NiCl$_2$ Cathode with the High Load Capacity for High Specific Power Thermal Battery

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Abstract. The advanced thermal batteries with CoS$_2$ cathode are applied to provide high energy, delivering lower specific power, because it is not suitable for high current discharge. NiCl$_2$, possessing a high potential and large current discharge capacity, is considered as one of the cathode candidates for high power thermal battery. Li-B/NiCl$_2$ couple outputs effectively specific power of $\sim 17.3$ kWkg$^{-1}$ in this work at 500$^\circ$C and 0.5 Acm$^{-2}$ (8 Ag$^{-1}$). However, NiCl$_2$ has highly dissolution in LiF-LiCl-LiBr electrolyte (widely used in thermal batteries), resulting in the capacity loss and severe safety problem. Here, cross-sections between NiCl$_2$ cathode and LiF-LiCl-LiBr electrolyte have been characterised by SEM after discharge at 500$^\circ$C, and 0.5 Acm$^{-2}$-discharged interface exhibits blurrier boundary than that of 0.2 Acm$^{-2}$-discharged.

1. Introduction
Thermal battery is primary chemical power utilizing molten salts as electrolyte and generally starts discharge under a high temperature above 350$^\circ$C [1, 2]. Compared with the aqueous electrolyte, once the temperature provided is above its melting point, the molten salt electrolyte immediately becomes an ionic conductor with higher conductivity, such as 3.45 cm$^{-1}$ at 500$^\circ$C for LiF-LiCl-LiBr eutectic salt [3]. Otherwise it is a solid state, which is beneficial to minimizing self-discharge and capacity loss. Thermal battery has lots of advantages including high current discharge, high specific power, high specific energy, and long storage life and so on. Therefore, they are primarily used as power sources for military weapon (torpedoes, guided missile, electronic guidance and aerospace exploration etc.) or emergency backup power. With the progress of the high-sophisticated weapons, requirements for high specific power output are proposed in the further. Previously, the commercial thermal batteries with cathode materials of both CoS$_2$ and FeS$_2$ operate at voltage lower than 2 V, as MoS$_2$ does [4]. Their single cells deliver poor specific power. For instance, for the first voltage platform from 1.8 V to 1.7 V, Li-Si/CoS$_2$ couple obtained the specific power of 2.7 kWkg$^{-1}$ with current density of 0.1 Acm$^{-2}$ (1.5 Ag$^{-1}$) under 500$^\circ$C [5, 6]. However, Li-Si/FeS$_2$ thermal battery only delivered specific power of 0.9 kWkg$^{-1}$ at current density of 0.32 Acm$^{-2}$, which restricted their high-specific power application.
The power of the thermal battery is determined by the product of voltage and current. For acquiring the high specific power output of the single cell, selecting a cathode material with the high load capacity and potential is necessary. Vanadium oxide (β-Li$_{0.3}$V$_2$O$_5$, γ-Li$_{1+x}$V$_3$O$_8$ and CuO-V$_2$O$_5$ system materials, transition metal halides (NiCl$_2$, CuF$_2$, NiF$_2$, FeF$_3$,CoF$_3$ etc.) were developed as cathode materials with high potential in batteries [7-13]. The battery using CuO-V$_2$O$_5$ as cathode exhibited a voltage plateau of 3.4V and 2.5V at a current load of 0.1 and 0.31 Ag$^{-1}$, respectively, but its electrochemical performance at higher current density was relatively poor [14]. LiV$_3$O$_8$, a high-rate cathode material, suffered from fast capacity decay during discharge processes, which severely restricted its large-scale applications [15]. Besides, the FeF$_3$, NiF$_2$ and CoF$_3$ exhibited high open voltage of 3.4V, 2.6V and 3.4V, at 500℃, respectively, but their multiple-discharge platform would reduce the voltage accuracy.

