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Thin cathode for thermal batteries using a tape-casting process

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ABSTRACT

Thin cathodes for thermal batteries with good homogeneity and a reproducible thickness were prepared using a tape-casting process. A single cell fabricated with a 100 μm thick cathode using tape-casting process exhibited a specific capacity of 1934.08 A s/g. In contrast, a single cell fabricated with a pellet type 500 μm thick cathode demonstrated a specific capacity of 1000.25 A s/g. The thin cathode, which exhibited excellent utilization of the electrode material due to the optimal thickness from an electrochemical point of view, showed good mechanical strength and excellent electrochemical properties making it suitable for use in thermal batteries.

1. Introduction

Thermal batteries are primary batteries that use molten salts as an electrolyte and employ an internal pyrotechnic source to bring the battery stack to the operating temperature. Thermal batteries are used primarily for military applications, such as missiles and ordnance, and in nuclear weapons because of their excellent mechanical robustness, reliability, and long shelf life [1–5]. Fig. 1 presents the basic structure of a single cell of a thermal battery. As a representative thermal battery electrode, Li-Si is used as an anode and FeS_2 (pyrite) is used as a cathode; LiCl-KCl is used mainly as an electrolyte [6]. To realize such material properties, the molding and manufacturing process of each material is very important, and sufficient mechanical strength and durability are essential for military applications [7].

Generally, the constituent materials are produced in the form of pellet with a thickness of several hundreds of micrometers using a pressing process. However, the formed pellets are thicker than the optimum thickness in terms of utilization of the electrode material, since they must maintain a minimum mechanical strength. For these reasons, an electrolyte material is added to the electrode to compensate for the lower utilization of the electrode material but this approach makes the electrode becomes thicker and reduces the ratio of the active material in the electrode. When the thickness of the electrode pellet is greater than a certain level, the utilization of the electrode is lowered significantly, which may cause a decrease in the energy density of the thermal battery. To solve such a problem, it is essential to choose a process for thinning the electrode, which can ensure sufficient mechanical strength with optimal electrochemical performance of the electrode. Therefore, this study examined the thinning of the cathode of a thermal battery using the tape-casting process.

Tape-casting is a method of continuously producing thin sheets composed of ceramic powder and organic matter, and it is possible to manufacture a thin sheet with a thickness of 0.01–1.2 mm as well as possible to control the density, surface condition, and flexibility of the synthesized sheet at the same time [8,9]. The organic additive and solvent present during sheet production are partially evaporated during the drying process and are completely evaporated during the burnout process, resulting in a dense sintered body with a higher filling density than that obtained from the powdery molding method. In addition, it is possible to make sheet with uniform thickness by using doctor blade method, which is the most commonly used method for coating slurry in the tape-casting process. Tape casting is one of the methods for reproducing the proper thickness by deriving the viscosity of the slurry suitable for the electrode production of a thermal battery. In the present study, a thin cathode for thermal batteries with excellent mechanical strength was manufactured using a tape-casting process. In addition, the discharge characteristics of the thin cathode and pellet type cathode were compared in terms of the utilization ratio of the electrode in the cathode.

2. Experiments

All the sample preparations were conducted at room temperature in a dry room with a humidity less than 20%. The following materials were used to make a slurry for the tape-casting process. FeS_2 powders (mean size of 98 μm, 99%, LinYi, China) were used as an active

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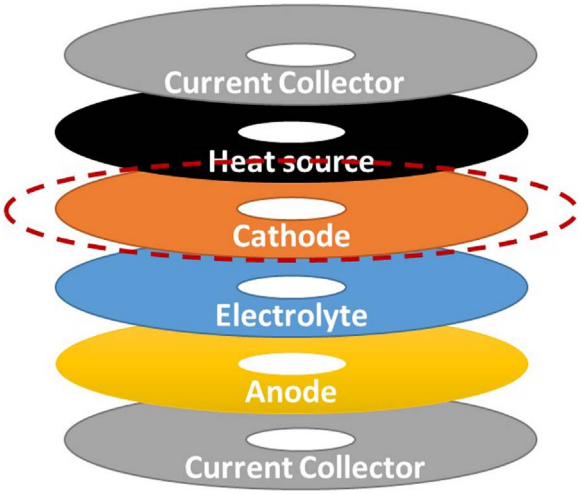

Fig. 1. Structure of a single cell for the thermal battery.

material; acetone (≥99.9%, Sigma-Aldrich) and benzene (≥99.9%, Sigma-Aldrich) were used as the solvents. BYK-110 (Altana) dispersant was used to improve the dispersion of FeS_2 powders in the solvent, and silicic acid (Sigma-Aldrich, −80 mesh) and polysiloxane (OFX-8040, XIAMETER) were used as binders to form the binding force between the FeS_2 powders. A wet ball mill process was performed to mix the slurry materials and control the particle size of the FeS_2 powders. To maximize the dispersion of the FeS_2 powder, the ball milling process was carried out two times (24 h each) before and after adding the binder. The balls used in the ball milling process were zirconia with diameters of 10 mm and 5 mm at a 1:1 ratio. The slurry was prepared from a dispersant containing 0.1 wt% of the active material and a binder containing 10 wt% of the active material. Silicic acid and polysiloxane were used as the binder materials that were mixed at a 1:5 ratio. After the ball milling process, the bubbles contained in the slurry were removed in a vacuum chamber. The prepared slurry was uniformly coated using the doctor blade method with a constant thickness. The substrate was a 50 μm thick SUS plate used as a current collector. After the application of the slurry, the samples were dried at 70 °C for 1 h to vaporize the solvent. The dried samples were cut into circular-shaped pieces with a diameter of 56.2 mm to assemble as a cathode in the single cell of a thermal battery. Fig. 2 presents manufacturing process for the thin cathode and a schematic diagram of the tape-casting process.

