



## Short communication

# High capacity and cyclic performance in a three-dimensional composite electrode filled with inorganic solid electrolyte



Kai Chen, Yang Shen\*, Yibo Zhang, Yuanhua Lin, Ce-Wen Nan\*

State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

## HIGHLIGHTS

- Surface capacity of  $\sim 9 \text{ mAh cm}^{-2}$  is obtained.
- Excellent cycling performance and good rate capability at various discharge rates.
- The novel composite cathodes are highly compact with a relative density of 92%.
- No electronic conductive additive or polymer binder is used.
- The one-step sintering approach may be readily applied to other cathode systems.

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## ABSTRACT

Three-dimensional (3-D) composite electrodes are prepared by one-step sintering of the laminated  $\text{LiCoO}_2$  and  $0.44\text{LiBO}_2 \cdot 0.56\text{LiF}$  pellets, in which the amorphous  $0.44\text{LiBO}_2 \cdot 0.56\text{LiF}$  solid electrolyte melts during the sintering process and fills the interspaces in the underlying highly conductive 3-D frame formed by  $\text{LiCoO}_2$ . The one-step sintering process yields a compact electrode structure of  $\sim 92\%$  in relative density, which contains no electronic conductive additives or polymer binder. For better characterization of the composite electrode, liquid electrolyte is used in the battery test, but the vast majority of the active material is in the all-solid-state environment. The specific capacity of the 3-D composite electrode is dependent on the thickness of the composite electrodes. The  $100\text{-}\mu\text{m}$ -thick 3-D composite electrode possesses high specific discharge capacity of  $131 \text{ mAh g}^{-1}$  at C/20 rate (96% utilization of the active material), excellent cycling performance for the measured 20 cycles and good rate capability at various discharge rates. The  $200\text{-}\mu\text{m}$ -thick 3-D composite electrode delivers 88% of the theoretical capacity, i.e.,  $120 \text{ mAh g}^{-1}$ , and a significantly enhanced surface capacity of  $\sim 9 \text{ mAh cm}^{-2}$ , which is much higher than that of the electrode used in the conventional all-solid-state lithium battery.

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## 1. Introduction

Safety issues and substantial demand for higher energy density are two major challenges for the lithium ion batteries [1,2], which slow down their applications in electric vehicles and energy storage for power stations. All-solid-state lithium ion batteries, with solid state electrolytes and new battery structure designs, are the ultimate solution for the safety issues and have attracted ever-increasing attentions for the past few years. The thin film type all-solid-state batteries prepared by film deposition techniques have been thoroughly investigated [3–8]. Limited by the very thin

cathodes employed, the surface capacities of these thin film type batteries are only  $9.9\text{--}250 \mu\text{Ah cm}^{-2}$ , though they could deliver excellent capacity retention over thousands of cycles [9]. Bulk-type all-solid-state batteries are thus considered more promising to be used in the scenarios where high capacity is crucial. In principle, the capacity and cycle lifetime of all-solid-state batteries are determined by the microstructure of the cathode especially the interfaces between the active cathode materials and the solid electrolytes. Recently, a number of efforts have been made in constructing porous cathodes with pores of three-dimensional (3-D) connectivity inside [10,11]. With the ionic electrolyte filled in the pores, these 3-D composite cathodes are capable of providing higher capacity due to their significantly larger specific areas and much shorter diffusion path for the lithium ions during the charging/discharging process. For instance, Lai et al. reported that porous 3-D  $\text{LiCoO}_2$  electrode with liquid electrolyte filled-in

\* Corresponding authors. Tel.: +86 10 62773587; fax: +86 10 62772507.  
E-mail addresses: [shyang\\_mse@tsinghua.edu.cn](mailto:shyang_mse@tsinghua.edu.cn) (Y. Shen), [cwnan@tsinghua.edu.cn](mailto:cwnan@tsinghua.edu.cn), [cwnan@mail.tsinghua.edu.cn](mailto:cwnan@mail.tsinghua.edu.cn) (C.-W. Nan).

