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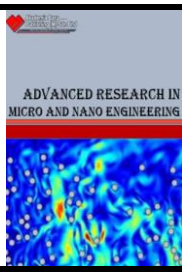

Synthesis, Structure and Characterization of $Sr_{0.9}Y_{0.1}Ti_{1-x}V_xO_3$ (x = 0.1, 0.2) Anodes for Solid Oxide Fuel Cell

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ABSTRACT

The current anode materials used in solid oxide fuel cells face challenges regarding their thermal stability and performance under varying operating conditions with the commonly used electrolyte (yttria stabilized zirconia), prompting the need for the development of alternative anode materials with superior thermal compatibility. $Sr_{0.9}Y_{0.1}Ti_{1-x}V_xO_3$(x=0.1, 0.2) was synthesized via the traditional solid-state reaction method and characterized as potential anode materials for SOFCs. The crystal structure, phase purity, electrical conductivity, and microstructure of the synthesized materials were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), thermogravimetric analysis (TGA), and conventional four-probe techniques. Results obtained from the experimental investigations showed a negligible weight loss in $Sr_{0.9}Y_{0.1}Ti_{1-x}V_xO_3$(x=0.1, 0.2) samples of about 18.81%, and a 2.2% weight gain for x = 0.2. The negligible weight loss indicates that $Sr_{0.9}Y_{0.1}Ti_{1-x}V_xO_3$(x=0.1, 0.2) would be a highly stable material under the high operating temperature of SOFC. At 900 ℃, the electrical conductivity in air for $Sr_{0.9}Y_{0.1}Ti_{1-x}V_xO_3$(x=0.1, 0.2) was measured to be 0.32 Scm^{-1} and 0.2042 Scm^{-1}, respectively. The result of linear thermal elongation investigation revealed that $Sr_{0.9}Y_{0.1}Ti_{1-x}V_xO_3$(x=0.1, 0.2) has a favourable thermal expansion coefficient. This will help reduce the challenges of thermal compatibility associated with commonly used electrolytes in SOFC.

1. Introduction

Solid Oxide Fuel Cell (SOFC) is a technological device that produces electricity through the direct oxidation of fuels (usually hydrogen). SOFC is known for its high energy density, low emissions, and a good alternative solution for clean energy generation. It offers significant advantages since it can operate at high temperatures (800 – 1000 ℃), enabling it to use a variety of fuels without the need for a complex and expensive external reformer [1].

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Critical to the performance and commercial viability of SOFCs is the development of advanced materials for their various components, including the anode, cathode, and electrolyte [2]. The anode plays a vital role in SOFC performance, as it serves as the site for the electrochemical oxidation of fuel, typically hydrogen, methane, or other hydrocarbons. Over the last two decades, extensive research efforts have focused on enhancing anode materials to improve their electrocatalytic activity, stability, and durability at the high operating temperatures of SOFCs. One class of materials that has garnered significant attention in recent years are perovskite oxides [3]. Perovskite oxides are known for their versatile properties, excellent crystal structure, and tunability. This group of metal oxides has demonstrated great potential as anode materials in SOFC applications. The tunability of perovskite materials allows for the optimization of their electrical conductivity, thermal expansion coefficients, and catalytic activity, making them promising candidates for several energy conversion devices.

Figure 1 illustrates the traditional SOFC and its various components. The primary challenge with conventional anode materials, such as nickel-based cermet, is their susceptibility to coking and carbon formation during fuel cell operation [4]. Carbon deposition onto the anode surface leads to reduced electrochemical activity, resulting in performance degradation and the need for frequent maintenance. This issue is particularly acute when using hydrocarbon-based fuels, such as natural gas. Another significant challenge arises from the thermal expansion mismatch between the anode, electrolyte, and cathode components [5]. During the high operating temperature of SOFC, such mismatch can lead to mechanical stress, microcracking, and ultimately, the failure of the cell. These challenges limit the long-term durability of fuel cells. The SOFCs are sensitive to impurities present in fuel streams, especially sulphur compounds. Conventional nickel-based anodes are prone to sulphur poisoning, leading to a decrease in cell performance and requiring additional purification steps for fuel streams, adding complexity and cost to the system design.

