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Synergetic proton conduction in $BaZr_{0.8}Y_{0.2}O_{3-\delta}$–carbonate composite electrolyte for intermediate-temperature solid oxide fuel cells

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ABSTRACT

In the present study, electrical properties of a composite electrolyte composed of a $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY) and a perspective of defect chemistry. A DFT first-principles calculation further confirmed that proton transfer in molten carbonates was a low-energy process.

1. Introduction

Intermediate-temperature solid oxide fuel cell (IT-SOFC) is a commercially viable product because of its advantages in cost and reliability over its high-temperature counterpart. However, the development of IT-SOFC is currently hampered by the lack of high-conductivity solid oxide-ion electrolytes. A focus of the recent research on electrolyte development has been on proton conducting perovskites such as acceptor-doped $BaZrO_3$ and $BaCeO_3$. The $BaZrO_3$-based conductors are chemically stable over a wide range of temperatures and atmospheres, but very difficult to sinter [1–3]. By contrast, the $BaCeO_3$-based conductors are easy to sinter, but chemically unstable in CO_2-containing atmospheres [4–6]. To address the sintering issue of the $BaZrO_3$-based perovskites, we have recently demonstrated the use of molten carbonate (MC) as a sintering aid to promote the densification of $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY), while introducing CO_3^{2-} into the ionic conduction, making it a mixed H^+ and CO_3^{2-} conductor [7]. Similar work of combining oxide-ion conductors such as doped-CeO_2 and molten carbonates as an IT-electrolyte has also been reported by other groups with excellent SOFC performance [8,9].

In the present study, we report a systematic investigation into ionic conduction in the MC–BZY composite electrolyte, aiming to understand the role of proton conduction in the enhanced conductivity observed in the MC–BZY electrolyte system.

2. Experimental procedure

2.1. Sample preparation

The BZY ($BaZr_{0.8}Y_{0.2}O_{3-\delta}$) electrolyte was synthesized via conventional solid-state reaction. The staring materials were $BaCO_3$ (99.8%, Alfa Aesar), ZrO_2 (99.7%, Alfa Aesar) and Y_2O_3 (99.9%, Alfa Aesar). Stoichiometric amount of the starting materials was first weighed, intimately mixed and pelletized, followed by firing at 1100 °C for 5 h. The calcined pellets were then broken into powders and calcined again at 1300 °C for another 5 h. After ball milling, the powders were then blended with ~10 wt% of carbon-black as a pore former, pelletized and finally sintered at 1500 °C for 5 h. Thus made samples were porous and ready for molten carbonate infiltration.

Two molten carbonate systems were selected for this study: Li_2CO_3–38 mol% K_2CO_3 (denoted as LK) and Li_2CO_3–48 mol% Na_2CO_3 (denoted as LN); these compositions reflect a eutectics. They were first melted and homogenized in an Al_2O_3 crucible at 650 °C for 2 h. The porous BZY pellet pre-loaded in a silver basket was then slowly immersed into the MC. After a roughly 2-h soaking, they were gradually pulled out of the melt and suspended above the crucible before slowly cooling the finance to room temperature. Thus fabricated MC–BZY composites were slightly polished to remove the residual carbonate on the surface. The samples were then ready for microstructural and electrical characterizations.

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2.2. Characterization

The phase purity of the BZY powder and MC–BZY composites was examined by X-ray diffraction (XRD) (D/max-A, Rigaku, Japan), while microstructures of the BZY as well MC–BZY composites were captured by a field emission scanning electron microscopy (FE-SEM, Zeiss Ultra).

The ionic conductivity of the MC–BZY composites was assessed by electrochemical impedance spectroscopy (EIS) on a symmetrical cell configuration consisting of the MC–BZY composite sandwiched by two identical silver-based electrodes and current collectors. The EIS measurements were carried out using an electrochemical workstation (IM6, Zahner) under open-circuit conditions within a frequency range of 10^5 to 0.01 Hz and under a 10 mV of stimulus AC amplitude. The ionic resistance was extracted from the high-frequency intersection of the spectrum with the real-axis. The temperature was varied from 400 to 650 °C, covering the solid-to-liquid transition of the carbonate phase (the melting temperature of the carbonate phase is ~490 °C). To understand the nature of ionic conduction, the ionic conductivity was also measured in both oxidizing (air) and reducing atmospheres (H_2–N_2 mixture) with a range of varied partial pressures of H_2O and H_2. The different partial pressures of H_2O were generated by a homemade water bubbler system and monitored by an on-line humidity sensor (Vaisala model 332). To verify the involvement of protons in ionic conduction, D_2O was also used as an alternative to H_2O. In addition, the effects of MC loading and MC type on ionic conductivity were also studied.

2.3. DFT modeling of proton transfer in molten carbonates

The energetics of proton transfer in a MC was analyzed by Gaussian09 suite of quantum chemistry programs [10]. The disordered MC phase was simulated by a cluster of $(Li_2CO_3)_8$. The B3LYP hybrid functional [11,12] in combination with the basis set of 3-21G(d, p) were used to calculate the energetics of H^+-transfer in $[(Li_2CO_3)_8H]^+$ cluster.

