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Effect of titanium doping on chemical and structural stability and electrical properties of proton-conducting solid electrolyte $BaCe_{0.8}Sm_{0.2}O_{3-\delta}$

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ABSTRACT

In this study, the effects of Ti substitution for Ce on chemical and structural stability and electrical properties of proton-conducting solid electrolyte membrane $BaCe_{0.8-x}Ti_xSm_{0.2}O_{3-\delta}$ (BCST) are investigated. Our results show that both chemical and structural stability of the BCST samples in CO_2 containing and moist atmospheres are remarkably enhanced with increasing the content of Ti which is higher electronegative than Ce. However, the proton conductivity of the sample decreases with increasing Ti content, which may be due to the increasing difficulty of lattice hydration and smaller grain size (corresponding to more grain boundaries) caused by Ti doping. The activation energy for proton migration increases with Ti content, which is mainly related with the weaker hydrogen bond. The results show that the $BaCe_{0.75}Ti_{0.05}Sm_{0.2}O_{3-\delta}$ has a great electrical conductivity (1.03×10^{-2} S cm^{-1} at 650 °C) and it also demonstrates good chemical and structural stability in CO_2 and water containing atmospheres. Therefore, $BaCe_{0.75}Ti_{0.05}Sm_{0.2}O_{3-\delta}$ can be considered as a promising proton conducting electrolyte for intermediate temperature solid oxide fuel cells.

1. Introduction

Rare-earth oxide doped perovskite materials such as $BaCeO_3$, $SrCeO_3$ and $BaZrO_3$ have attracted considerable attentions because of their proton-conduction properties under hydrogen or water vapor containing atmosphere at intermediate temperatures [1–7]. Among these perovskites, $BaCeO_3$ exhibits the highest proton conductivity, and is regarded as one of the most promising candidate materials for electrolyte membrane in solid oxide fuel cells (SOFCs) [7]. Previous results have shown that introduction of trivalent rare-earth dopants such as Nd [8], Yb [9], Y [10] and Sm [11] into B site (Ce site) of $BaCeO_3$ crystal lattice can create oxygen vacancies, which produces protonic defects in the moist atmosphere via the hydration reaction shown in Eq. (1):

$$H_2O + V_o^{\bullet\bullet} + O_o^{\times} \rightarrow 2OH_o^{\bullet} \quad (1)$$

In addition to proton conductivity, the long-term chemical and structural stability in operating conditions is another important criterion to classify a perovskite material as a good electrolyte for SOFCs. However, $BaCeO_3$ suffers from poor chemical and structural stability in moist and CO_2 containing atmospheres as it tends to decompose to CeO_2 in these two atmospheres according to (Eqs. (2) and (3)), respectively [12]:

$$BaCeO_3 + H_2O \rightarrow Ba(OH)_2 + CeO_2 \quad (2)$$

$$BaCeO_3 + CO_2 \rightarrow BaCO_3 + CeO_2 \quad (3)$$

Therefore, the performance degradation of $BaCeO_3$-based materials in moist and CO_2 containing atmospheres greatly limits their applications. For example, it had been reported that the $BaCe_{0.8}Gd_{0.15}Pr_{0.05}O_{3-\delta}$, $BaCe_{0.85}Sm_{0.15}O_{3-\delta}$ and $BaCe_{0.85}Eu_{0.15}O_{3-\delta}$ compounds were reactive with CO_2 at elevated temperatures and they were also unstable when boiled in water [13]. Tanner and Virkar [14] reported that, $La_{0.05}BaCe_{0.95}O_{2.95}$ decomposed into CeO_2 and $Ba(OH)_2$ in moist atmosphere within 72 h even the operating temperature was lowered to 500 °C. Taniguchi et al. [15] also demonstrated that the degradation rate of single cell voltage with $BaCe_{0.8}Gd_{0.2}O_{3-\delta}$ as electrolyte was increased from 7%/1000 h to 24%/1000 h when 20% CO_2 was added into the pure H_2 fuel under a certain discharge current density (100 mA cm^{-2}) at 800 °C. In addition, it has been suggested that, the decomposition rate for doped $BaCeO_3$ samples was even faster than undoped ones in moist atmosphere. Several works [14,16,17] have implied that the reaction

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of $BaCeO_3$ with CO_2 and H_2O is more favored at low temperatures, which greatly hampers the application of $BaCeO_3$-based materials as electrolyte for intermediate temperature SOFCs.

