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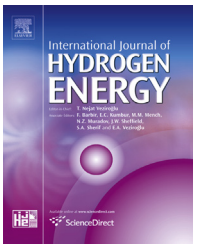

Synthesis and characterization of B-site doped $La_{0.20}Sr_{0.25}Ca_{0.45}TiO_3$ as SOFC anode materials

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ABSTRACT

In this paper, B-site doping of an optimized A-site deficient composition, calcium-doped lanthanum strontium titanate, $La_{0.2}Sr_{0.25}Ca_{0.45}TiO_3$ ($LSCT_{A-}$) with Ni and Fe is presented. The doped compositions were successfully synthesized by the Pechini method and then characterized by XRD, SEM, dilatometry, ac impedance, and dc conductivity. The doped analogues preserved the orthorhombic symmetry of the parent, $LSCT_{A-}$. The observed dilatometric results were correlated with the particle size. Ac impedance studies revealed their semi-conducting behaviour in air. Furthermore, the doped compositions showed higher conductivity values in reducing atmosphere. Compared to bare pre reduced $LSCT_{A-}$ having conductivity of 38 S cm^{-1}, the pre reduced 5% Ni doped $LSCT_{A-}$ (LSCTN5) and 5% Fe doped $LSCT_{A-}$ (LSCTF5) showed conductivity values of 47 S cm^{-1} and 66 S cm^{-1} at 880 °C, respectively. B-site doping could affect the electrical and catalytic properties of $LSCT_{A-}$ materials making them viable alternatives for fuel cell applications.

Introduction

The innate limitations of Ni/YSZ have led scientists and researchers to modify Ni/YSZ cermet as well as to explore alternative anode materials for solid oxide fuel cells (SOFCs) [1,2]. In this aspect, Ni/YSZ has been modified by replacing Ni with other metals like Ru or Cu and replacing YSZ with other alternate oxide ion conductors such as ceria stabilized zirconia, calcium-doped ceria, yttria-doped ceria, titania doped yttria stabilized zirconia or samarium doped ceria.

The modification and improvement of metal cermets have resulted in good performance using either hydrogen or methane as the fuel however none of them is as efficient as Ni/YSZ. However, the issues related with the metal cermets like sintering and volume instability yet need to be addressed. To reduce the structural mismatch between the anode and the electrolyte, single phase oxide anodes have been developed. Major attention has been given to mixed ionic and electronic oxides because these result in enhancement of reaction zone over the three phase boundary thereby affecting the reaction kinetics. The anode development for SOFCs has been detailed in various reviews [3–6].

Among single phase oxides, perovskites have gained major interest due to good stability and reasonable electronic conductivity in reducing conditions. The general formula of perovskite oxides is ABO_3 where A and B cations are 6-fold and 12-fold coordinated to the oxygen anions, respectively. The structure consists of BO_6 octahedra sharing the corners of the cube containing the A cation at the centre. The A-site is

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usually occupied by alkaline earth and/or rare earth metal ions while small transition metal ions (usually from 3d series) occupy the B site.

The structures, redox properties, conductivity as well as the electro-catalytic properties of the parent perovskite are largely affected by B site dopants [7]. The B-site network plays its role in electronic conduction in perovskites. The existence of multiple oxidation states of the transition metals at B-site such as Ti, Cr, Mn or Mo facilitate electronic conductivity due to electron hopping from $B^{(n-1)+}$ to B^{n+} cations. Thus, one of the strategies to improve the electrical conductivity is via B-site doping.

In the family of perovskites, titanate-based oxides have good stability and reasonable n-type electronic conductivity in reducing conditions. In reducing conditions, Ti^{+4} reduces to a lower oxidation state accompanied by creation of oxygen vacancies as the lattice oxygen is removed. The electronic charge carriers formed in this process (see the equation below) take part in enhancing the conductivity [8];

$$2Ti_{Ti}^{X} + O_{O}^{X} \rightarrow 2Ti_{Ti}^{'} + V_{\ddot{O}} + \frac{1}{2}O_2 \quad (1)$$

This defect chemistry makes them attractive as potential anode materials for SOFCs. Among titanates, $SrTiO_3$ has always remained in focus due to its good electronic conductivity in fuel cell conditions and its resistance to sulphur which is one of the limitations of Ni-YSZ cermet anodes. Both A and/or B sites of the strontium titanate have been doped to tune and tailor its properties. Special attention has been given to enhance its electrical conductivity by partial substitution of Sr^{2+} on A-site and/or Ti $^{4+}$ on B site [9,10].