Compared with common CoS$_2$, FeS$_2$ and NiS$_2$ cathodes, NiCl$_2$ possess relative higher potential (2.64V vs Li) and higher thermal stability (above 700℃) and has only one reduction reaction (Ni$^{2+}$+2e$^-$$\rightarrow$Ni). NiCl$_2$ cathode material is conductive to large current discharge, which could be attributed to its sheet structure to facilitate the reduction rapidly. So, NiCl$_2$ has the capacity of high specific power output. Liu et al. found that Li-B/LiF-LiCl-LiBr/NiCl$_2$ thermal battery can output specific power as high as ~6.0kWkg$^{-1}$ with current density of 0.28Acm$^{-2}$ at 500℃ [16]. Hu et al. demonstrated that NiCl$_2$ cathode with nickel metal foam substrate obtained specific power of 10.8kWkg$^{-1}$ at current density of 0.3Acm$^{-2}$ [17]. Jin et al. indicated that carbon-coated modification reduced the dissolution of the NiCl$_2$ cathode in LiF-LiCl-LiBr electrolyte and obtained specific power of 10.5kWkg$^{-1}$ at current density of 0.5Acm$^{-2}$ under 480℃ [18].

As mentioned above, NiCl$_2$ has the capacity of the high power output in thermal battery. High power output requires high voltage and large current density. Li-B/LiF-LiCl-LiBr/NiCl$_2$ thermal battery system is usually designed to achieve the high power output. The Li-B alloy with ultrahigh Li activity and NiCl$_2$ material are able to meet the high power requirement. And LiF-LiCl-LiBr molten salt is considered as a preferred electrolyte with a relative high Li$^+$ transport capacity at high discharge temperature. Therefore, based on this high power system and the NiCl$_2$ cathode material, the high current discharge and dissolution investigation under different current density at 500℃ were carried out.

2. Experimental

2.1. Anhydrous nickel chloride preparation

Anhydrous nickel chloride (NiCl$_2$) was successfully prepared via one-step high-temperature treatment of the raw material nickel chloride hexahydrate (NiCl$_2$$\cdot$6H$_2$O). NiCl$_2$$\cdot$6H$_2$O was transformed into pure NiCl$_2$ by sintering at 600℃ for 2h in the quartz tube with an argon atmosphere. The dehydrated NiCl$_2$ powers were then ground in an agate mortar in the gloved-box providing a dry Ar-filled operating atmosphere. Subsequently, the powders were hermetically sealed and preserved.

2.2. Material characterization

The phase analysis of anhydrous NiCl$_2$ and overflowing from stack were identified by X-ray diffraction (Rikagu MiniFlex 600) with Cu Ka radiation at a rate of 10$^\circ$ min$^{-1}$ from 10$^\circ$ (2θ) to 90$^\circ$ (2θ).

The microscopic morphology of the dehydrated NiCl$_2$ and the cross sections from discharged cells were observed by a field emission scanning electron microscope (FE-SEM, JSM-6700F, Japan).

2.3. Electrochemical measurements

The single cell is constructed with electrolyte, cathode and anode. The electrolyte is a mixture of 50wt.% eutectic salt (9.6wt.%LiF-22wt.%LiCl-68.4wt.%LiBr, melting point of 436℃) and 50wt.% binder (MgO, purity of over 99%). The cathode consists of 60wt.% NiCl$_2$ active material and 20wt.% LiF-LiCl-LiBr electrolyte to improve the conductivity and 20wt.% MgO binder. The anode is the commercial Li-B alloy (40 wt.%Li and 60 wt.%B) provided from Zhijian Liu Research Group (Central
South University). Following operations were conducted in the dry Ar-filled glove box to protect samples from contamination. The cathode and electrolyte were laminated into pellet with a diameter of 17.5mm under a static compaction pressure of 30MPa. The cathode-electrolyte and the anode of Li-B alloy were stacked into a single cell in a heat resisting die sleeve, and then sandwiched between two nickel metal collectors (Fig. 1a).

Subsequently, the assembled battery was placed in preheated device (Fig. 1b) providing constant temperature. Single cells were tested at 500℃ with 0.1, 0.2 and 0.5Acm⁻² provided by electronic load (ITECH, IT8511, USA), respectively. Considering the practical applications of thermal battery, the cut-off voltage was set to be as high as 85% of the voltage platform. For characterization of interface between cathode and electrolyte, transferring instantly the discharged cells into the glove box, the cooling batteries were split through the stacks center and exposed cross-sections.

3. Results and Discussion
The prepared NiCl₂ sample is the deep orange powders. Its XRD pattern (Fig. 2a) is well indexed to the pure-phase of hexagonal NiCl₂ (JCPDS card No. 71-2032), which suggests that sintered NiCl₂ powders have been removed water completely. NiCl₂ power shows observable flaky morphology with smooth surface and each piece consists of several layers as shown by the orange frame (Fig. 2b). Its average size in the two-dimensional direction is 17μm.