A pellet type cathode with the same diameter was fabricated for comparison with the thin cathode. Pellet type cathode was fabricated using powder compaction process. The contents of the substances

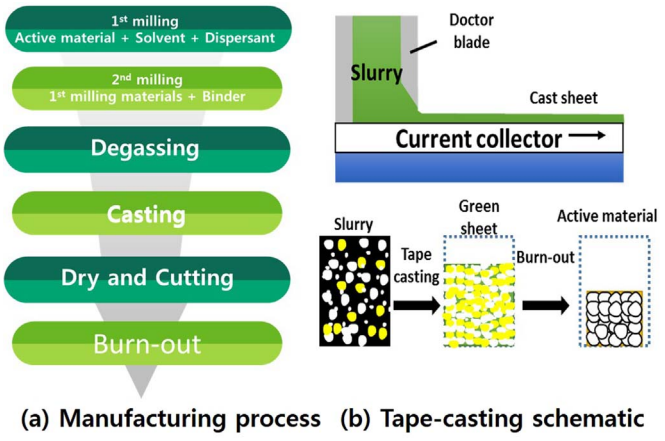

Fig. 2. (a) Manufacturing process and (b) Schematic of tape-casting for thin cathode.

Table 1
The contents of the substances contained in the thin cathode and the pellet type cathode.

Thin cathode		Pellet type cathode	
FeS_2 (Active material)	90 wt%	FeS_2 (Active material)	75 wt%
Silicic acid (Binder)	1.67 wt%	MgO (Binder)	8.75 wt%
Polysiloxane (Binder)	8.33 wt%	LiCl-KCl (Electrolyte)	16.25 wt%

contained in the thin cathode and the pellet type cathode are shown in Table 1.

The single cells were discharged at 500 °C while applying a consecutive pulse current profile (10 A, 4.5 s→0 A, 0.5 s). The cell discharge was terminated when the voltage dropped below 1.3 V.

FESEM (Field Emission Scanning Electron Microscopy; Hitachi S-4200) was used to examine the morphology of the slurry constituents. TGA – DTA (Thermo Gravimetric Analysis – Differential Thermal Analysis; TA Instruments, SDT Q600) was used to investigate the thermal stability of the slurry constituents. XRD (X-Ray Diffraction; Rigaku RINST) was performed to analyze the structural changes to FeS_2 before and after the ball milling process.

3. Results and discussion

The performance of the battery varies according to the particle size of the active material FeS_2 as the cathode material manufactured by tape casting method. The thermal stability is decreased when the particle size of FeS_2 is reduced to a certain size or less, and the decomposition rate at 500 °C, which is the operating temperature of the thermal battery, increases, causing a decrease in discharge capacity. On the other hand, if the particle size of FeS_2 is too large and non-uniform, the pores in the electrode increase, resulting in an increase in internal resistance. Therefore, a ball milling process was applied to control the particle size of FeS_2, and the evaluation was carried out to determine the appropriate ball milling time. Fig. 3 presents SEM images of the FeS_2 powder according to the ball milling time. Fig. 3(a) shows the particle size and shape of the pristine FeS_2 powder; the particle size was more than 60 μm and showed a non-uniform distribution. Fig. 3(b) and Fig. 3(c) shows the particle size and shape of the FeS_2 powder ball milled for 24 and 48 h, respectively. As the ball milling time increases, the particle size of the FeS_2 powder decreased and became uniform.

In general, when the particle size of the electrode material was reduced, the electrical contact between the electrode active materials was improved, the resistance was decreased, and the utilization ratio of the electrode was increased, resulting in an increase in capacity [10,11]. On the other hand, the thermal battery is a special cell that operates at high temperatures, (e.g., 500 °C). The active material of the electrode must have excellent thermal stability up to 500 °C. For this reason, TGA-DTA was conducted to investigate the thermal stability of the FeS_2 powder prepared by using the above-mentioned conditions (Fig. 4). The pristine FeS_2 powder in Fig. 4(a) showed excellent thermal stability with a mass reduction rate of approximately 2% up to 500 °C. The 24 h ball-milled FeS_2 powder showed a mass reduction rate of approximately 5% at 500 °C (Fig. 4(b)) and the 48 h ball-milled FeS_2 powder had a mass reduction rate of approximately 12% at 500 °C (Fig. 4(c)). In the SEM image of Fig. 3, the ball milling time between 24 and 48 h appears appropriate in terms of the uniformity of the FeS_2 powder. Considering the thermal stability, however, 24 h ball milling time was considered the optimum.

After ball milling for 24 h in the solvent, XRD was performed to determine if there were any changes in the crystal structure due to chemical or physical damage, as shown in Fig. 5. A comparison of the XRD peaks of the pristine FeS_2 powder (Fig. 5(a)) with those of the