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Thermal batteries with ceramic felt separators – Part 1: Wetting, loading behavior and chemical stability

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ABSTRACT

The use of a thermally and chemically stable ceramic felt separator for thermal batteries is believed to enhance the reliability by minimizing the sudden failure of an electrolyte upon shock compared to the conventional pellet-pressed one. To achieve desirable electrochemical properties for applications in thermal batteries, the separator should hold a sufficient amount of molten electrolyte with a minimal **leakage** to prevent physical contact between the cathode and anode. In addition, the chemical stability of the separator materials should be maintained under a very reactive molten Li-salt electrolyte environment to confer high ionic conductivity and reliability. To assess the feasibility of 3 types of ceramic felt as a separator for thermal batteries, 2 types of Al_2O_3 felt with different porosity and one ZrO_2 felt are examined using binary LiCl-KCl and ternary LiF-LiCl-LiBr as the electrolytes. This Part 1 explains the wetting, loading and leakage behaviors of the ceramic felts for molten electrolytes along with the chemical stability. The ionic conductivity of the electrolytes and electrochemical properties of the resulting thermal batteries will be presented in Part 2.

1. Introduction

The thermal battery is an important primary battery that has been used widely as a power source for missiles, torpedoes, guided bombs, and radar since the Second World War [1]. Because of the nature of military weapons, the thermal battery should offer a high level of reliability, including long storage life of more than 10 years, without a significant decrease in capacity. The most commonly used electrochemical system in thermal batteries is Li(Si) (or Li(Al))/FeS_2 (or CoS_2), where a Li-based solid electrolyte is located between them [2,3]. After stacking the periodic layers of the unit cell to realize a desired output voltage along with a Fe/$KClO_4$ heat pellet at the end of the stack to activate the battery pyrotechnically, the thermal battery is hermetically sealed [2]. Although the electrolyte is inactive under normal conditions, the battery is activated instantly into an excellent Li-ionic conductor by melting the electrolyte upon the ignition of a heat pellet. Guidotti et al. provided a systematic explanation of both electrode materials and electrolytes for thermal batteries [2–7].

The components for thermal batteries, such as the cathode, anode and electrolytes, have been synthesized by simple pellet pressing using a ceramic powder, which are inherently fragile during handling, particularly with a thin (<0.5 mm thick) and large (diameter >5 cm) dimension prepared to enhance the electrochemical properties. With this pellet-pressed structure, moreover, the electrolyte needs to contain approximately 30 vol% MgO binder to prevent an electric short circuit between the two electrodes, which is generally caused by serious leakage of the molten electrolyte or sudden failure upon an external shock [8]. To prevent the fracturing of electrolyte that causes the short circuit, as an alternative, the use of separators with porous membranes instead of ceramic pellets has been suggested [9–16]. A systematic approach to the use ceramic membranes, such as fiberglass, borosilicate, quartz and zirconia tape, has been made by Guidotti and Reinhardt [9], where they obtained approximately 85% of active lives with the cells containing ceramic membranes compared to that with the pellet-pressed electrolyte.

Additional advantages of using ceramic felts loaded with electrolyte with an increased mechanical strength originate from the reduced thickness of the resulting separator, compared to the pressed-pellet structure. A thinner separator results in lower impedance for the battery, all other factors being equal. In addition, the lower electrolyte mass involved requires a lighter heat pellet, which results in a higher power density. Moreover, the chances for thermal runaways by electric short would be dramatically reduced compared to the conventional separator, which will make the battery intrinsically safer. To realize these advantages, the porous separator should hold a sufficient amount

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Table 1
Physical properties of 2 types of electrolytes [17].

Electrolytes	Composition (Mole %)	Melting point (°C)	Density (liquid) (g cm^{-3})	Density (solid) (g cm^{-3})	Surface tension (dyne cm^{-1})
LiCl-KCl	58.8–41.2	354	1.59	2.01	123
LiF-LiCl-LiBr	21–31–47	443	2.17	2.91	70

