

Surface modified ceramic fiber separators for thermal batteries

Hae-Won Cheong*, Sang-Hyeon Ha and Yu-Song Choi

Agency for Defense Development, Yuseong P.O. Box 35-41, Daejeon 305-600, Korea

A wide range of possible hazards existing in thermal batteries are mainly caused by thermal runaway, which results in overheating or explosion in extreme case. Battery separators ensure the separation between two electrodes and the retention of ion-conductive electrolytes. Thermal runaways in thermal batteries can be significantly reduced by the adoption of these separators. The high operating temperature and the violent reactivity in thermal batteries, however, have limited the introduction of conventional separators. As a substitute for separators, MgO powders have been mostly used as a binder to hold molten salt electrolyte. During recent decades the fabrication technology of ceramic fiber, which has excellent mechanical strength and chemical stability, has undergone significant improvement. In this study we adopted wet-laid nonwoven paper making method instead of the electrospinning method which is costly and troublesome to produce in volume. Polymeric precursor can readily be coated on the surface of wet-laid ceramic paper, and be formed into ceramic film after heat treatment. The mechanical strength and the thermo-chemical stability as well as the wetting behaviors of ceramic separators with various molten salts were investigated to be applicable to thermal batteries. Due to their excellent chemical, mechanical, and electrical properties, wet-laid nonwoven separators made from ceramic fibers have revealed positive possibility as new separators for thermal batteries which operate at high temperature with no conspicuous sign of a short circuit and corrosion.

Keywords: Thermal batteries, Ceramic fiber separator, Molten salt electrolyte.

Introduction

Thermal batteries are very attractive power sources for missiles, torpedoes and other military systems that need separate and instant electric power [1]. They offer long storage life, more than 15 years without any notable loss in capacity, which exceeds that of other maintenance-free reserve battery systems and therefore makes them suitable for many military, space and emergency power applications [2, 3].

In this study, Li/FeS₂ electrochemical system has been adopted for its high current capability [4]. Thermal batteries have solid electrolyte which is inactive at room temperature. As soon as the heat pellets are fired by an igniter, all the insulating solid electrolytes are melted into excellent ionic conductors, and the thermal battery is instantly activated and produces electric power. An anode and a cathode are separated by an electrolyte layer, in which molten salt is held in place by an inorganic binder [5].

The defects in electrolytes, such as broken edges, cracks, low-density parts, compositional fluctuation or unintentionally added impurities, can give rise to bridging the electrodes and cause the catastrophic failures. To relieve these problems, about 40 wt% MgO binder in powder form is generally added to hold the molten

electrolyte [4, 6]. At high operating temperature around 500 °C under a closing force, however, the leakage of molten electrolyte is inevitable to some degree [6, 7]. The excessive leakage can cause serious problems such as a short between electrodes and a shortage of ion-conductive electrolyte, posing reliability troubles as well as deterioration of performance. There is a strong possibility of these failures when a thermal battery is exposed to high temperature, excessive closing force, acceleration force, vibration, shock or combination of all these conditions, which are familiar environments to most thermal batteries. Although these failures in thermal batteries may be rare in real applications, they can end in fatal consequences.

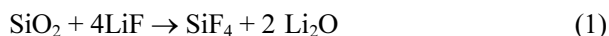
In order to prevent the short-circuit problems generated by the direct contact of electrodes, battery separators are widely used [5]. Battery separators are porous membranes placed between electrodes, permeable to ionic flow while preventing electric contact. They separate the electrodes physically and electrically and hold sufficient amount of ionic conductive electrolyte during the discharge, providing excellent ion conductivity with enhanced handling strength. The absence of these separators under abusing conditions could outbreak various failures, sometimes fires or even explosions of thermal batteries.

The highly corrosive molten salt together with high operating temperature, however, has limited the introduction of conventional separators. Most common separators are made of chemically and electrochemically inert polymeric materials. However, polymeric separators cannot be used

*Corresponding author:
Tel : +82-42-821-3688
Fax : +82-42-823-3400
E-mail : imchw@add.re.kr

for thermal batteries because of their instability at high operating temperature.

When a silica-based glass fiber separator is used with LiF-containing molten salt, gaseous SiF₄ is formed during the discharge, resulting in the total destruction of glass network structure [7, 8].



Glass fiber separators were thoroughly attacked by the reaction that they easily crumbled by a light pinch. When LiCl-KCl eutectic salt is impregnated into a glass fiber separator, surface toughening phenomenon by the ion exchange of K⁺ into Na⁺ site at the sodium-added glass surface was observed [7].

