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Effect of fluorine, chlorine and bromine doping on the properties of gadolinium doped barium cerate electrolytes

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ABSTRACT

The high temperature proton conductors have attracted considerable interest for their potential application in gas sensors, hydrogen separators and fuel cells. Among various kinds of proton conducting materials, rare earth doped barium cerate based ceramics display the highest conductivity, but their practical applications are limited because their well-recognized poor chemical stability against CO₂ and/or H₂O steam. In this work, F, Cl and Br doped BaCe_{0.90}Gd_{0.10}O_{3-δ} (BCG) materials were prepared via a solid-state reaction method with CuO as sintering aid to improve the materials chemical stability. The experimental results display that the added F, Cl or Br enters into the lattice of BCG without causing structure and morphology change. Halogen (F, Cl and Br) doping effectively enhances chemical stability of BCG in CO₂ and H₂O steam due to decreasing the materials basicity. Br doped BCG exhibits the best chemical stability as well as relatively high electrical conductivity. CuO addition reduces sintering temperature by 150 °C.

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Introduction

When trivalent rare earth cations mostly, such as Y³⁺, Gd³⁺ or Sm³⁺, partially substitute Ce⁴⁺ in BaCeO₃ or SrCeO₃ or Zr in BaZrO₃, oxide ion vacancies are formed in crystal lattice in order to keep charge neutrality. If the materials are exposed to hydrogen-containing atmosphere at high temperature, incorporated protons through the filling of oxygen vacancies can hop between oxygen ions in the crystal and as a result, the materials exhibit proton conduction [1–6]. The kind of

materials called high temperature proton conductors (HTPC) have extensively been investigated and shown potential applications in fuel cells, steam electrolyzers, gaseous sensors, hydrogen separators and catalytic membrane reactors [7–15].

One ideal HTPC material should display high protonic conductivity and excellent chemical stability as well under its application conditions. Previous research work shows that among various kinds of HTPC materials, Y- or Gd-doped BaCeO₃ possesses the highest proton conductivity because of the favorable factors associated with the structural features of perovskite materials [16–20]. For example, Amsif and

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Kikuchi et al. [21,22] recently reported that $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_3$ ceramic sample has the highest ionic conductivity among $\text{BaCe}_{0.9}\text{Ln}_{0.1}\text{O}_3$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Yb}, \text{Tb}$) materials due to the optimal combination of lattice distortion and tolerance factor. However, their well-recognized poor chemical stability against CO_2 and H_2O steam limits their practical applications [23–27]. BaCeO_3 -based materials reacting with CO_2 or H_2O to form barium carbonate or barium hydroxide and cerium oxide not only reduces their proton conductivities, but also makes electrochemical devices based on the materials loss of function.

A lot of research efforts have been made for improving the chemical stability of BaCeO_3 -based ceramic materials. The reduction of basicity of the materials is one of methods for increasing their chemical stability. Elisabetta [28] prepared $\text{BaCe}_{0.9-x}\text{Nb}_x\text{Y}_{0.1}\text{O}_{3-x}$ and found that Nb-doping effectively improved the chemical stability of barium cerates against carbonation, which was attributed to the decreased basic character of the $\text{BaCe}_{0.9-x}\text{Nb}_x\text{Y}_{0.1}\text{O}_{3-x}$ compared to $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$ due to relatively high electronegativity of Nb over Ce. The sample with the highest Nb content shows the highest stability in pure CO_2 . However, the sample conductivity decreases as Nb doping content increases. Ta-substituted barium cerate also shows more tolerant to CO_2 due to the same reason [29]. However, Ta_2O_5 is limited dissoluble in barium cerate and the sample preparation procedure is relatively complicated [29].

Compared with doped BaCeO_3 , BaZrO_3 -based materials show better bulk proton conductivity and chemical stability in general fuel cell operating conditions [30]. However, the apparent electrical conductivity of polycrystalline BaZrO_3 -based materials is lower than that of BaCeO_3 -based materials under the same conditions because of the high grain boundaries resistances [31]. Furthermore, BaZrO_3 -based materials are of a very refractory nature, and thus, sintering temperatures of at least 1700°C are needed in order to obtain 95% density. Fortunately BaZrO_3 can easily form solid solutions with BaCeO_3 across the composition range, so BaCeO_3 - BaZrO_3 solid solutions [32] and Zr-substituted, Y-, Gd- or In-doped barium cerates were obtained by solid state reaction method [33–36]. The prepared materials show improved chemical stability against CO_2 and H_2O steam and their chemical stability increases with the increase of Zr content. However, the materials stability improvement is at the cost of reducing protonic conductivity. For example, 50 mol % Zr-substituted barium cerate typically leads to 50% drop in proton conductivity, which is considered to be due to grain-boundary effects [37]. Additionally, Zr-substituted barium cerates still need to be sintered at high temperature to achieve dense sinters due to their poor sinterability.

