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# Ceria-carbonate composite for low temperature solid oxide fuel cell: Sintering aid and composite effect

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## ABSTRACT

In this study, the effect of carbonate content on microstructure, relative density, ionic conductivity and fuel cell performance of  $Ce_{0.8}Sm_{0.2}O_{1.9}-(Li/Na)_2CO_3$  (SDC-carbonate, abbr. SCC) composites is systematically investigated. With the addition of carbonate, the nano-particles of ceria are well preserved after heat-treatment. The relative densities of SCC pellets increase as the carbonate content increases or sintering temperature rises. Especially, the relative density of SCC2 sintered at 900 °C is higher than that of pure SDC sintered at 1350 °C. Both the AC conductivity and DC oxygen ionic conductivity are visibly improved compared with the single phase SDC electrolyte. Among the composites, SDC-20 wt%  $(Li/Na)_2CO_3$  (SCC20) presents high dispersion, relative small particle size, and the dense microstructure. The optimized microstructure brings the best ionic conductivity and fuel cell performance. It is hoped that the results can contribute the understanding of the role of carbonate in the composite materials and highlight their prospective application.

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## Introduction

As a promising energy-conversion device, solid oxide fuel cell (SOFC) possessing many notable advantages, such as high efficiency, environmental friendly and flexibility of fuels has

received a great attention in recent years [1–3]. However, due to its relative high operation temperature (~800 °C), tremendous challenges are remained, especially in the fields of fuel cell materials and fabrication technology. Lowering the operation temperature becomes one of the hot topics in SOFC community. For years, intermediate/low-temperature solid

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oxide fuel cells (IT/LTSOFCs, below 800 °C) have been perused [3–5] with different research strategies, such as employment of thin electrolyte film and high ionic conductive electrolytes. The fluorite structural stabilized zirconia and doped ceria are common electrolyte materials for SOFCs. Unfortunately, at a reduced temperature, the conductivity of yttria-stabilized zirconia (YSZ) cannot meet the requirement. Ceria-based single phase electrolyte possessing superconductivity has been studied widely. In order to improve the  $O^{2-}$  conduction, i.e., increasing the concentration of oxygen vacancies, different lower valence cation ions are used as the dopants or co-dopant, e.g.,  $Sm^{3+}$ ,  $Gd^{3+}$  and  $La^{3+}$  [6–8]. For example, Eguchi et al. [6] studied the electrical properties of different ions doped ceria-based oxides. They found that, because of their close ionic radii to that of  $Ce^{4+}$ , samaria and gadolinia doped ceria-based (SDC and GDC) electrolytes exhibit the highest electrical conductivities. Andersson et al. [8] revealed that the ideal dopant should have an effective atomic number between 61 (Pm) and 62 (Sm) which could balance between repulsive elastic and attractive electronic interaction, leading to the optimal conductivity.

In recent years, doped ceria-based composite electrolytes have been successfully developed. Different salts [9–11] and oxides [12,13] have been chosen as the second phases for ceria-based composite electrolytes, in which ceria-carbonate composite gives the most promising characteristics: the high ionic conductivity of  $0.01\text{--}1\text{ Scm}^{-1}$  in the LT region, excellent fuel cell (FC) performances and improvement of mechanical properties compared with the single phase electrolyte. For example, a power density of  $300\text{--}1100\text{ mW cm}^{-2}$  between 400 °C and 600 °C has been obtained using these composites as electrolytes [5,14].