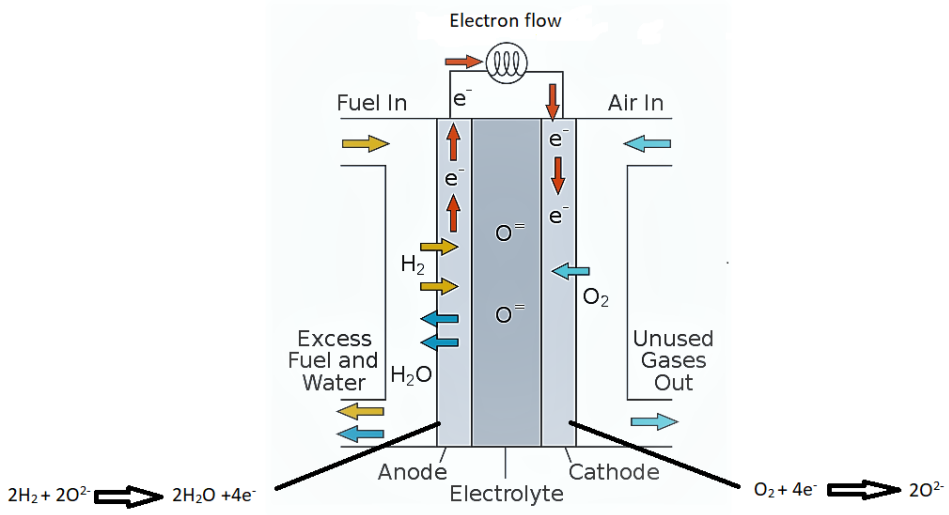

Fig. 1. Convectional SOFC and its basic components

Yttrium-doped strontium titanate (STO) has emerged as a promising candidate for anode material in SOFC due to its advantageous properties, which include redox stability, compatibility with other cell components, and a favourable tolerance for sulphur coking [6]. When yttrium is introduced onto the A-site of the STO, it induces a compensatory transition from Ti^{4+} to Ti^{3+} under ambient air and low oxygen partial pressure conditions, which is accomplished through the creation of oxygen vacancies. This dual conductivity exhibited by STO under fuel-related conditions makes it catalytically

active for methane (CH_4) oxidation, with performance levels similar to Ni/YSZ cermet anodes at high operating temperatures [7]. Liu *et al.,* [8] investigated the effect of strontium-doped lanthanum vanadate on crystal structure, conductivity and vanadium valence state of a $La_{1-x}Sr_xVO_3$ anode for SOFC application. The material was synthesized via a solid-state reaction technique. The varying of x (0-1) alters the material's properties from antiferromagnetic insulator to metallic conductor. XRD reveals structural changes to a more symmetrical perovskite phase, while XPS confirms V's valence change, impacting conductivity via exchange interactions and charge transfer mechanisms. Despite their unique findings, investigations into linear thermal expansion revealed low thermal compatibility of this material with commonly used electrolytes. This issue may be attributed to lanthanum, which experiences nearly 15% weight loss at high temperatures [9,10]. Lee *et al*., [11] investigated $Sr0_{0.92}Y_{0.08}TiO_{3-\delta}$ (SYT) as an alternative anode for solid oxide fuel cells (SOFC) using humidified CH_4 fuel, comparing it with the conventional Ni/yttria-stabilized zirconia (Ni/YSZ) anode. The cell performance of SYT decreased by 20% compared to the 58% decrease observed with the Ni/YSZ anode. Severe degradation of cell performance in the Ni/YSZ anode resulted from carbon deposition due to methane thermal cracking. Carbon was significantly less detected in the SYT anode due to catalytic oxidation, while a substantial amount of bulk carbon was found in the Ni/YSZ anode. Several studies have also reported the use of similar materials as anodes in SOFC, resulting in improved electrochemical performance [8,11–16]. Nevertheless, the material's performance is still considered inadequate due to its high operating temperature requirement and limited electronic conductivity. The substitution of vanadium ions at the B-site offers a potential avenue for enhancing oxide ion conductivity and other catalytic properties. In the present study, $Sr_{0.9}Y_{0.1}Ti_{1-x}V_xO_3$ (x=0.1, 0.2, YVST-1) was synthesized and analyzed as possible anode materials for solid oxide fuel cells. The findings from this study reveal a highly stable material with negligible weight changes and a promising thermal expansion coefficient.