exhibited ultrahigh energy density and good cycling performance [12]. Thick film cathodes filled with solid oxide electrolyte have also been reported [13]. However, a composite of thick oxide electrolyte pellets of about 0.5–1 mm and thin cathode layer of only about 10  $\mu\text{m}$  result in low capacity and energy density [13]. By increasing the thickness of the composite electrode to 400  $\mu\text{m}$ , a higher surface capacity of 2.2  $\text{mAh cm}^{-2}$  was achieved in a monolithic solid-state lithium battery with  $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$  as solid electrolyte and  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  as electrodes [14], which is much higher than that in the thin film type all-solid-state batteries. Another report on filling solid inorganic electrolyte into the open pores of the porous 3-D  $\text{LiCoO}_2$  electrode was carried out by repeatedly infiltrating  $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$  sol into the pores of the pre-sintered  $\text{LiCoO}_2$  substrate and the subsequent heat treatments. The 100- $\mu\text{m}$ -thick electrode thus prepared could deliver a specific discharge capacity of only 115  $\text{mAh g}^{-1}$ , and no cycling data was given [15]. Moreover, the infiltration and firing process needs to be repeated many cycles and is time-consuming and labor intense.

In this contribution, a high performance composite electrode is prepared via a simple one-step sintering process by using  $\text{LiCoO}_2$  as active cathode material and  $0.44\text{LiBO}_2 \cdot 0.56\text{LiF}$  as amorphous solid electrolyte. Instead of direct co-firing or infiltrating the porous cathode with precursor sol of solid electrolyte, laminated  $\text{LiCoO}_2$  pellet and  $0.44\text{LiBO}_2 \cdot 0.56\text{LiF}$  pellet was uni-axially pressed together, as shown in Fig. 1. With a melting temperature of  $<700^\circ\text{C}$  [16],  $0.44\text{LiBO}_2 \cdot 0.56\text{LiF}$  solid electrolyte was melted during the sintering process at  $950^\circ\text{C}$  and infiltrated the underlying  $\text{LiCoO}_2$  frame. The one-step sintering process yielded a 3-D composite electrode of  $\sim 92\%$  in relative density. Without any electronic conductive additive or polymer binder, the novel composite cathodes are highly compact as compared with their counterparts in the conventional liquid lithium battery. A rather high specific discharged capacity of 131  $\text{mAh g}^{-1}$  (or a high surface capacity of 5  $\text{mAh cm}^{-2}$ ) was achieved in a 100- $\mu\text{m}$ -thick composite electrode, which is up to 96% of the theoretical capacity of  $\text{LiCoO}_2$  (137  $\text{mAh g}^{-1}$ ). Further increase in the thickness to 200  $\mu\text{m}$  led to an even higher surface capacity of 9  $\text{mAh cm}^{-2}$ . Given the low sintering temperature and the amorphous nature of  $0.44\text{LiBO}_2 \cdot 0.56\text{LiF}$  solid electrolyte, this one-step sintering approach is promising to be extended to other cathode systems.

## 2. Experimental

Battery-grade  $\text{LiCoO}_2$  powder was ball-milled for 12 h, and used as active material of the composite electrodes.  $\text{LiBO}_2$  and  $\text{LiF}$  with a molar ratio of 0.44:0.56 were mixed using an agate mortar to act as solid ionic electrolyte. The active material and solid ionic electrolyte were pressed into pellets with a diameter of 12 mm, separately. Then the active material pellet and solid electrolyte pellet with a mass ratio of 2:1 were stacked as shown in Fig. 1a, and sintered at  $950^\circ\text{C}$  for 90 min. During the sintering process,  $\text{LiCoO}_2$  particles in the lower pellet connected together and formed a 3-D frame, while

the upper pellet consisting of  $\text{LiBO}_2$  and  $\text{LiF}$  melt and filled into interspaces of the  $\text{LiCoO}_2$  frame (Fig. 1b), forming the 3-D composite electrode (Fig. 1c). For comparison, pure  $\text{LiCoO}_2$  and  $0.44\text{LiBO}_2 \cdot 0.56\text{LiF}$  pellets were also sintered under the same condition.

