Development of tysonite-type fluoride conducting thin film electrolytes for fluoride ion batteries

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ABSTRACT
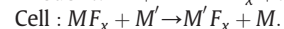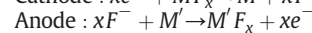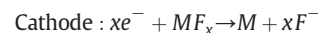
Thin films of $La_{1-x}Ba_xF_{3-x}$ ($0 \leq x \leq 0.15$) have been fabricated via a sol–gel spin coating method on stainless steel substrates. The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and electrochemical impedance spectroscopy (EIS). All the compositions possessed a tysonite-type structure without any detectable impurity; the thickness of the films was 5–6 μm. Fluoride ion conductivity of LaF_3 was greatly improved by BaF_2 doping. Similar to bulk material, $La_{0.9}Ba_{0.1}F_{2.9}$ showed the highest ionic conductivity within the measured compositions. An ionic conductivity of 8.8×10^{-5} S·cm^{-1} was observed at 170 °C. Apparent activation energy for the ion conduction measured from 60 °C to 170 °C was determined, as well.

1. Introduction

In the search of new concepts to build batteries with high energy densities [1–6], a novel type of secondary solid state battery was reported recently with the fluoride anion as a charge transfer ion [7]. With certain materials combinations, up to more than 5000 Wh·L^{-1} are theoretically possible, which is close to twice the theoretical volumetric energy density of the Li/S battery [8–10].

Fluoride ion battery (FIB) consists of a metal anode and metal fluoride cathode, separated by fluoride transporting electrolyte. Fluoride anion acts as a charge transfer ion between a metal/metal fluoride pair. Generally, the anode contains a metal or an alloy of metals, whose fluorination leads to a generation of fluoride or fluorides during discharge. The cathode is typically a transition metal fluoride. The cathodic and anodic reactions during discharge are as follows:

$$\text{Cathode}: xe^- + MF_x \rightarrow M + xF^-$$
$$\text{Anode}: xF^- + M' \rightarrow M'F_x + xe^-$$
$$\text{Cell}: MF_x + M' \rightarrow M'F_x + M.$$

A critical component to obtain a good electrochemical performance of the FIB is the electrolyte, which should provide fast F anion conduction. Solid ion conductors based on tysonite and fluorite structures are known for fluoride ion [11,12]. Liquid electrolytes for selective fluoride ion transport are still in development [13]. In the previous studies, the FIB was assembled as bulk-type battery which contained a pressed pellet consisting of cathode, electrolyte, and anode layer [7,9]. Up to 70% of the theoretical capacity was observed in the first discharge, at a discharge voltage close to the open circuit voltage (OCV). However, also a capacity drop was observed upon cycling and the battery cells were operated at around 150 °C, mainly due to the thick electrolyte layer which, for mechanical reasons, had a thickness of 700–800 μm in the first studies (Fig. 1a). The thickness caused a high resistance of the ionic conductor [14,15]. Moreover, resistance may also be created due to an insufficient contact at the solid state interface of electrode and electrolyte [16,17]. Thus, it should be beneficial to reduce the thickness of the electrolyte in order to reduce the electrolyte resistance. Furthermore, the contact between electrode and electrolyte should be optimized to reduce the interfacial resistance. From a practical point of view, it is reasonable to employ thin film technology to serve the purpose. The schematic representation of the thin film fluoride ion battery is shown in Fig. 1b.

Among the fluoride ion conductors, Ba doped LaF_3 with tysonite-type structure has been reported to apply as a solid state electrolyte due to its superionic conductivity for fluoride and its large electrochemical stability window [8,18,19]. After doping the trivalent LaF_3 with small amounts of divalent Ba, point defects are created at different sites of the anionic sublattice to compensate the charge and maintain the electroneutrality of the crystal [20]. These defects enable high anionic conductivity in tysonite structures [18,19].

In order to replace the so far utilized thick electrolyte powder layers by thin films with similar composition but potentially higher conductance,

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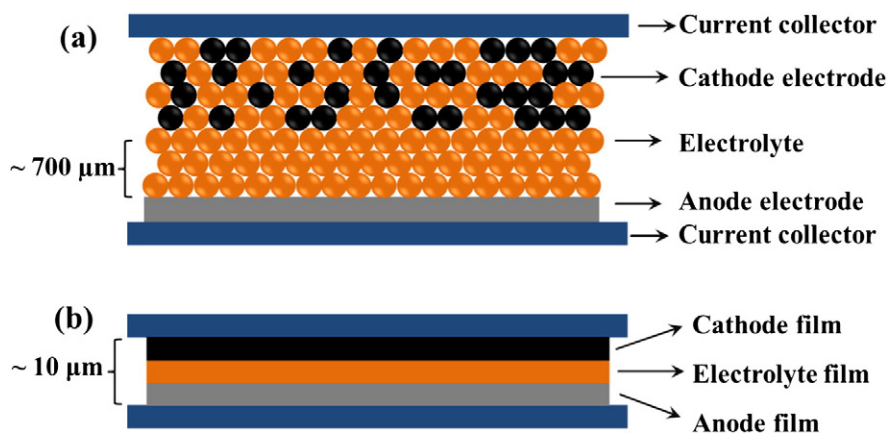E-mail address: m.fichtner@kit.edu (M. Fichtner).

Fig. 1. Schematic illustrations of (a) bulk-type solid state battery and (b) thin-film electrolyte battery.

the sol–gel spin coating technology could be a suitable approach as thin films of various metal fluorides have already been prepared by this method, mostly for optical applications [21–23]. To the best of our knowledge, ionic conductivities of such systems have not been studied so far.