Recently, there is some reviews on the possible adoption of ceramic fiber separators [9]. Ceramic fibers made of Al₂O₃, ZrO₂, SiOC, or MgO can be used as alternatives for glass fibers. Ceramic separators can also prevent short circuits caused by the dendrites, metal spines of current collector or any other protrusions [7].

The availability of mass producible battery separator is also an important factor to be put into the practical application. In the previous study, two nonwoven fabrication methods of ceramic fiber separators were proposed and evaluated for a potential alternative to the conventional MgO powder binders for molten salt electrolyte [7]. One is based on the electrospinning, and the other wet-laid paper making method. The electrospun separators with fine fiber diameter turned out to be effective for holding molten salt electrolyte. However, the low yield rate of electrospinning method has to bear high manufacturing costs. Therefore, we chose commercially available Al₂O₃ fibers fabricated into paper by the wet-laid nonwoven method as an accessible production process on a large scale with relatively inexpensive costs even compared with conventional MgO-based electrolyte.

In this study two kinds of polymeric precursors, polycarbosilane (PCS) and magnesium acetate (Mg-acetate), were adopted, which can be readily coated as films on the surface of Al₂O₃ fibers, and be formed into ceramics by the subsequent heat treatment [10, 11].

Experimental

Wet-laid paper-making process

Commercial alumina fibers (97 % Al₂O₃) with various additives and water were wet-laid to ceramic paper. The binders for the ceramic paper used were polycarbosilane (Nippon Carbon Co.) and magnesium acetate (Samchun chemical Co.). First, the ceramic fibers were chopped into 3 mm lengths and mixed with cellulose pulp to improve the mechanical properties. The resulting mixture was stirred with an agitator for the effective dispersion and was properly cohered by adding organic additives, such as flocculants and dispersing agents. After the slurry was wet-laid into

nonwoven paper form, the papers were dried at 130 °C under applied force.

Alumina papers were coated with polymeric precursors by dipping them into PCS or Mg-acetate solution. After drying at around 250 °C to remove the solvent and organics, PCS and Mg-acetate precursors were heat treated into SiOC and MgO on the surface of Al₂O₃ fibers [10, 11].

Material characterizations

Microstructural analysis was carried out using SEM and EDS. Porosity and pore size distribution of separators were measured using mercury intrusion porosimetry. To evaluate the ceramic fiber separators for potential alternatives to the conventional MgO binders for molten salt electrolyte, LiF-LiCl-LiBr eutectic salt was impregnated into the porous ceramic separators in a vacuum furnace at 500 °C for 20 min. Li(Si)/FeS₂ single cells with ceramic separators and current collectors were fabricated to test the discharge characteristics.

Characterization of discharge performance

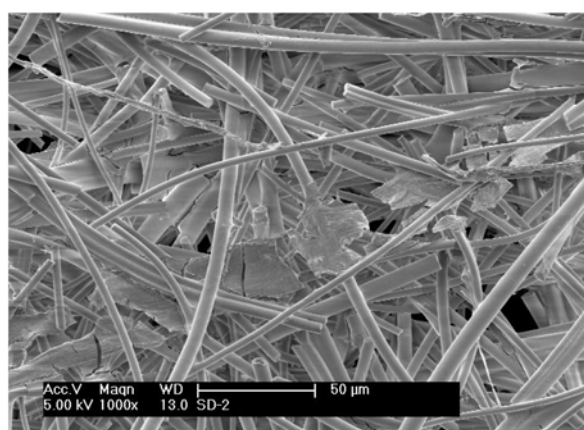
Li/FeS₂, Li(Si) for anode and FeS₂ for cathode, is adopted in this system for its high stability and current capability [4]. As for the electrolyte, LiF-LiCl-LiBr eutectic salt is used to meet the high current requirements. Separators made of ceramic fibers were adopted for they have no blind or closed pores but through pores, which allow excellent passages for ion conduction. The separators were cut into 56 mm diameter discs. All the separators impregnated with salt electrolyte and Li(Si)/FeS₂ electrodes were prepared in dry air condition. A single cell to be discharge-tested consists of a current collector, anode, electrolyte, cathode, and another current collector in series. The detailed fabrication procedure for Li(Si)/FeS₂ single cells was described in the previous paper [4, 7]. The uniaxially applied force on a cell was 250 kgf and the temperatures of the heating platens were maintained at 500 °C.