X-ray diffraction (XRD, Rigaku D/max-2500 diffraction meter with a  $\text{Cu K}\alpha$  radiation source) was used for the phase identification in the sintered composite electrode. The microstructure of the  $\text{LiCoO}_2$  ceramics sintered with and without solid electrolyte was observed by scanning electron microscopy (SEM, JEOL JSM-7001F). The composition of the 3-D composite electrode was determined using inductively coupled plasma spectroscopy (ICP-AES, Varian Vista-MPX) and ion chromatography (IC, Metrohm 761 compact). Electrochemical impedance measurement was carried out with an impedance analyzer (ZAHNER-elektrok IM 6) in the frequency range from 100 kHz to 10 mHz with an AC voltage amplitude of 5 mV.

As the first step towards the goal of all solid state battery, we focus on the preparation and evaluation of the composite electrode. In order to better test the performance of the composite electrodes, liquid electrolyte is used here, but the liquid electrolyte is only wetting the surface of the dense composite electrode and only some of  $\text{LiCoO}_2$  particles on top surface could be contacting to the liquid electrolytes, and thus the vast majority of the active material inside the composite electrode is in the all-solid-state environment not contact with the liquid electrolyte (see Fig. 1c). In this scenario, Lithium ions as well as electrons are transported solely by the solid electrolyte and the  $\text{LiCoO}_2$  inside the composite electrode. For battery measurement, the composite electrodes were polished to different thickness ranging from 100  $\mu\text{m}$  to 500  $\mu\text{m}$ . Au was sputtered onto one side of the composite electrode as the current collector. A piece of lithium foil was then pressed onto another collector, on top of which one layer of Celgard 2400 separator was placed. Then, the prepared composite electrode was centered over the separator. The whole laminated construction was sealed in a LIR 2032 cell with electrolyte solution of 1 M  $\text{LiPF}_6$  dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1). The cells were galvanostatically cycled between 2.5 and 4.2 V vs.  $\text{Li/Li}^+$  at C/20. For investigation of the rate capability of the 100- $\mu\text{m}$ -thick 3-D composite electrode, CC charging was used, with constant current C/10 applied until cell voltage reached 4.2 V, after which cells were galvanostatically discharged at various rates to 2.5 V. Cyclic tests indicate that the  $0.44\text{LiBO}_2 \cdot 0.56\text{LiF}$  solid electrolyte is stable against the liquid electrolyte solution (see Fig. S1 in the Supporting information).

## 3. Results and discussion

### 3.1. Structure and composition

Fig. 2 shows the XRD patterns of the fresh surface and interior of the sintered 3-D composite electrode. For the upper and lower fresh surfaces, diffraction peaks corresponding to  $\text{LiCoO}_2$  (PDF 50-0653)

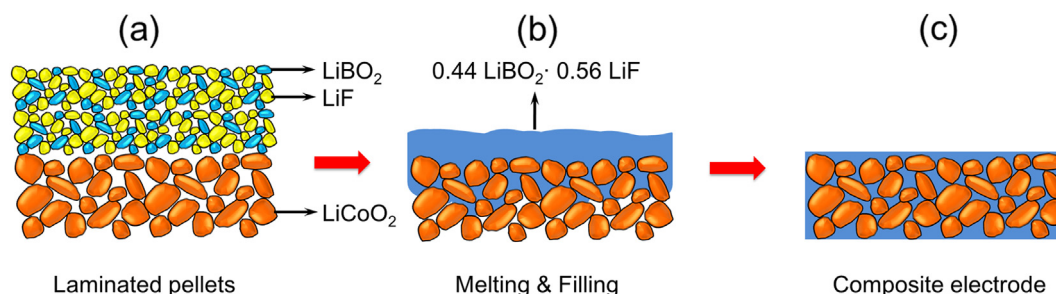


Fig. 1. A schematic illustration for the preparation process of the 3-D composite electrodes.

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