Int. J. Electrochem. Sci., 15 **(2020)** 10406 – 10411, doi: 10.20964/2020.10.49

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Short Communication

High specific energy of CuO as a thermal battery cathode

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Received: 5 June 2020 / *Accepted:* 26 July 2020 / *Published:* 31 August 2020

As the high specific energy and long working time of the thermal battery development requires the cathode that has high thermal stability and excellent conductivity. As a semiconductor, the microstructure of CuO keeps stability below 830°C. In this of case, the CuO has been first designed as the cathode material for thermal battery. With a cut-off voltage of 1.5 V, the specific energy of CuO thermal battery is up to 1040 Wh/kg under the working environment of 500°C, 100 mA/cm^2. That is higher than commercial FeS_2 and CoS_2 of 327 Wh/kg and 256 Wh/kg, respectively. We believe that our work will afford insights into the alternative of the cathode materials in the high specific energy thermal batteries.

Keywords: CuO; Cathode material; Thermal battery; High specific energy.

1. INTRODUCTION

The single thermal battery usually consists of heat piece, collector, anode, electrolyte and cathode. The battery discharges only the non-conductive electrolyte when melt at high temperature and become conductivity [1]. It is characterized by being able to work with high power and high specific energy, quick activation (below 0.1 s), long shelf life (above 15 years), good mechanical performance and high reliability [2-4]. Thermal battery is the ideal reserve power supply of modern weapons like a variety of missiles, shells, rockets, decoy radars, sonar buoy, and plays an important role in the military field.

Owing to the high utilization of Li metal in Li-B anode, and high ionic conductivity of LiF-LiCl-LiBr electrolyte (above 3.4 S cm^{-1}) after melt [5], as far as we know, the cathode material has become the key factor restricting the development of thermal battery. For example, the commercial FeS_2 cathode has theoretical specific capacity of 890mAh g^{-1}, but the actual specific capacity is lower than 200 mAh·g^{-1} because of low decomposition temperature (≤ 530°C), which make the discharge early invalid at high temperature [6]. Since the higher decomposition temperature (about 650℃) of CoS_2, it has been developed [7]. As the long working time and high specific energy of the thermal battery development requires the cathode that has high thermal stability and excellent conductivity. Many researches present that metal chalcogenide and metal oxide could be applied to the high specific energy of thermal cathode, such as NiS_2, $NiCoS_4$, $FeCoS_4$, $CuVO_3$. While these materials do not satisfy either the high thermal stability or high conductivity [2, 8-12]. Therefore, it is of great significance to develop a new type of cathode with both high actual capacity and high thermal stable.

At present, copper oxide (CuO) as the electrode material of lithium-ion battery has been widely studied. The theoretical specific capacity of CuO thermal battery reaches 670 $mAh \cdot g^{-1}$. Moreover, the CuO is good at semiconductor, which improves the actual discharge ability. For example, Rai et al. [13] synthesized dumbbell and spherical CuO porous three-dimensional structures by simple chemical solution method and subsequent annealing, which have a good rate performance (dumbbell shaped CuO is 569 $mAh \cdot g^{-1}$, spherical CuO is 467 $mAh \cdot g^{-1}$, at 5℃). Moreover, CuO nanowires unfolded the first discharge capacity of 752 $mAh \cdot g^{-1}$ [14]. These studies present that CuO has higher actual discharge performance than commercial FeS_2 and CoS_2. Thermogravimetric analysis also shows that CuO has high thermal stability. It slowly decomposed to Cu_2O and O_2 as the temperature increased above 830℃ [15]. Thus, the high specific capacity and thermal stable of CuO conforms to the high energy thermal battery cathode materials development.

In addition, copper oxide also has the advantages of simple preparation, low price, non-toxic, rich resources, environmentally friendly and so on, which makes it have high research value. In this of case, the CuO has been first applied to the cathode for thermal battery. The discharge parameters and performances have been tested. The results presented the CuO has higher specific energy of 1100 $Wh \cdot kg^{-1}$ than the metal chalcogenides.

