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Advanced materials for SOFC application: Strategies for the development of highly conductive and stable solid oxide proton electrolytes

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ABSTRACT

The basic strategies of improving the stability of proton-conducting electrolytes based on barium cerate ($BaCeO_3$) by means of: (i) co-doping, (ii) doping by nonmetallic elements and (iii) composites development, are considered in the present review work. The reasons of the stability enhancement in these systems, as well as the correlation between stability and electrical conductivity are also presented and discussed. On the base of literature data comparative analysis, the electrolytes with sufficient phase structural, chemical, thermal stabilities and acceptable conductivity are identified.

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1. Introduction

$BaCeO_3$ based oxides are the most widely and intensively studied materials as representative of the solid proton conductors' class [1–5]. The proton conductivity in such unique systems appears due to the interaction between water vapor and oxygen vacancies (the Kröger–Vink nomenclature is used here and further [6]):

$$V_O^{\cdot\cdot} + H_2O + O_O^x \leftrightarrow 2OH_O^{\cdot}. \quad (1)$$

The oxygen vacancies are generated within the structure by acceptor doping of the basic oxide:

$$R_2O_3 \xrightarrow{BaCeO_3} 2R_{Ce}^{/} + V_O^{\cdot\cdot} + 2Ba_{Ba}^x + 5O_O^x, \quad (2)$$

$$RO \xrightarrow{BaCeO_3} R_{Ce}^{//} + V_O^{\cdot\cdot} + Ba_{Ba}^x + 2O_O^x, \quad (3)$$

where R_2O_3 and RO are oxides of three- and bi-valent elements (for example, Y_2O_3, Gd_2O_3, In_2O_3, CaO).

The presence of the proton conductivity, which is caused by $OH_O^{\cdot}$ defects along with the oxygen conductivity and defined by $V_O^{\cdot\cdot}$, makes such co-ionic systems effective as functional materials for a number of electrochemical devices (solid oxide fuel cells (SOFC), electrolyzers, hydrogen and oxygen pumps, gas sensors, electrochemical reactors for ammonia synthesis, dehydration of alkanes, etc.) [7–9]. The application of co-ionic electrolytes in SOFC, for instance, is more effectively visibly compared with unipolar oxygen-ionic electrolytes (materials based on ZrO_2, CeO_2, (La,Sr)GaO_3, Bi_2O_3), as the conversion effectiveness of fuels' chemical energy into electricity is significantly higher [10–12].

For long time researchers have been seeking for the material with the highest proton conductivity. Thus, different groups of oxides with fluorite, braunmillerite, apatite, perovskite and some other structures were extensively studied. The perovskite structure (ABO_3) was found to be the most favorable, because it permits high concentration and mobility of proton defects [1–5].

Among investigated systems of scandates, hafnates, tantalates, indates, yttrates and zirconates of alkali-earth elements, materials based on barium cerate ($BaCeO_3$) exhibited the highest proton conductivity [1,2,4]. This may be explained from: (i) the structural perspective by the large ionic radius cation, which occupies A and B positions of ABO_3 perovskite, (ii) its relatively low electronegativity and (iii) from the microstructural perspective by the rather low grain-boundary resistance impact on the total resistance of ceramic samples.