The effect of calcium doping on A-site deficient lanthanum strontium titanate was investigated earlier which showed enhancement of its electrical conductivity and maximum conductivity was observed for $La_{0.20}Sr_{0.25}Ca_{0.45}TiO_3$ ($LSCT_{A-}$) composition [11]. Furthermore, the same composition was tested as an anode in fuel cell conditions where good performance was achieved [12]. Recently, we have reported the solution phase synthesis of $LSCT_{A-}$ [13].

In this work, we investigated the effect of B-site doping on the conductivity of $LSCT_{A-}$. Fe and Ni were chosen as B-site dopants having good catalytic activity. Additionally, the doping level (1% and 5%) was kept low to have good solubility and preservation of dense network of Ti on B-site of perovskite. The doped compositions were synthesized, characterized and investigated for dc conductivity.

Experimental

All materials were prepared by modified Pechini method described previously [11]. Briefly, an aqueous solution containing stoichiometric amounts of metal salts was mixed with a solution of ethylene glycol and citric acid in a fixed molar ratio of 1:16:4. The resulting solution was heated on the hot plate at 80–100 °C. The obtained viscous gel was dried and calcined in air at 1000 °C for 5 h to get the powders. Room temperature powder X-ray diffraction (XRD) was performed on a Philips XRD diffractometer using Cu-Kα_1 radiation in the 2θ range of 20° to 80° in the reflection mode. Diffraction peaks were fitted with STOE WinXPOW software to calculate the values of lattice parameters. The morphology of the sintered pellets was studied using a JEOL 5600 scanning electron microscope. Sinterability of the doped analogues was investigated using a Netzch DIL 402C instrument. For dilatometry, powder was pressed into pellets of 13 mm diameter under pressure of 1 ton and heated in air in the dilatometer to 1400 °C. For ac impedance, the pellets were sintered in air at 1400 °C for 6 h and the surface of sintered pellets was polished and coated with Pt paste which was then consolidated at 900 °C for 1 h. Impedance data were taken using a Solartron 1260 impedance/gain phase analyzer in the frequency range of 1 Hz–13 MHz. The measured impedance data were analyzed by the Z view program. van der Pauw method was used to measure dc conductivity of the synthesized samples. The observed conductance value was corrected for samples' thickness and area. The geometry was determined by measuring the dimensions (thickness and diameter) of the sintered pellets before conductivity measurements. Table 1 lists the investigated doped analogues of $LSCT_{A-}$.

Results and discussion

Crystal structure of doped samples

XRD patterns of as prepared doped analogues show characteristic reflections of perovskite crystal structure as shown in Fig. 1. Similar XRD pattern was observed in all compositions and no impurity peak was detected in any of X-ray diffraction patterns displaying full solubility of these dopants up to the doping level added. XRD of parent $LSCT_{A-}$ is also given for comparison.

The ionic radii of Fe^{+3} (0.645 Å) and Ni^{+2} (0.690 Å) are greater than that of Ti^{+4} (0.605 Å) thus unit cell volume is expected to increase with these dopants. The ionic radii of Ni^{+2} is greater than Fe^{+3} so it is anticipated that Ni^{+2} doping would result in more expansion in unit cell volume. Similar trend was noticed in XRD pattern where the peaks shifted slightly to low angle theta upon doping. The shifting suggests that Ti^{+4} was successfully substituted by larger Ni^{+2} and Fe $^{+3}$ ions.

The peaks were indexed in orthorhombic symmetry with space group Pbnm using WinXPOW software. An increase in lattice parameters was observed upon doping with Fe and Ni. The variation of lattice parameters and volume *V* in the doped compositions is presented in Table 2 where the trend can be explained by considering the ionic sizes of the dopants.

It can be seen that the doping results in an expansion of unit cell. The expansion in volume with Ni^{+2} as dopant is more than Fe^{+3} in accordance with their sizes.

Table 1 – Studied doped analogues of $LSCT_{A-}$.

Doped analogues	Codes
$La_{0.2}\ Sr_{0.25}\ Ca_{0.45}\ Ti_{0.99}\ Ni_{0.01}\ O_3$	LSCTN1
$La_{0.2}\ Sr_{0.25}\ Ca_{0.45}\ Ti_{0.95}\ Ni_{0.05}\ O_3$	LSCTN5
$La_{0.2}\ Sr_{0.25}\ Ca_{0.45}\ Ti_{0.99}\ Fe_{0.01}\ O_3$	LSCTF1
$La_{0.2}\ Sr_{0.25}\ Ca_{0.45}\ Ti_{0.95}\ Fe_{0.05}\ O_3$	LSCTF5

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