substance content of cathode materials, further affecting the discharge performance and reducing the specific energy. Thus we should improve the next dehydration step. It is necessary to ensure dehydration and the active substance content.

Considering the reaction conditions, energy consumption and structural stability, synthetically, the optimum temperature for low-temperature pre-dehydration in air

Figure 1 XRD patterns of different low-temperature pre-dehydration materials (a) and XRD patterns of the 500°C-treated materials (b).

was 270°C, since the samples treated at temperatures between 270 and 400°C had almost the same structure. In contrast, temperatures below 270°C would be lower than its dehydration temperature, and the stability of the material would be seriously affected [29]. If the temperature was raised to 500°C, a new impurity phase would appear, as seen from Fig. 1b.

The XRD patterns of the high-temperature-sintered materials obtained in an Ar-filled atmosphere were further examined, as shown in Fig. 2. The patterns display sharp peaks corresponding to nickel chloride (JCPDF#002-0765) at temperatures over 600°C and there are no obvious impurity diffraction peaks. Which temperature condition would be favorable for cathode materials would be further examined by the electrochemical performances of single cells.

The SEM images show that the particles treated at 270, 600, and 900°C have different surface structures. As shown

in Fig. 3a, the NiCl_2 samples obtained at 270°C were aggregated into irregular particles with a broad particle size distribution. However, the NiCl_2 samples obtained at higher temperatures like 600 and 900°C had a layered structure with larger grain size. Compared with NiCl_2 obtained at 600 and 900°C (Fig. 3b, c), NiCl_2 obtained at 270°C (Fig. 3a) showed smaller grain sizes with larger specific surface area. The smaller grains agglomerated to larger particles. This was advantageous in increasing the tap density of the cathode material, which was attributed to better interfacial contact of the material and better particle–particle contact among the nickel chloride particles.

Electrochemical properties of single cells

To evaluate the electrochemical performances of single cells using materials sintered at different high temperatures as cathode powders, their discharge characteristics were studied. The single cells were discharged at constant currents of 0.5 and 2.0 A until the potential fell to 1.5 V. The discharge curves of the single cells are shown in Fig. 4a, b. As shown in Fig. 4a, the control group was a one-step discharge result at high temperature, and the discharge plateaus of the experimental groups were approximately 2.40 V at a constant current of 0.5 A; the discharge plateau with 600°C-treated material ran about 1200 s until the potential dropped below 1.5 V, much longer than the materials treated at other temperatures. This was about 400 s longer than the 900°C material and 200 s longer than the 500°C material. At a constant current of 2.0 A, seen from Fig. 4b, the discharge plateau with the 600°C-sintered materials ran about 350 s, which was still longer than the materials sintered at other temperatures. However, at 2.0 A, the voltage delay was more obvious than that at 0.5 A (details shown in Table 1), and the delay voltage rose with the sintering temperature, but the plateau voltage declined.

Figure 2 XRD patterns of materials sintered at different temperatures.

Figure 3 SEM images of materials pre-dehydrated at 270°C (a), sintered at 600°C (b), and sintered at 900°C (c) (scale bar: 20 µm).

Table 1 The voltage data relative to the single cells at a constant current of 2.0 A

Temperature	500°C	600°C	700°C	800°C	900°C
Standing voltage (V)	2.595	2.594	2.594	2.589	2.591
Initial voltage (V)	2.262	2.243	2.071	2.002	1.850
Plateau voltage (V)	2.418	2.417	2.390	2.338	2.316
Delay voltage (V)	0.156	0.174	0.318	0.336	0.466

In order to further examine the electrochemical performances with 600°C-sintered materials, the cells were discharged at different constant currents and discharge temperatures. As shown in Fig. 4c, when the current was 1.0 A, its specific capacity was 221.74 mA h g⁻¹ with a high discharge plateau. From Fig. 4d, when the discharge temperature was raised to 520°C, its specific capacity was 188.65 mA h g⁻¹ with a flatter discharge plateau.