Results and Discussion

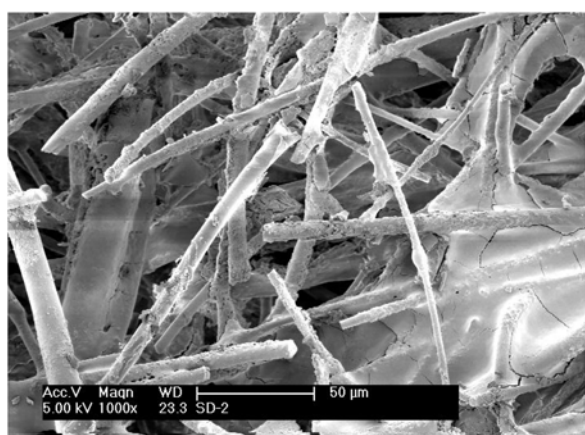
Microstructure characteristics

The microstructures of wet-laid alumina fiber separators after heat treatment are shown in Fig. 1. With the addition of PCS, the vacant spaces among Al₂O₃ fibers are partially filled with relatively dense SiOC flakes as shown in Fig. 1(a). With the addition of Mg-acetate, however, the surface morphology of Al₂O₃ fibers becomes more porous, as shown in Fig. 1(b) and (c), which could offer better microstructure to hold molten salt effectively. Ceramic separators exhibited excellent corrosion resistance against LiF-containing molten salt, while glass separators showed poor chemical stability [10, 11].

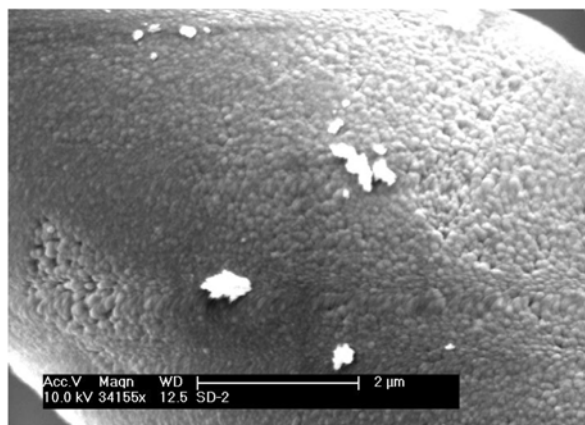
To check the holding capability of fiber separators impregnated with electrolyte, leakage tests were carried out as a function of pore size of separators at 500 °C



(a)



(b)



(c)

Fig. 1. SEM images of wet-laid alumina fiber separators with the addition of (a) polycarbosilane (PCS), (b) and (c) Mg-acetate with different magnification.

for 30 min in a furnace. The separators used in the tests were glass microfiber filters of GF/A, GF/C and GF/F (Whatman Ltd.) and the eutectic salts were LiCl-KCl and LiF-LiCl-LiBr. As shown in Fig. 2, the release rates of molten salt for glass separators decreased as the pore size decreased. The rates in Fig. 2 are expressed in the ratio of the weight of salt to that of ceramic fiber.

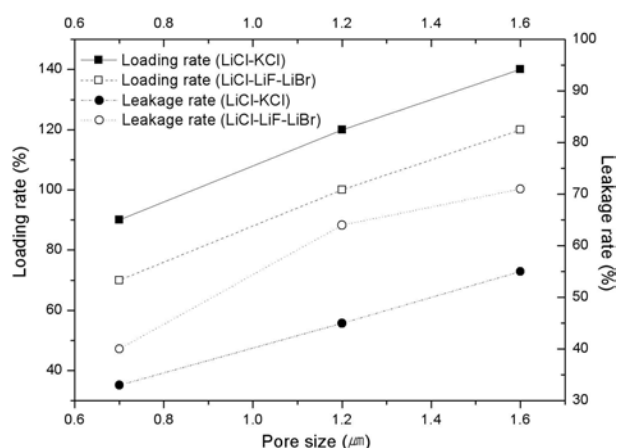


Fig. 2. Loading and releasing rates of electrolyte as a function of pore size.