In this work, thin-film electrolytes of $La_{1-x}Ba_xF_{3-x}$ ($0 \leq x \leq 0.15$) were prepared by sol–gel spin coating method. The fluoride ionic conductivity of the films has been determined and the potential conduction mechanism is discussed.

2. Experimental

2.1. Fabrication of $La_{1-x}Ba_xF_{3-x}$ thin-film electrolyte

$La_{1-x}Ba_xF_{3-x}$ ($x = 0, 0.05, 0.1, 0.15$) thin films were fabricated through a sol–gel spin coating method. Metal acetates $La(CH_3COO)_3 \cdot 1.5\ H_2O$ (99.99%) and $Ba(CH_3COO)_2$ (>99.0%) were used as raw materials, obtained from Alfa Aesar and used without further purification. In a typical process, a coating solution was prepared by dissolving $La(CH_3COO)_3 \cdot 1.5\ H_2O$ and $Ba(CH_3COO)_2$ in isopropanol (20 mL) and subsequently adding trifluoroacetic acid (CF_3COOH (4 mL)) and H_2O (2 mL). The final concentration of the metal ions was 0.19 M, and the molar ratio of fluorine/metal ions was in the order of 32. The resulting solution was stirred for 4 h at room temperature to ensure the sol formation.

Prior to the spin coating, round stainless steel substrates ($\Phi = 10$ mm) were polished, ultrasonicated in distilled water and dried in an oven at 80 °C. By using a Laurell WS-650Mz-23NPPB spin coater, thin films of the sol were coated on the substrates at 2650 rpm for 30 s. The films were immediately transferred into a furnace and kept at 300 °C for 5 min in air. This procedure was repeated 7 times to increase the film thickness. Finally, the films were sintered at 400 °C for 20 min in air followed by quenching.

2.2. Structural characterization and EIS measurement

The phase composition of the films was characterized by X-ray diffraction (XRD, Philips X'PERT diffractometer, Cu-Kα radiation). The surface and cross-section morphologies of the films were investigated using a Leo-1530 scanning electron microscope and an atomic force microscope from Digital Instruments-Multimode SPM.

The fluoride ionic conductivities were determined at different temperatures by EIS on the as-prepared thin films using a Zahner IM6 device. Gold was sputtered on the surfaces of the films as an ion-blocking electrode. The frequency range was 1 Hz to 4 MHz, and the voltage amplitude was 10 mV. All the measurements were performed under a dynamic vacuum. The impedance spectra were fitted using the EIS Spectrum Analyzer software from Zahner.

3. Results and discussions

In this work, trifluoroacetic acid was used as a complexing and fluorinating agent. The addition of trifluoroacetic acid to the metal acetates in a solution leads to the formation of a metal trifluoroacetate complex, due to the strong ligand strength of trifluoroacetate compared to the acetate [24,25]:

$$M(CH_3COO)_x + CF_3COOH \rightarrow M(CF_3COO)_x + CH_3COOH.$$
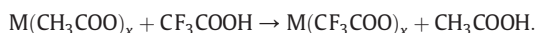
The metal trifluoroacetates are soluble in isopropanol. However, as the metal acetates have limited solubility in isopropanol, a small amount of water was added to promote the formation of the metal trifluoroacetate complex. Thermal decomposition of the trifluoroacetate complex between 250 °C–300 °C leads to the formation of respective metal fluorides according to the following reaction [26,27]. Previously, this method was demonstrated for the synthesis of various pure metal fluorides, but mostly for optical applications.

$$M(CF_3COO)_x \xrightarrow{\Delta} MF_x + (CF_3CO)_2O + CO_2 + CO.$$
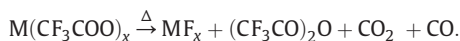
Ba doped LaF_3 compounds $La_{1-x}Ba_xF_{3-x}$ with four different compositions ($x = 0, 0.05, 0.1, 0.15$) were prepared by this method. The XRD patterns of the samples sintered at 400 °C in air are given in Fig. 2. For all BaF_2 concentrations, a single phase tysonite-type structure with the space group of $P63/mcm$ was obtained. This indicates that the method allowed for the preparation of LaF_3 thin films and that Ba^{2+} was successfully integrated in the lattice of the tysonite. Moreover, the applied doping level did not lead to detectable formation of a secondary phase. Compared to pure LaF_3, the peaks were shifted to lower angles when increasing x (see Fig. 2b), indicating an increase of the lattice parameter in accordance with Vegard's law of solid solution as Ba^{2+} is larger than La^{3+}. In addition, the full widths at half-maximum of the reflections became larger because of the formation of nano-sized crystalline domains, which was determined by Rietveld refinement. The average crystallite size was found to decrease with increasing Ba doping, similar to that of the materials prepared by mechanical milling [7]. The unit cell parameters and average crystallite sizes are given in Table 1.

In the tysonite-type structure, F anions are distributed in three structurally and dynamically nonequivalent positions with ratios $F_1:F_2:F_3 = 12:4:2$. However, the behaviors of F_2 and F_3 were found to be very similar and can be considered equivalent [28,29]. The F conduction mechanism in tysonite is due to a vacancy mechanism. It's very unlike to form the F interstitials, because the size of the interstitial sites in tysonite structure (0.84 Å) is smaller than the radius of the F anion (1.19 Å) [12]. The charge carrier density increases with the temperature. At low temperatures, the F vacancies are located preferentially in the F_1