One of the approaches to address these issues is to partially replace Ce in $BaCeO_3$ with higher electronegative elements, such as Zr and Nb, which can help to decrease the basicity of the oxide [18,19]. For example, Xie et al. [20] reported that $BaCe_{0.7}Nb_{0.1}Sm_{0.2}O_{3-\delta}$ powders exhibited higher chemical stability compared with $BaCe_{0.8}Sm_{0.2}O_{3-\delta}$. Although basic oxides were thought to easily react with acidic gases or H_2O [21], a high basicity of the oxide was in favor of forming protonic charge carriers, which was beneficial to protonic conductivity. Therefore, a compromise between chemical and structural stability and protonic conductivity should be considered when one selects a dopant from the viewpoint of basicity of materials. Among the potential elements, titanium (Ti) might be a most promising candidate because it has a relatively high electronegativity and suitable ionic size. Xie et al. [22] reported that Ti-doping enhances the structural stability of $BaCe_{0.8}Y_{0.2}O_{3-\delta}$ in CO_2/H_2O atmosphere at the expense of conductivity. The prepared $BaCe_{0.7}Ti_{0.1}Y_{0.2}O_{3-\delta}$ exhibited a conductivity of 0.0062 $S\ cm^{-1}$ at 700 °C in humid hydrogen (~3% H_2O). Obviously, Ti doping level has large influence on the structural stability and protonic conductivity. Therefore, further optimization of Ti doping amount is required to achieve excellent integrate properties from a point of view of practical application.

The electrolyte of 20 mol% Sm doped $BaCeO_3$ (BCS) was reported to exhibit a high protonic conductivity (0.017 $S\ cm^{-1}$ at 600 °C) in moist H_2/Ar atmosphere [11]. To further enhance the structural stability of BCS against CO_2 and/or H_2O atmospheres, in this work, a series of Sm and Ti co-doped $BaCeO_3$ electrolyte composites, $BaCe_{0.8-x}Ti_xSm_{0.2}O_{3-\delta}$ ($x=0$, 0.05 and 0.1), were prepared. The effects of Ti doping level on the lattice structure, material microstructure, chemical and structural stability as well as electrical conductivity were investigated. The possible reaction mechanisms of $BaCe_{0.8-x}Ti_xSm_{0.2}O_{3-\delta}$ with different atmospheres (H_2O and CO_2) were also examined and discussed.

2. Experimental

2.1. Sample preparation

$BaCe_{0.8-x}Ti_xSm_{0.2}O_{3-\delta}$ ($x=0$, 0.05 and 0.1, referred to as BCS, $BCST_{0.05}$ and $BCST_{0.1}$, respectively) powders were synthesized via a combined EDTA-citrate sol-gel method using $Ba(NO_3)_2$, $Ce(NO_3)_3 \cdot 6H_2O$, $C_{16}H_{36}O_4Ti$ and Sm_2O_3 as starting materials, and citric acid and ethylenediaminetetraacetic acid (EDTA) as complexants. The Sm_2O_3 was annealed at 1000 °C for 10 h before use to remove the possibly adsorbed water and carbon dioxide. First, $C_{16}H_{36}O_4Ti$ was dissolved in ethanol at a molar ratio of 1:30 to form a transparent solution, into which a citric acid solution (pH=5) was added at a molar ratio of citric acid: $Ti^{4+}=2:1$ to acquire solution A. Then, solution A was treated at 80 °C for 1 h in a water bath. Stoichiometric amounts of Sm_2O_3 and barium and cerium nitric salts were dissolved in a dilute nitric acid solution under magnetic stirring to form solution B, where citric acid with a molar ratio of 2:1 with regard to metallic ions was then introduced. The pH of the solution B was adjusted to 5 with ammonia. The solution A and B were mixed homogeneously, to which EDTA was added in the molar ratio of 1:1 relative to total metallic ions. The pH value of the resultant solution was adjusted to ~8 by ammonia. After being mixed homogenously by magnetic stirring, the obtained solution was evaporated in a water bath at 80 °C to form a viscous gel, which was then heated at 250 °C for 2 h in an oven to obtain a bouffant precursor. The ground powders were calcined at 1000 °C for 10 h and were uniaxially pressed into pellets with appropriate amounts of polyvinyl alcohol (PVA, 8 wt%) as organic binders. The green pellets were sintered at 1500 °C for 4 h in air to obtain dense pellets.

