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Modified coin cells to evaluate the electrochemical properties of solid-state fluoride-ion batteries at 150 °C

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ABSTRACT

In the scope of developing new chemistries for electrochemical energy systems, rechargeable solid-state fluoride-ion batteries are attractive devices owing to their high theoretical energy density. State of the art of fluoride ion conductors require the use of high temperature electrochemical cells to overcome the low ionic conductivity of the electrolyte at room temperature. In this work, we modify a coin cell to evaluate the electrochemical properties of fluoride-ion batteries at elevated temperature, over long periods of time and outside a glovebox. The coin cell is covered by a high-temperature epoxy resin that enables efficient sealing and therefore protection against air atmosphere at 150 °C. The suitability of the setup is confirmed by electrochemical investigation performed on a symmetrical cell assembled with composite electrodes made of Bi and BiF_3. Notably, a reversible capacity of around 190 mAh/g after 3 cycles is reached with the modified coin cell setup.

1. Introduction

Owing to the high electronegativity of fluorine, the electrochemical reaction of a metal M with fluoride ions F^- to form a metal fluoride MF_x can lead to a large change in Gibbs free energy, inducing high theoretical electromotive forces (emf) in electrochemical cells. Although the study of systems relying on fluoride shuttle started in the mid 70's [1–5], Anji Reddy and Fichtner were recently the first to validate the concept and the feasibility of a rechargeable Fluoride-Ion Battery (FIB) [6]. Upon discharge, the MF_x cathode is reduced down to its metallic state M, while the metal anode M' is simultaneously oxidized to give $M'F_x$, according to the following reactions:

$$\text{At the cathode}: \quad MF_x + xe^- \rightarrow M + xF^- \tag{1}$$

$$\text{At the anode}: \quad M' + xF^- \rightarrow M'F_x + xe^- \tag{2}$$

$$\text{Overall}: \quad M' + MF_x \rightarrow M'F_x + M \tag{3}$$

These reactions, which may be classified as conversion reactions, are multi-electronic processes. Associated with large emf, some combinations of fluorides could deliver theoretical energy densities as high as 5000 Wh L^{-1} [7], values much larger than those obtained with conventional lithium-ion batteries.

However, considering the relatively poor conductivity of solid fluoride electrolytes [8–13], it is required to evaluate solid-state FIBs at higher temperatures, typically 150 °C. Indeed, performing electrochemical testing at 150 °C decreases the cell internal resistance and enables the use of higher current densities (10 $\mu A/cm^2$ [7,14]). These current densities are in the order of magnitude of those typically employed in solid state lithium batteries operating at room temperature ($\geq$64 $\mu A/cm^2$ [15–20]).

Typical battery testing systems rely on coin cells or Swagelok type cells. Coin cells generally use polyethylene (PE) or polypropylene (PP) sealing O-rings that soften and age quickly at high temperatures, leading to the loss of sealing properties of the cell, and therefore, to the oxidation of the battery materials. Similar observations can be made with Swagelok type cells. The sealing of Swagelok type cells is generally ensured by polytetrafluoroethylene (PTFE) rings. While PTFE presents a higher fusion temperature than PE or PP, it is also subject to softening and to significant creeping at elevated temperature, due to its glass transition temperature of 115 °C. The creeping of PTFE eventually leads to a loss of the sealing properties of the Swagelok type cell. Early experiments carried out with a conventional Swagelok type cell placed in an oven at 150 °C confirmed that the sealing

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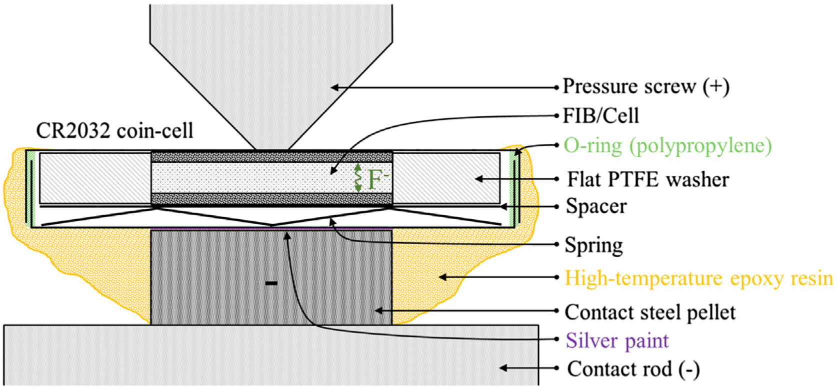

Fig. 1. Schematic representation of the cross-section of the modified coin-cell placed on the test bench.

properties were lost after a few days. Moreover, the PTFE sealing rings were permanently damaged as they were significantly deformed. Other commercial systems are available, but they all rely on polymeric seals which are not adapted for high temperature operation. The development of a high-temperature (300 °C) Swagelok type cell has already been reported elsewhere [21], but its development requires significant modifications and machining work.