2. EXPERIMENTAL

2.1 Materials

The copper oxide powders used as active ingredient were obtained through purchase (Purity ≥ 99%, Shanghai Medicine). The anode is the commercial Li-B alloy (40 wt.% Li and 60wt.% B) provided from Hunan Ruilin Ltd. The separator consists of 60 wt.% electrolyte (9.6 wt.% LiCl-22 wt.% LiF-68.4 wt.% LiBr, m.p. = 436℃) and 40 wt.% magnesium oxide binder with grain size of 1~3 μm (Purity ≥ 99%, Hunan Ruilin Ltd). The phase structure of copper oxide powders was measured by X-ray diffractometer (XRD) on a Miniflex 600 with Cu-Kα radiation. The surface morphology was characterized by scanning electron microscopy (SEM). The particle size and specific surface area are measured with HYL-2076 laser particle size distribution analyzer. The thermal stability was characterized by Thermogravimetry analysis. The morphological feature of cathode after discharge was observed by transmission electron microscope (TEM) with an HAADF, SAED and EDS for elemental distribution analysis.

2.2 Preparation of single cells

A single cell testing system consisted of cathode, anode and separator. The cathode consisted of active material CuO and separator ground and mixed in a 4:1 ratio. Each cathode pellet contained 0.15 g CuO. The anode consisted of Li-B alloy (0.1 g) pressed to pellet at 40 MPa. 0.35 g separator powders and 0.2 g cathode powders were pressed into two pellets with a diameter of 17 mm at 5 MPa. Finally, the single cell was conventionally assembled by lamination. And it was sandwiched between two collectors. The preparation process of single cells was carried out in glove box with argon atmosphere. Water and oxygen content were controlled below 5 ppm.

2.3 Electrochemical measurement

The high temperature discharge performances of thermal battery were tested by the self-made equipment under different experiment conditions. The single cell was tested at 500℃ with current density controlled at 100 mA/cm^2. The discharge above was plotted as relationship between voltage and specific capacities to investigate the effect of current density and temperature on discharges. Pulsed discharge was carried out on a regime of a background current density of 100 mA/cm^2 for 10 s, a pulse current density of 300 mA/cm^2 for 1 s.

3. RESULTS AND DISCUSSION

Figure 1a showed the XRD pattern of CuO powders. Only CuO has been observed (JCPDS NO. 48-1548), which indicated that the sample has high purity, monoclinic crystal structure. CuO powder particles were irregularly shape with an average particle size of 19.5 μm (Figure 1b).

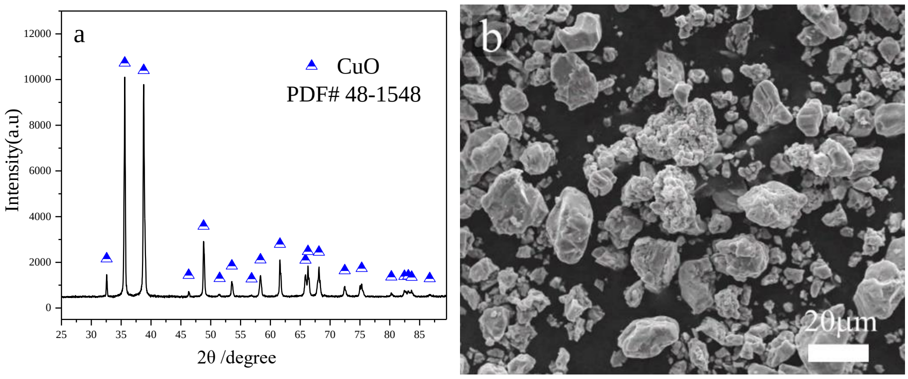

Figure 1. X-ray diffraction pattern (a) and SEM image (b) of CuO material.

This size made the thermal decomposed temperature above 854℃ (TG curve was not given here). It was higher than that of commercial FeS_2 and CoS_2. The high thermal stability and purity enhanced the active material utilization of CuO cathode as thermal battery cathode.