3. Results and discussion

3.1. XRD patterns and microstructures

The XRD patterns of BZY synthesized at 1500 °C for 5 h are shown in Fig. 1(a), indicating two cubic phases, which have been previously reported [13]. The reactivity between BZY and LN was also studied by firing a mixture of BZY and LN (1:1 vol%) at 650 °C for 2 h. The XRD patterns are shown in Fig. 1(b), indicating no phases formed other than the original BZY and LN, which is consistent with that reported in Ref. [9]. Rietveld refinements of XRD patterns resulting from the pure BZY and BZY-LN indicated that the mole ratio of the two cubic $BaZrO_3$ phase was consistently 59:41. The two $BaZrO_3$ cubic phases exhibited a lattice parameter of a = 4.2021 Å and a = 4.2366 Å, respectively. For the composite sample, the lattice parameters for the two $BaZrO_3$ cubic phases were a = 4.1999 Å and a = 4.2358 Å, further suggesting no reaction occurred between BZY and molten carbonate.

The microstructures of BZY and MC–BZY composite are shown in Fig. 2(a) and (b), respectively. It is evident that BZY even after being sintered at 1500 °C contains poorly connected grains, indicating the refractory nature of BZY materials. By contrast, Fig. 2(c) and (d) of the MC–BZY composite shows a dense microstructure with the MC phase filling the pores.

3.2. Conductivity vs. MC loading

The effect of MC loading on the ionic conductivity of a LK–BZY is shown in Fig. 3. Since the MC loading is determined by the initial porosity in BZY, different contents of carbon-black pore former were used during preparation of porous BZY. Fig. 3 clearly indicates that higher MC loading (or higher initial porosity in BZY) results in a higher ionic conductivity over the entire temperature range tested. This is an expected result as

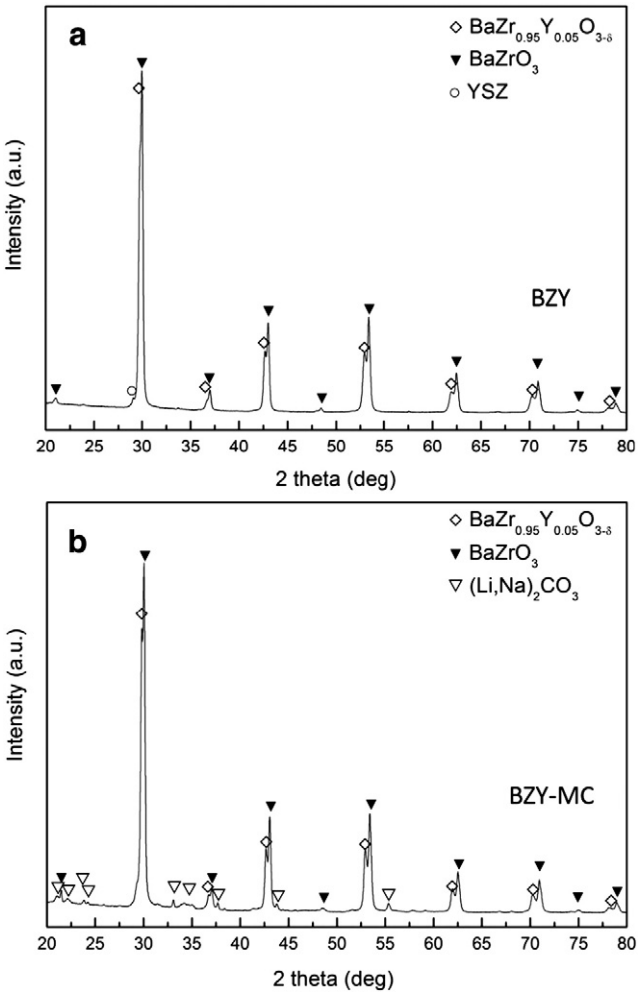

Fig. 1. XRD pattern of (a) BZY sintered at 1500 °C for 5 h and (b) MC–BZY fired at 650 °C.

the primary conductor in MC–BZY is the MC phase, which is also evidenced by the activation energy E_a = 0.29–0.30 eV close to that of pure molten carbonate. In practice, however, the high conductivity of the MC phase could be limited by the amount of MC that can be retained within the BZY skeleton, analogous to the case of MC in $LiAlO_2$ matrix used in commercial molten carbonate fuel cells.

3.3. Conductivity vs. MC type

The effect of MC type, i.e. LK vs. LN, on ionic conductivity of MC–BZY is shown in Fig. 4. To ensure a fair comparison, the MC loading of the two samples was fixed at 48 vol%. Clearly, LN–BZY has a higher conductivity than LK–BZY at t > 500 °C. This observation is consistent with the literature showing higher conductivity for LN than LK system [14]. In addition, E_a = 0.30 and 0.40 eV at above the melting temperature for the LN–BZY and LK–BZY system, respectively, are comparable to the literature values [14]. The LN system was selected for the subsequent electrical characterization because of its high conductivity.

3.4. Conductivity vs. atmosphere

Fig. 5 shows the conductivity of a LN–BZY with an MC loading of 57 vol% measured in both oxidizing and reducing atmospheres. It is evident that conductivity measured in reducing 3% H_2O–(5% H_2–N_2) is higher than that measured in oxidizing 3%H_2O–air over the entire temperature range. The result suggests that the enhanced conductivity by H_2 be associated with the MC phase since the BZY's conductivity