2. Experimental

High-purity powders of $Sr_{0.9}Y_{0.1}Ti_{1-x}V_xO_3$ (x=0.1, 0.2, YVST-1, YVST-2) were synthesized via conventional solid-state reaction technique, using commercial precursors of SrO, TiO_2, V_2O_5 and Y_2O_3. The precursors were mixed in stoichiometric ratio using acetone as the mixing reagent. The resulting homogenous mixture was ball milled for 24 hours, which was then dried in an oven at a temperature of 70 ℃ for 2 hrs. The synthesized samples were calcined at 1100 ℃ for 4 hrs at a heating and cooling rate of 4 ℃min^{-1}. The calcined samples were then pressed into pellets before being fired in the air at 1450 °C for 2.5 hrs at a heating and cooling rate of 4 °Cmin^{-1}. Table 1 presents the chemical compositions of the synthesized anode materials.

Table 1
Chemical composition of synthesized $Sr_{0.9}Y_{0.1}Ti_{1-x}V_xO_3$ (x=0.1, 0.2, YVST-1, YVST-2)

Composition	abbreviations	Sintering temperature (℃)
$Sr_{0.9}Y_{0.1}Ti_{0.9}V_{0.1}O_3$	YVST-1	1450
$Sr_{0.9}Y_{0.1}Ti_{0.8}V_{0.2}O_3$	YVST-2	1450

The crystal structure of the powder samples was investigated using X-ray diffraction (XRD), which was performed on a Shimadzu XRD-7000 (Cu, Kα1 radiation). The obtained XRD profiles were analyzed to determine the crystal structure and cell parameters. Checkcell software was used to index the peak position of the synthesized anode materials. The weight loss as a function of temperature changes was investigated with the aid of thermogravimetric analysis (TGA) and the coefficient of thermal elongation was obtained using dilatometers. The electrical conductivity of the

materials was measured using the conventional four-probe technique. The surface morphology was obtained using a scanning electron microscope (SEM), and energy dispersive X-ray (EDX) spectroscopy was used to obtain information on the chemical composition of the synthesized anode materials.

3. Results and Discussion

3.1 Structural Characterization and Conductivity Measurement

X-ray diffraction (XRD) analysis confirmed that YVST-1 and YVST-2 samples formed a cubic structure when sintered in air at a temperature of 1450 ℃. The phase formation and indexing were confirmed using checkcell software as pm-3m. The obtained structures are consistent and in agreement with other reported cubic materials [17]. Figure 2 illustrates the x-ray diffraction profiles obtained for the synthesized anode materials at 2θ to 80 °. The peak positions which were indexed via checkcell are indicated as delta (Δ) and asterisk (*) in the XRD profile [18]. The diffraction profiles exhibited sharp and well-defined peaks, indicating a high degree of crystallinity and phase purity. Notably, the major diffraction peaks observed at 2θ between 25° to 70 ° closely matched the expected positions for the pm-3m space group described in various literature [19]. The cell parameters obtained from checkcell are in agreement with those obtained for cubic structures [20].