Extensive studies have been performed on the ceria-carbonate composite, from the aspects of preparation methods and parameters, composition, ionic conductivity, materials interaction, FC performance and stability. For instance, the effects of different kinds of carbonates, e.g.,  $(Li/Na)_2CO_3$ ,  $(Li/K)_2CO_3$  and  $(Na/K)_2CO_3$  on the electrical performances of ceria-carbonate composite were investigated by Huang et al. [15]. The FC with SDC- $(Li/Na)_2CO_3$  electrolyte exhibits the best performances. Xia et al. [16] tried to reveal the relationship between the microstructure and ionic conductivity of doped ceria- $(Li/Na)_2CO_3$  composites by varying the heat-treat temperatures. It has been revealed that 675 °C is the optimized sintering temperature for obtaining good microstructure as well as high conductivity. In our previous studies, the electrical properties of ceria-carbonate composites have also been deeply studied. The conductivities of SCC composites were measured and compared in various atmospheres (argon, air and hydrogen) and the concentration cells [17]. Furthermore, through optimizing the composite electrolyte fabrication process and measurement technology, an impressive power density of  $916\text{ mW cm}^{-2}$  has been obtained at 550 °C [18]. Significant improved electrochemical performance was ascribed to the hybrid-ionic conduction. The hybrid  $H^+/O^{2-}$  conduction behavior was latterly proved by the DC four probe method in hydrogen and oxygen conditions [19]. In addition, Mizuhata's group in Japan devoted to study the interaction between inorganic materials and carbonates by polarized Raman spectroscopy. The symmetrical

stretching mode of carbonate is slightly disturbed by the presence of ceria-based oxide and the ceria-carbonate gives a higher stability compared with  $Al_2O_3$ -carbonate composite [20]. Recent works from the France group leading by Professor Cassir M. demonstrated that the ceria-carbonate composite showed a stable ionic conductivity over 6000 h [21,22]. And Prof. Tao et al. [23] reported that the FC with ceria-carbonate composite and perovskite oxide cathode presented a stable 100 h nonstop operation in hydrogen/air condition. The ceria-carbonate has been come a star but magical material in LTSOFC field.

On the other hand, one of the general requirements for electrolyte layer is its densification to avoid the gas-cross during FC operation. For most single phase electrolyte materials, sintering temperature up to 1400 °C is needed [24]. However, such high temperature results high energy consumption, also causes detrimental reaction between cell components and the sintering of cermet anode. Fortunately, decreasing sintering temperature by adding sintering aids has been proved to be an effective solution. Various transition metal oxides, such as ZnO, CuO and  $Co_2O_3$  [25], could reduce the required sintering temperature by 100–200 °C. But it should be noted that the transition metal oxide aids may result reduced ionic conductivity and induced electronic conductivity [26]. Recently, lithium compounds including  $LiNO_3$  [27],  $Li_2O$  [28] and LiF [29] were used as sintering aids for doped ceria oxide electrolytes. For example, the addition of  $LiNO_3$  [27] reduced the sintering temperature to 800 °C and the resulting dense electrolyte got a relative density of 96%. The lithium salts/oxides bring complex but interesting results, such as (1) lowering sintering temperature; (2) increasing ionic conductivity and lowering electronic conduction; (3) enhancing the mechanical properties [27–29]. However, few papers examined the effect of  $Li_2CO_3$  as a sintering aid on the densification of doped ceria electrolyte, and hence the electrochemical performances of the ionic conductor.

In this paper,  $Li_2CO_3$  was used as the sintering aid for ceria based electrolyte. To make an effective comparison and reduce the superionic phase transition temperature, it is combined with  $Na_2CO_3$  in the molar ratio of 52Li: 48Na to form a binary carbonate eutectic with a melting temperature around 490 °C. Especially, the electrical composite effect is also investigated for probably use as electrolyte for ITSOFC. The effect of carbonate content from 0 to 40 wt% on the microstructure, relative density, AC and DC conductivity and subsequent FC performance is systematically investigated.

## Experimental

### Preparation of the composite electrolyte

$Ce(NO_3)_3 \cdot 6H_2O$ ,  $Sm_2O_3$  and concentrated  $HNO_3$  were used as raw materials.  $H_2C_2O_4 \cdot H_2O$  was employed as precipitant. The preparation procedure is similar to the early report [30].  $Ce(NO_3)_3 \cdot 6H_2O$  and  $Sm_2O_3$  were first dissolved in deionized water with the assistance of concentrated  $HNO_3$ .  $H_2C_2O_4 \cdot H_2O$  solution was dropped into metal nitrate solution with  $H_2C_2O_4$ : cation ions of 2:1 under stirring. Then the precipitate was filtered, rinsed with deionized water for three times. The

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