Generally, specific capacity is the most important indicator to evaluate a thermal battery [9,29]. The single cells with the 600°C-sintered materials at a constant current of 0.5 A ran for 1200 s with specific capacity of 210.42 mA h g⁻¹; at 2.0 A, it ran for 268 s with specific capacity of 242.84 mA h g⁻¹. Compared with the other materials, the reduction in lifetime and specific capacity were related to the morphology of materials, due to the effects of different sintering temperatures.

According to the above results, the two-step variable-temperature preparation method is beneficial in improving the thermal stability of NiCl₂ cathode materials. During the low-temperature pre-dehydration process, crystal water and oxide impurity mainly affect the thermal stability of NiCl₂. Lower contents of crystal water and oxide impurity result in improved thermal stability. In addition, when the sintering temperature was over 400°C, the oxide impurity increased, which can lead to declining thermal stability. In contrast, during high-temperature sintering, it helps to further dehydrate the powders and prevent the mate-

rial from being oxidized, further improving thermal stability. Thermal stability is also related to its own morphology, and it increases with temperature due to the NiCl₂ materials recrystallizing and forming regular crystal structures after high-temperature sintering.

As shown in Fig. 4 and Table 1, the best performance was obtained with 600°C treatment, while at temperatures below 600°C, poor performances were obtained. This might be due to the incomplete removal of the crystal water, and the existence of the crystal water affected the thermal stability of materials and the electrochemical performances. Meanwhile, when the temperatures were over 600°C, the materials' morphology was the dominant factor, and changes to surface morphology deteriorated the electrochemical activity and electrolyte compatibility, as shown in Fig. 5. The internal resistance and polarization would increase, and finally these factors affected the electrochemical performance.

The two step variable-temperature preparation method for NiCl₂ materials related to thermal batteries is suitable for the rapid and extensive production of cathode materials, since it is relatively easy to control the preparation process of the materials. With the two-step preparation method, it can ensure dehydration, protect dehydrated equipment from contamination and corrosion, and reduce the energy and material consumption, especially the consumption of argon gas, further lowering the manufacturing cost. Therefore, this method is a novel economic and

Figure 4 Discharge curves of Li-B/LiCl-LiBr-LiF/NiCl₂ cells at 500°C and constant currents of 0.5 A (a) and 2.0 A (b) with different high-temperature-sintered materials, and different constant currents (c), and different discharge temperatures (d) with 600°C-sintered materials.

Figure 5 Total internal resistance values of Li-B/LiCl-LiBr-LiF/NiCl₂ cells at 500°C and 2.0–4.0 A with different high-temperature-sintered materials.

technologically viable preparation method for NiCl₂ related to thermal batteries.

CONCLUSIONS

NiCl₂ materials for Li-B/NiCl₂ cells with an all-Li LiCl-LiBr-LiF electrolyte were synthesized by a novel two-step variable-temperature method using nickel chloride hexahydrate and the effect of temperature was systematically studied. The process with pre-dehydration at 270°C and sintering at 600°C can remove crystal water quickly and effectively and make the particles recombine to form coarse particles and present an obvious layered structure. Measured at constant currents of 0.5 A and 2.0 A, the single cells made with the 600°C-treated cathode provided better specific capacity than the materials treated at other temperatures. It is therefore possible that the materials made with the two-step variable-temperature method will lead to dramatic electrochemical performance and significant increase in lifetime and specific capacity.

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热电池正极材料氯化镍的变温法制备及其性能研究

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摘要 本文采用两步变温法制备了无水氯化镍材料. 并以所制备的氯化镍为正极, 锂硼合金为负极, LiCl-LiBr-LiF 为电解质, 组成单体锂热电池. 通过XRD、SEM和单体电池电化学测试分析了温度对氯化镍材料的结构、表面形貌以及电化学性能的影响. XRD结果表明270°C预处理2 h, 600°C高温烧结5 h后, 氯化镍中的结晶水能够被完全去除; SEM结果表明氯化镍热处理后晶粒重组长大并呈现层状结构. 经600°C热处理后的氯化镍材料在0.5 A和2.0 A恒流放电时的比容量分别可达210.42和242.84 mA h g⁻¹, 表明以热处理后的氯化镍为正极的锂热电池具有良好的放电性能. 本文研究结果表明氯化镍是一种非常有潜力的热电池正极材料, 而两步变温法是制备无水氯化镍材料的一种简单实用的方法.