2.2. Characterization

X-ray diffraction (XRD, Rigaku D/MAX-RB) with Ni filtered Cu Kα radiation at room temperature was employed for phase purity and crystal structure identification of $BaCe_{0.8-x}Ti_xSm_{0.2}O_{3-\delta}$ ($x=0$, 0.05, 0.1) samples. The XRD data were collected over a 2θ range of 10–100° with a step size of 0.02°. Rietveld refinements on collected XRD patterns were performed using GSAS/EXPGUI software [23,24]. Scanning electron microscopy (SEM, LEO-1450) was employed to observe the surface and cross-section microstructure of dense ceramics. The relative density of the sintered pellets was measured and calculated based on Archimedes principle. The actual density (ρ_{actual}) of sample is calculated by dividing the sample mass with its volume, which is obtained by water displacement method. The theoretical density (ρ_{th}) of the samples is automatically got from the Rietveld refinement results of XRD pattern of each samples. Then the relative density (ρ%) of sample is derived from the ratio of ρ_{actual}/ρ_{th}. The elemental compositions of the prepared samples were examined by X-ray fluorescence spectrometry (XRF, Axios advanced, PANalytical B. V.), which is $Ba_{0.97}Ce_{0.79}Sm_{0.21}O_{3-\delta}$, $Ba_{0.96}Ce_{0.73}Ti_{0.06}Sm_{0.21}O_{3-\delta}$, $Ba_{0.96}Ce_{0.69}Ti_{0.11}Sm_{0.20}O_{3-\delta}$ for samples $BaCe_{0.8-x}Ti_xSm_{0.2}O_{3-\delta}$ with nominal $x=0$, 0.05 and 0.1, respectively, very close to the designed compositions.

Chemical and structural stability of the samples in CO_2 containing atmospheres were tested by annealing the sintered and crushed pellets at 650 °C for 6 h in dry 100% CO_2 and dry 10% CO_2/Ar, respectively. The resultant samples were examined by XRD to identify the phase change. The surface and cross-section micrographs of the pellets were observed by SEM. The purity of CO_2 and Ar used in the experiments is 99.99%.

Chemical and structural stability of the samples in water containing atmosphere were examined by placing the crushed samples in boiling water for 3 h. The composition and microstructure change of the treated samples were evaluated by XRD and SEM.

The infrared spectra were collected on power samples of BCS, $BCST_{0.05}$ and $BCST_{0.1}$ by Thermo Nicolet 670 with wave number ranging from 400 to 4000 cm^{-1} to illustrate the proton status in materials. Before collecting the infrared spectra, all the samples were treated at 500 °C for 10 h in wet 5% H_2/Ar ($p(H_2O)=0.074$ atm) to ensure that the proton defect concentration of the three samples to reach the maximum. Desired $p(H_2O)$ was obtained by bubbling the carrier gas through water at an identified temperature.

Electrical conductivity measurement was performed in wet 5% H_2/Ar ($p(H_2O)=0.074$ atm, 60 $mL\ min^{-1}$) from 250 to 750 °C by Solartron 1260 Frequency Response Analyzer combined with a Solartron 1287 interface controlled by the Zplot software (Advanced Measurement Technology Inc. Solartron Analytical, Type SI-1287). Ag paste was applied as current collector to both sides of the sintered pellets which were elaborately polished. Then, silver wires used as lead wire for both electrodes were attached to the surface of the pellets, followed by calcination at 700 °C for 0.5 h to remove the organic binders. The AC impedance data were collected in the frequency range from 10^6 to 0.1 Hz with a signal amplitude of 30 mV. The recorded data were fitted with appropriate equivalent circuit by Zview 2 software.

3. Results and discussion

3.1. Crystal structure and microstructure

The XRD patterns of BCS, $BCST_{0.05}$ and $BCST_{0.1}$ samples sintered