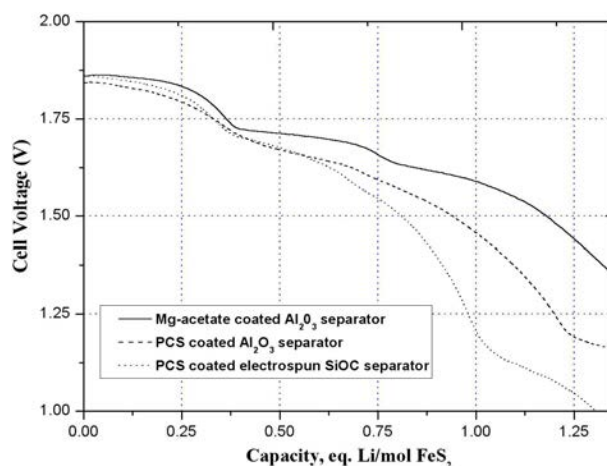


Fig. 3. Discharge characteristics of single cells with wet-laid nonwoven ceramic fiber separators and an electrospun SiOC-based separator.

The lowered loading rate and increased release rate of LiF-LiCl-LiBr salt can be attributed to its high reactivity with glass fibers [11].

The glass separators impregnated with molten salt in vacuum showed enhanced holding capability compared to that impregnated in normal atmospheric pressure with the reduced leakage rate from 33% to 25% for LiCl-KCl electrolyte. These results showed that smaller pores and vacuum atmosphere endow higher capillary force, resulting in deep infiltration of electrolyte into the separator. The loading rate of electrolyte increased as the pore size increased.

Discharge characteristics

The resistance of electrolyte, which occupies a large portion of the total voltage drop of a cell or a battery, increases as the molten salt content in electrolyte decreases. The pore volume of ceramic separators (~85 % for Mg-acetate coated Al₂O₃ fiber separators) is higher than the electrolyte volume of conventional MgO binder (~54 %), which suggests that ceramic

separators could provide superior ion conductivity. The discharge characteristics of single cells with different ceramic separators are shown in Fig. 3. The wet-laid alumina separators coated with Mg-acetate and PCS showed better effective capacities than that of electrospun SiOC separators. Mg-acetate coated Al_2O_3 separators showed the best discharge characteristics. This can be explained by its large surface area as shown in Fig. 1 (b) and (c).

When commercially available ceramic fibers surface-coated with inert ceramics are adopted for battery separators, the cost for the ceramic separators can be greatly reduced. With the adoption of the conveyor-type paper making machine for the wet-laid nonwoven method, productivity for the ceramic separators will be further improved. The mechanical strength and the thermo-chemical stability as well as the wetting behaviors of ceramic fiber separators with various molten salts were found to be applicable to thermal batteries.

Conclusions

The present study showed that the wet-laid nonwoven fabrication method of ceramic fiber separators can be a potential alternative to the conventional MgO powder binders for molten salt electrolyte. Compared with the electrospinning paper making method, the wet-laid method is cost-effective and exhibits relatively good discharge performances. The porosity and pore size can be further controlled by the precursor coating as filler. Due to their excellence in chemical, mechanical and electrical properties, ceramic-based fabric separators are considered to be one of the most promising candidates

as novel separators for thermal batteries which can endure at high temperature with no conspicuous sign of short circuit.

Acknowledgements

The technical supports of Yong-Sik Chung at Chonbuk National University, Kwang-Youn Cho at Korea Institute of Ceramic Engineering and Technology and Young-Ok Ko and Sang-Jin Lee and many others at Vitzrocell Co., Ltd. are appreciated.

References

1. R. Guidotti, P. Masset, *Journal of Power Sources* 161 (2006) 1443-49.
2. H.P. Kim et al., *Key Eng. Materials* 227-279 [2] (2005) 625-30.
3. D. Linden, in "Handbook of Batteries, Second edition" McGraw-Hill, Inc. (1994) 22.1-22.20.
4. J. Choi et al., *Proceedings of 43rd Power Sources Conference* (2008) 169-72.
5. P. Arora, Z. Zhang, *Chem. Rev.* 104 (2004) 4419-62.
6. P. Masset, R. Guidotti, *Journal of Power Sources* 164 (2007) 397-414.
7. H. Cheong et al., *Proceedings of 44rd Power Sources Conference* (2010) 261-64.
8. F. Reinhardt, R. Guidotti, (SAND2006-2244, Sandia National Laboratories (2006).
9. T. Kaun et al., *Proceedings of 43rd Power Sources Conference* (2008) 365-68.
10. K. Lim et al., *Journal of the Korean Ceramic Society* 46 (2009) 648-52.
11. K. Cho et al., *Journal of the Korean Ceramic Society* 45 (2008) 423-29.