The voltage increased to the peak value of 2.33 V within a few seconds after the battery was activated, except discharging at 450℃ (Figure 2a). It suggested the battery has a higher resistance at 450℃ compared to other high temperature. As the discharge, the voltage decreased along with three platforms of 2.1 V, 1.85 V and 1.75 V, respectively. The discharge time decreased with the discharge temperature increased, especially between 500℃ and 550℃. So, the specific energy decreased from 1020 Wh·kg^{-1} of 500℃ to 648 Wh·kg^{-1} of 550℃ and 558 Wh·kg^{-1} of 600℃ (Figure 2a). As shown in the Figure 2b and Table 1, the specific energy of CuO is not only twice that of commercial FeS_2 and CoS_2, but also higher than that of new cathode materials in recent years, such as Cu_2O, MoS_2, $CrCl_3$ and so on [7, 8, 16-19]. The Li^+ transmission rate increased with the discharge temperature increased, and coupled with CuO good electrical conductivity, leading the pulse resistance decreased (Figure 3). So the activation time decreased at higher temperature (Figure 2a). However, the infiltration between CuO cathode and LiF-LiCl-LiBr electrolyte dramatically amplification at 550℃, which induced to short circuit and invalidation. That why the best discharge performance can be detected at 500℃ during discharge.

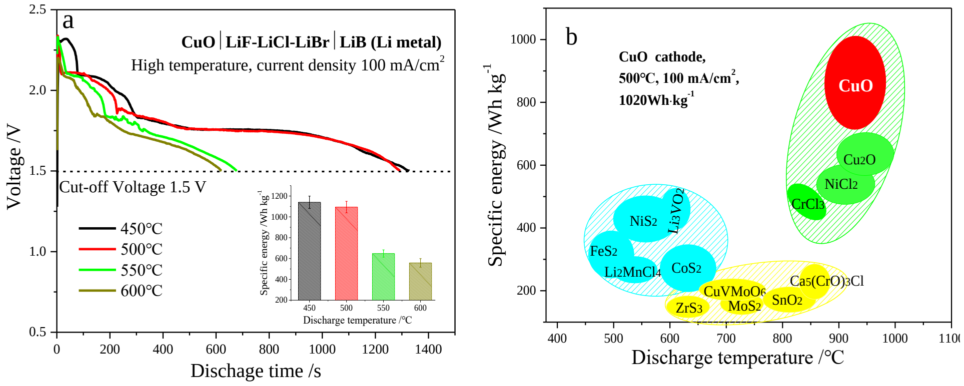

Figure 2. Discharge curves and specific energy of CuO cathode at 100 mA/cm^2 with cut-off voltage 1.5 V (a), and the specific energy of different cathodes as function of discharge temperature (b).

Table 1. Comparison of different cathode materials for thermal battery reported in the literatures.

Cathode materials	Thermal decomposition temperature (℃)	Discharge condition	Specific energy (Wh kg^{-1})	Ref.
FeS_2	550	0.2 A cm^{-2}, 520℃	450	[7]
CoS_2	634	0.1 A cm^{-2}, 500℃	387	[16]
$CrCl_3$	> 800	0.2 A cm^{-2}, 550℃	540	[17]
MoS_2	740	0.05 A cm^{-2}, 450℃	337	[18]
Cu_2O	> 900	0.1 A cm^{-2}, 500℃	665	[8]
CuO	854	0.1 A cm^{-2}, 500℃	1020	This work

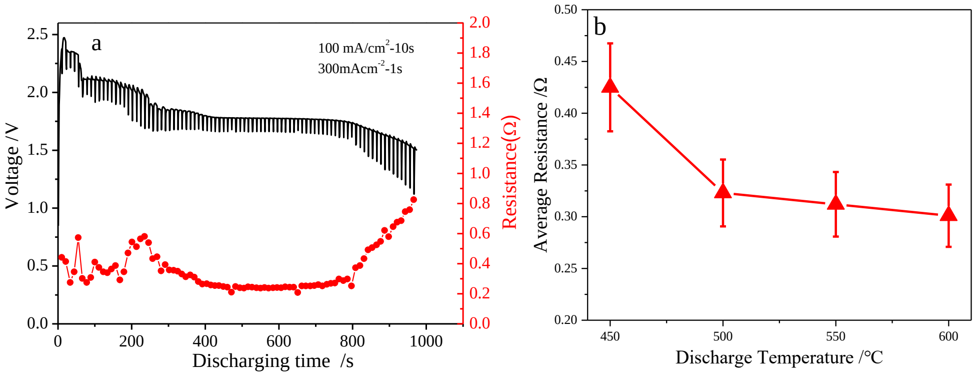

Figure 3. Discharge curve and pulse resistance of CuO cathode at 500°C (a), average resistance as function of discharge temperature (b).

