Solid State Batteries (SSBs) Prepared with Powder Metallurgy Route

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Abstract: The solid state batteries (SSBs) were prepared by powder metallurgy route. For making SSBs, a special die was designed. LiNiO\textsubscript{2} and face centre cubic (fcc) TiB powders\textsuperscript{[1]} were used to make cathodes for SSBs while such metals as Zn or Mg were used to make anodes. The SSBs made with LiNiO\textsubscript{2} powder generated relatively low currents (1 to 2 \(\mu\text{A}\)) and voltage (0.4~0.9 V) at room temperature. The SSBs made with fcc-TiB cathode generated more power than do the SSBs made with LiNiO\textsubscript{2} powder.

Keywords: Solid state batteries; LiNiO\textsubscript{2} powder; Fcc-TiB powder; Powder metallurgy route; Output power.

1. Introduction

Powder metallurgy technology has been widely employed to make various mechanical components. In this study, we use powder metallurgy route to fabricate the solid state batteries (SSBs). SSBs that convert chemical energy into electrical energy have supported power for portable computers, sensors, and electric vehicles\textsuperscript{[1-4]}. These batteries have a peculiar advantage over those containing liquid electrolyte; they can avoid liquid leakage to spoil their performances by chemical reactions. The SSBs are long-lived and inherently safe; they can be used in both low-power and high-energy versions.

The SSBs consists of anode (negative electrode), electrolyte and cathode (positive electrode). The oxidation occurs at the anode and releases electrons into the external circuit while the reduction occurs at cathode and gets electrons from the external circuit. The electrolyte that acts as a physical separator for the electrodes must be insulator for electrons to prevent self-discharging of the battery; at the same time, it must be good ionic conductor. The choice of materials for the anode and cathode is affected also by cost. The stability of SSBs mainly depends on the quality of cathode and anode materials.

In present paper, we use LiNiO\textsubscript{2} and fcc-TiB as electrode materials to fabricate different solid state batteries through powder metallurgy route. LiNiO\textsubscript{2} is frequently used for making cathode materials\textsuperscript{[5]} Fcc-TiB has similar crystal structure with TiO\textsuperscript{[6]}.

For making SSBs, a special die was designed. The electrical properties of various 

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batteries were measured.

2. Experimental materials

LiNiO\textsubscript{2} powder is commercial product with 99.9% pure (it is a very promising cathode material of Li-ion battery for its high capacity, low pollution and appropriate cost); fcc-TiB is a kind of conductive ceramic synthesized in our laboratory with Ti-boronizing method [7].

Zn and Mg were used as anodes. Two kinds of electrolytes were employed. One is solid state electrolyte (SSE). SSE was prepared by following previous reported method [8]. Ce\textsubscript{0.8}Gd\textsubscript{0.2}O\textsubscript{2}, NiAl and NaOH powders were used to fabricate the SSE powder. The precursors used for preparing Ce\textsubscript{0.8}Gd\textsubscript{0.2}O\textsubscript{2} are Ce(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O and Gd(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O powders(99.9% pure). Each powder was dissolved in distilled water; the solutions were then mixed to obtain compositions corresponding to Ce\textsubscript{0.8}Gd\textsubscript{0.2}O\textsubscript{2}. The resulting solution was dropped into (1:1) solution of NH\textsubscript{3}-(NH\textsubscript{4})\textsubscript{2}CO\textsubscript{3} for precipitation; then the precipitate was dried after filtration and rinsing. The dry powder was sintered at 600 °C for 1h. Subsequently, Ce\textsubscript{0.8}Gd\textsubscript{0.2}O\textsubscript{2} powder was mixed with 12wt%NiAl powder according to the reported method [9].

The structure of LiNiO\textsubscript{2}-type SSBs(battery No.1) was as follows:

(-) Zn (anode)/ SSE / LiNiO\textsubscript{2} (cathode) (+)

The current and voltage variations of different batteries were recorded under various conditions of temperature, time and humidity.

For another SSBs that use fcc-TiB as cathode, NaCO\textsubscript{3} saturated cloth was used as electrolyte while Mg metal was employed as anodes. The structure of this fcc-TiB type SSBs (battery No.2) was as follows:

Mg (anode )//cloth soaked with NaCO\textsubscript{3} solution// fcc-TiB (cathode )

3. Manufacture of Solid State Batteries

The tubular sample is basic components for making SSB. The powder metallurgy route is employed to make the tubular sample. For making the tubular sample, a special die was designed (Fig.1.).

![Fig. 1. Scheme of die for compacting tubular sample.](image-url)
It consists of punch, core rod and powder holder. The process of tubular sample consists of 3 steps: die fill, compaction and ejection, i.e. filling two kinds of powders into powder holder with the help of thin cylinder-shape separator (Fig. 2.)

![Fig. 2. Feeding of two kinds of powders.](image1)

and taking the thin cylinder-shape separator out from the powder holder, compression using the punch (Fig. 3.)

![Fig. 3. Compression of powders.](image2)

and ejection from the die (Fig. 4.).
All the steps were manually operated. For making battery No.1, the electrolyte (SSE) and cathode (LiNiO$_2$) powders are separately filled into the powder holder of the die as shown in Fig. 2. For making battery No.2, only fcc-TiB powders was used.

For making a complete battery No.1, metal powders are coated on the surface of the tubular samples as anode layer. For making battery No.2, the salt soaked cloth and metal net made from metal wire are taken as electrolyte and anode, respectively. Fig. 5. presents the size that is 10mm in diameter and cross section for a typical SSB made with LiNiO$_2$, solid electrolyte and Zn powder. LiNiO$_2$ layer black colour is in the outside; solid electrolyte layer (white color) is in the middle and the coated Zn layer black colour is in the inside.

Cu wires were used to connect the electrodes and the meter to measure the output power.
4. Electrical properties of Solid State Batteries

4.1. Battery No.1

4.1.1. Variation of output power with temperature

The influence of temperature on the output power of SSBs is shown in Fig. 6., it appears that both voltage and current increase with the temperature. The measurements reported in this figure were carried out under environment of relative humidity of 60%.

![Fig. 6. Variation of current and voltage with temperature.](image)

4.1.2. Variation of output powers with humidity

Fig. 7. shows that the output power of SSBs increases with the relative humidity. The measurements were carried out at a temperature of 25 °C.

![Fig. 7. Variation of current and voltage with relative humidity.](image)
4.2. Battery No.2

The SSBs made with fcc-TiB generated a voltage of 1.74 V and current 3.2 mA, with its larger power than do the SSBs fabricated with LiNiO$_2$; the every value is the average value of three measurements that were carried out at room temperature under environment of relative humidity of 60%.

5. Conclusion

The SSBs were successfully fabricated using powder metallurgy route. The designed die was applicable for making basic components for SSBs. The fabricated SSBs have shown their conductive properties. The values of output power of SSBs made with fcc-TiB have demonstrated that fcc-TiB can be used as electrode materials.

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6. References

Садржај: Батерије у чврстом стану (БЧС) припремљене су металурским обрадом праха. Посебне посуде су дизајниране за потребе прављења БЧС. LiNiO₂ и кубично центрирани прах TiB [1] су употребљени за катоду БЧС, док су метали као Zn или Mg употребљени за аноде. БЧС са прахом LiNiO₂ генеришу релативно ниске струје (1 до 2 μA) и волтажу (0,4–0,9 V) на собној температури. БЧС направљене са TiB катодом генеришу више снаге од БЧС са прахом LiNiO₂.

Кључне речи: батерије у чврстом стану; прах LiNiO₂; прах TiB; металурска обрада праха.