In Li-B/LiF-LiCl-LiBr/NiCl₂ thermal system, the galvanostatic discharge result shows an upper-voltage plateau for 2.51V under 0.1Acm⁻² and 500℃ (Fig. 3a). For the 500℃-discharge, it can be seen that with the current density increase, both the voltage platform and discharge time are gradually reduced. When current load increases from 0.1 to 0.5Acm⁻², the discharge time is greatly shorten from 429s to 123s. Although the discharge voltage of Li-B/NiCl₂ single battery reduces to 2.3V at 0.5Acm⁻², it still implies a higher voltage platform than NiS₂ and CoS₂ (about 1.9V) at 0.1Acm⁻², not to mention at 0.5Acm⁻². And the NiCl₂ cathode maintains a steady operating voltage, while both NiS₂ and CoS₂
cathodes include lower second voltage plateau. According to the discharge parameters of Table 1, the NiCl$_2$ cathode obtains 17.3kWkg$^{-1}$ of the specific power at 0.5Acm$^{-2}$ and 500°C showing the higher discharge ability than both NiS$_2$ and CoS$_2$ cathodes. And at small current density of 0.1Acm$^{-2}$, the single cell can output the specific energy of 472.3Whkg$^{-1}$ with cut-off voltage of 2.13V.

Table 1. The electrochemical parameters of the single cells at 500°C, the set-off voltage being 85% of the voltage platform.

| Cathode | Current density (Acm$^{-2}$) | Operating Voltage (V) | Discharge Time (s) | Specific Power (kWkg$^{-1}$) |
|---------|------------------------------|-----------------------|-------------------|-----------------------------|
| NiCl$_2$ | 0.1                          | 2.51~2.13             | 429               | 4.0                         |
|         | 0.2                          | 2.37~2.02             | 292               | 7.6                         |
|         | 0.5                          | 2.28~1.94             | 123               | 17.3                        |
| CoS$_2$  | 0.1                          | 1.94~1.65             | 231               | 3.0                         |
|         | 0.2                          | 1.92~1.63             | 259               | 5.9                         |
|         | 0.5                          | 1.74~1.48             | 97                | 13.0                        |
| NiS$_2$  | 0.1                          | 1.98~1.68             | 367               | 3.0                         |
|         | 0.2                          | 1.91~1.62             | 160               | 5.9                         |

Based on high-power Li-B/LiF-LiCl-LiBr/NiCl$_2$ system, the dissolution behavior with current density of 0.2Acm$^{-2}$ and 0.5Acm$^{-2}$ at 500°C are considered. Photographs of the Ni-based collectors from open-circuit discharge for two hours (Fig. 4a), manifests that discharge for too long operating time will cause plenty of overflowing from stack to the collectors. The collected overflowing from photograph Fig. 4a is nickel oxide (NiO) characterized by XRD. At the normal galvanostatic discharge also exists the overflowing phenomenon (Fig. 4b). To further evaluate the solubility of NiCl$_2$ cathode in LiF-LiCl-LiBr electrolyte, the cross-sections from discharged stacks were analyzed by SEM. In Fig. 4c and d, the cross section from 0.2Acm$^{-2}$-discharge still keep relative integrity and its interface between cathode and electrolyte is still obvious in comparison of 0.5Acm$^{-2}$-discharge at 500°C. It indicates that higher current load will cause more severe dissolution. The mechanism of how the cathode materials are dissolved into the electrolyte, we’ll further investigate in future.
Figure 4. (a) (b) The photographs of Ni-based current collectors and (c) (d) Cross-sectional views after discharge; the green circuit denoted the cathode (left) and anode (right), the overflowing located in red dash line; the deep blue and green frame denoted electrolyte and heat resisting substance, respectively.

4. Conclusion
High power delivery requires large-rate discharge and a high voltage platform. In the present of this work, it indicates that NiCl$_2$ has the capability of large current discharge. Li-B/LiF-LiCl-LiBr/NiCl$_2$ thermal battery outputs the high specific power of $\sim17.3$ kW kg$^{-1}$ under discharge temperature of 500$^\circ$C with current density of 0.5 A cm$^{-2}$.

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