A core-shell concept was proposed as a strategy for improving the chemical stability of the materials. The proton conductors of core-shell structured $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ (BZY10)- $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ (BCY10) were prepared via solid state reaction in combination with sol-gel method. The core-shell structured materials display higher conductivity and better chemical stability than that of BZY10/BCY10 physical mixture or solid solution with same composition [38,39]. It was considered that the conductivity increase is achieved by the improvement of the sintering property of BZY10 through coating BZY10 grains

by a thin layer of BCY10. In our previous work [40], the core-shell structured BZY10:BCY10 samples were prepared by similar method, but core and shell are inversed compared to aforementioned work. The samples achieve dense structure after sintered at 1300°C for 10 h with the help of ZnO sintering aid. The samples display not only high electrical conductivity but also enhanced stability against CO_2 and H_2O steam. In addition, a dual-layer electrolyte containing $\text{Ba}(\text{Ce}_{0.9}\text{Y}_{0.1})\text{O}_{3-\delta}$ as the higher-proton conducting phase and $\text{Ba}(\text{Zr}_{0.85}\text{Y}_{0.15})\text{O}_{3-\delta}$ as the chemically stable protecting phase also displays high electrical conductivity and good stability and the electrolyte was applied in fuel cell [41].

Recently, the improvement of the chemical stability of $\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$ (BCS) electrolyte was realized by Cl doping [42]. The Cl doped BCS shows better stability against CO_2 while its proton conductivity decrease is not obvious in humidified reducing atmosphere ($< 10\%$) [42]. The stability improvement of Cl doped BCS is attributed to the basicity reduction of BaCeO_3 perovskites by Cl doping. So, halogen doping may be a method to enhance chemical stability of barium cerates.

Because anions doping for improving barium cerate properties was hardly reported, based on Wang et al. work [42], we further investigated into effect of F, Cl, and Br doping on the chemical stability of $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$ (BCG) electrolytes against CO_2 and H_2O steam. BCG was usually sintered at above 1600°C to achieve dense sample [43]. The densification of the BCG ceramic materials will become more difficult with halogen addition. To overcome the problem, the sintering aids were introduced during the samples preparation for improve their sinterability. E. Gorbova et al. [44] have verified that MO_x (where $M = \text{Cu}, \text{Ni}, \text{Zn}, \text{Fe}, \text{Co}, \text{Ti}$) addition is very effective to improving BCG sinterability and electrical behavior. Among the samples with transition metal addition, the Cu-adding samples show the highest conductivity as well as reducing sintering temperature. So, in this work, 1 mol % CuO was selected as sintering aid for preparation of the halogen doped BCG. The results show that the Br doped BCG material displays the best chemical stability as well as relatively high electrical conductivity compared to undoped BCG electrolyte.

Experimental

The starting chemicals for samples preparation are BaCO_3 , CeO_2 , Gd_2O_3 , BaF_2 , BaCl_2 , BaBr_2 and CuO with analytical grade. Both the BCG and the 5 mol% F, Cl, Br doped BCG (BCGF, BCGCl, BCGBr) samples were fabricated by the high temperature solid state reaction and 1 mol % CuO was added to samples as sintering aid. The preparation process of BCG was described in our previous paper [40]. During preparation of BCGF, BCGCl and BCGBr, 5 mol% BaCO_3 was replaced with BaF_2 , BaCl_2 and BaBr_2 , respectively. Briefly, the raw powders with stoichiometry were fully mixed and ground, followed by calcining at 1150°C for 2 h in air. After 1% poly(vinyl butyral) (PVB) binder was added, the mixed powder was remixed. The dried powder was finally shaped into pellets and then sintered at 1450°C for 3 h in air.

Microstructure of the samples was characterized by S4800 field emission scanning electron microscopy. The phase

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