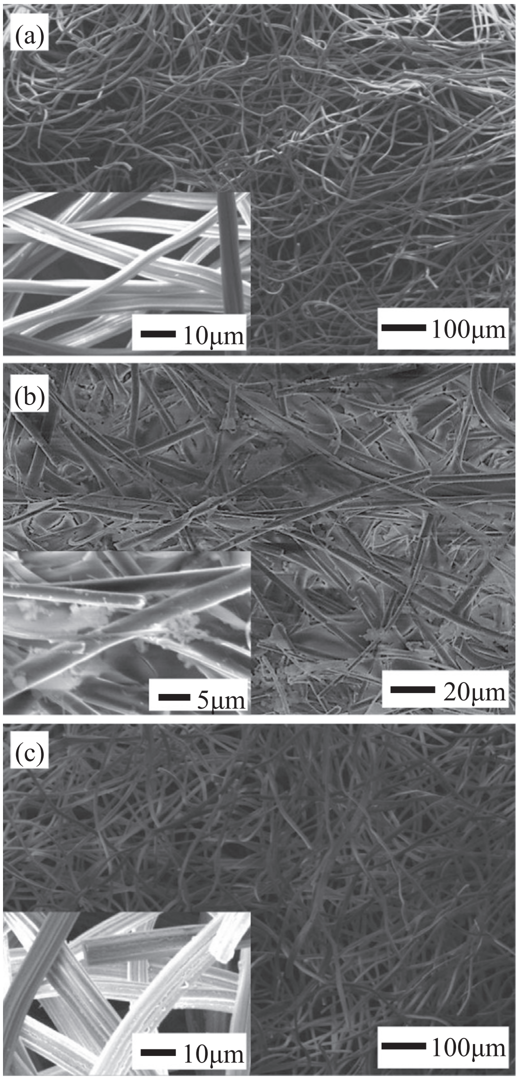

Fig. 1. SEM images of the ceramic felts used as a separator: (a) ALF-50, (b) APA-03, and (c) ZYF-50. The images at high magnification are shown in the inset.

of molten electrolyte to achieve high ionic conductivity, while still separating the cathode and anode to prevent a short circuit. In addition, the separator should be sufficiently stable thermally and chemically to resist the highly corrosive molten salt environment and maintain adequate mechanical strength for handling.

With this background, this study assesses the feasibility of 3 types of ceramic felt, i.e., 2 types of Al_2O_3 with different porosity and one ZrO_2 felt, as a separator for thermal battery. The use of ceramic felt as a separator is believed to enhance both mechanical and electrochemical properties of thermal batteries because of the high toughness of felt and increased electrolyte content by eliminating the MgO binder, respectively. Part 1 reports the wetting, infiltration, loading and leakage behaviors of these ceramic felts for the LiCl-KCl and LiF-LiCl-LiBr electrolytes along with the chemical stability at a corrosive molten electrolyte environment. The ionic conductivity of the electrolytes and the electrochemical properties of thermal batteries containing ceramic felt separators will be explained in Part 2 by a comparison with conventional pellet-pressed structures.

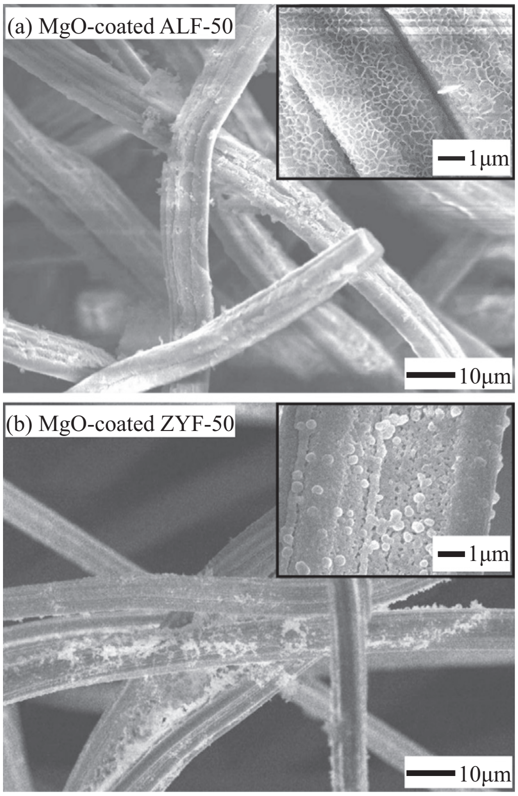

Fig. 2. SEM images of the MgO-coated (a) ALF-50 and (b) ZYF-50 ceramic felts. The images at high magnification are shown in the inset.

2. Experimental procedure

2.1. Starting materials and sample preparation

Three types of commercially available ceramic felt are used as a separator: high porosity Al_2O_3 (ALF-50, 97% porosity, >99 wt% pure), low porosity Al_2O_3 (APA-03, 79% porosity, 96 wt% pure containing 4 wt% SiO_2) and high porosity yttria-stabilized fused ZrO_2 (ZYF-50, 96% porosity, >99 wt% pure). The thickness of the ALF-50 and ZYF-50 felts is 1.27 mm, whereas that of APA-03 was 0.3 mm, according to the vendor. All felts are purchased from ZIRCAR Ceramics, NY, USA. The LiCl-KCl and LiF-LiCl-LiBr eutectic salts are used as a low and high temperature electrolyte, respectively. Table 1 lists the physical properties of both electrolytes.

To check the wetting behavior of the molten electrolytes on the separator materials, **20 mm** diameter pellets are prepared by hand pressing using Al_2O_3 (>99% pure, Baikowski, France), fused ZrO_2 (>99% pure, Zircomet, UK) and MgO (>99% pure, Scora, France) followed by sintering at 1550, 1450 and 1400 °C, respectively, for 2 h in air. The resulting density of the pellets is greater than 97%. The MgO sample is prepared as a reference sample because it has been used as a binder material for electrolytes in conventional thermal batteries [8].

In addition, the MgO coating on the ALF-50 and ZYF-50 felts is achieved by dipping into a stirred 2.5 wt% Mg-nitrate aqueous solution for 20 min. After drying at 80 °C, the impregnated felts are heat-treated at 400 °C for 1 h to convert the Mg-nitrate to MgO. This process is repeated 3 times to compare the electrolyte infiltration behavior into the felt with/without the MgO coating.