Here, we report a simple and rapid method to prepare modified coin cells particularly adapted to the study of FIBs at 150 °C, over long periods of time.

2. Results and discussion

2.1. Cell modification

CR2032 coin cells (MTI Corp) were chosen as the starting setup. In order to obtain a coin cell featuring high temperature resistance, the cell was covered with an epoxy resin (Loctite EA 9492) selected for its room temperature curing and high temperature resistance properties over long periods of time (*i.e.* no degradation of the strength retention after 3000 h at 150 °C, according to specifications). The use of an epoxy resin on the surface of the coin cell constitutes a simple and rapid approach to obtain electrochemical cells that can achieve high-temperature (150 °C) hermetical sealing.

A schematic representation of the modified CR2032 coin-cell is presented on Fig. 1. All parts are made from 304 stainless steel. The case sealing O-ring is made of PP, and is already mounted on the negative side of the case. Some modifications are necessary to adapt the CR2032 coin cell dimensions ($\emptyset_{int}$ 16.4 mm, 2.8 mm thickness when crimped empty) to the FIB's dimensions assembled for this study ($\emptyset_{int}$ 10 mm). A flat PTFE washer is used to maintain the FIB at the center of the coin-cell, and a flat wave spring ($\emptyset$14.4 mm, 1.5 mm thickness when fully expanded) and spacers ($\emptyset$15.4 mm, 0.5 mm thickness) are used to ensure electrical contact and to adjust the thickness of the FIB to the internal space available in the coin cell.

After assembling and crimping the coin cell within the glove box, the epoxy resin is deposited under air atmosphere. A steel pellet, used as a support and for electrical contact, is attached to the negative side of the coin-cell case with silver paint. Both the coin-cell and the contact steel pellet are thoroughly degreased with acetone prior to resin application. Additionally, the positive side of the coin-cell is masked with tape to avoid resin covering. The modified coin-cells obtained after curing (24 h) of the epoxy resin (Fig. 2a) are placed on the custom made electrochemical test bench (Fig. 2b) placed in an oven, heated to 150 °C for electrochemical evaluation.

The coin cells are tightened between a contact rod (bottom) and a screw (top) and connected to a potentiostat. The pressure screw maintains the modified coin-cell in place and keeps a constant pressure on the FIB placed within the coin-cell to maintain electrical contact.

To confirm the proper sealing provided by the epoxy resin, electrochemical testing is performed on pristine coin cells and coin cells covered by epoxy resin.

2.2. Electrochemical testing

A symmetrical cell relying on the Bi^{3+}/Bi redox couple was selected to confirm the sealing since its reversibility was demonstrated by Anji Reddy and Fichtner [6]. The electrolyte selected for our electrochemical investigation is Ba-doped LaF_3. Ball-milling LaF_3 and BaF_2 is an easy method to produce nano-crystalline $La_{1-x}Ba_xF_{3-x}$ ($0 \leq x \leq 0.15$) solid solutions of tysonite-type structure (trigonal, P-3c1) which offer a fluoride-ion

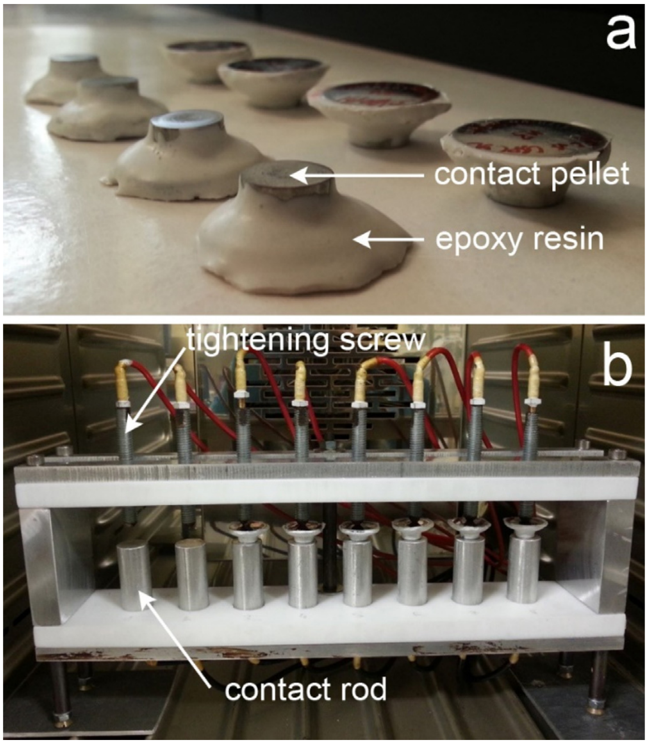

Fig. 2. Photograph of (a) the modified coin-cells and (b) the electrochemical test bench placed in an oven.