TEM image and corresponding elemental mapping present that the discharged product of cathode was composed of MgO, electrolyte, Cu and few CuO (Figure 4). The Cu also can be observed by the SAED of white zone inset of Figure 4a. Both the mapping and SAED indicated that most of the CuO have been transformed to the Cu after discharge at 100 mA/cm^2 and 500°C. By considering the discharge was cut off 1.5V, the discharge reaction was basically complete at large current density and high temperature, because of the high thermal stability and excellent conductivity. Namely, the CuO thermal battery cathode material can effectively discharge with a high specific energy.

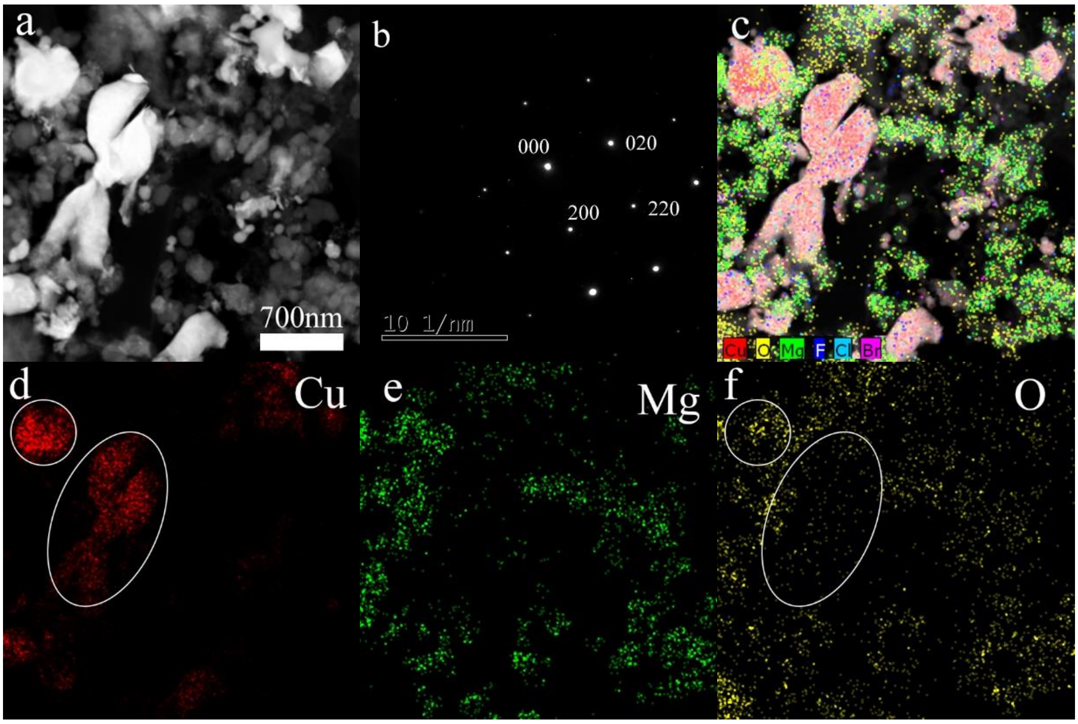

Figure 4. HAADF image of cathode after discharge at 500°C and 100 mA/cm^2 (a), the corresponding SAED, [001] zone axis (b), and the elemental mapping (c-f).

4. CONCLUSION

As cathode material of thermal battery, CuO has the advantages of high thermal stability, excellent conductivity and high theoretical capacity. In the presents of this work, the CuO has first been applied to the high energy thermal battery. The very high specific energy of 1040 Wh/kg has been obtained at temperature of 500°C and current density of 100 mA/cm^2, even with the cut-off voltage of 1.5 V. This is about three times of commercial cathode materials, such as FeS_2 and CoS_2. As a metallic oxide, CuO is expected to the high energy thermal battery in future.

ACKNOWLEDGMENTS
The research was carried out with financial support from the Young teacher development program of Hunan University (No. 2015031).

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