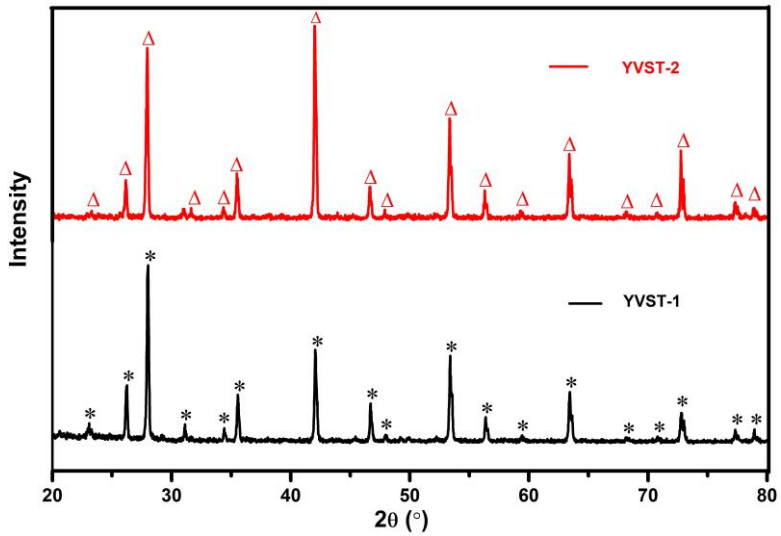

Fig. 2. X-ray diffraction profile of YVST-1 and YVST-2

A scanning electron microscope (SEM) was employed to examine the microstructural of YVST-1 and YVST-2 anode materials. The micrographs obtained provided valuable insights into the surface morphology, and particle size distribution of the synthesised anode materials. Figure 3 illustrates the micrograph for both compositions. SEM analysis revealed that the YVST-1 anode material has uniform particle distribution, and YVST-2 displayed a more porous structure with an irregular distribution of particles. YVST-1 has a larger particle size of about 25 µm compared to that of YVST-2, which has 15 µm. To further characterize the chemical composition of YVST-1 and YVST-2 anode materials, EDX analysis was conducted. The EDX profile in Figure 3 confirmed that YVST-1 and YVST-2 are composed of yttrium (Y), vanadium (V), strontium (Sr), and titanium (Ti) in the expected proportions. Moreover, the absence of any significant impurities indicates the high purity of the synthesized anode materials.

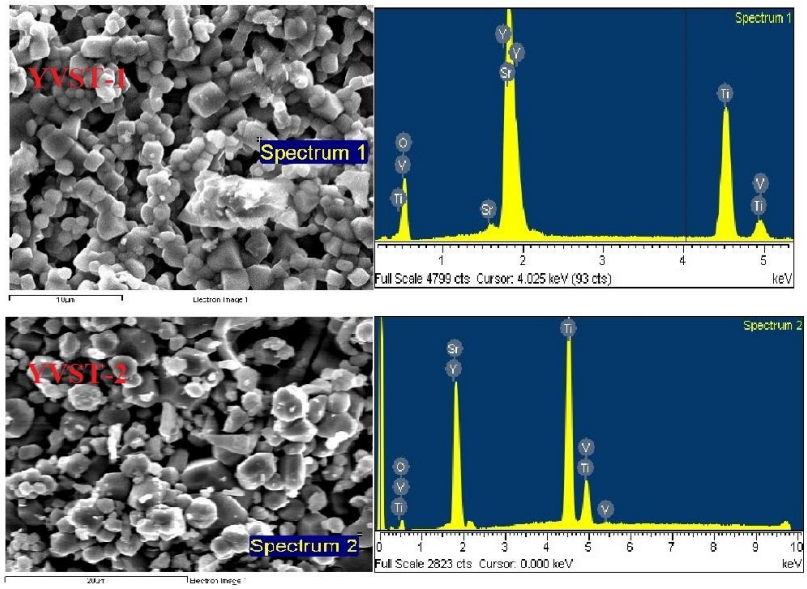

Fig. 3. SEM and EDX profiles for YVST-1 and YVST-2 anode materials

The thermal expansion coefficient (TEC) of YVST-1 and YVST-2 was investigated from 20 ℃ to 900 ℃. The TEC values of the synthesized samples are close to those reported for yttrium stabilized zirconia (YSZ), which show favourable thermal compatibility of the synthesized materials with ideal electrolyte (TEC~ 10.8 x 10^{-6} K^{-1}) [21]. Figure 4 shows the effect of increasing temperature on the thermal elongation of both materials. The favourable TEC suggests that YVST-1 and YVST-2 will be potential anode materials for SOFC, where dimensional stability under thermal cycling is an important factor.

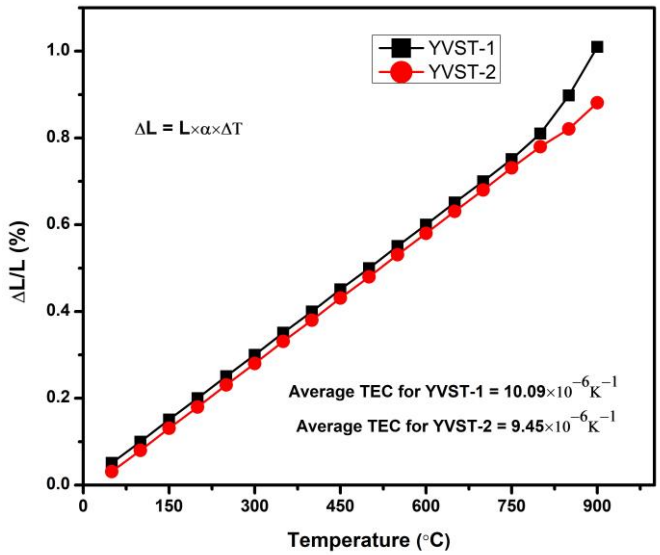

Fig. 4. Profile of thermal expansion analysis of $Sr_{0.9}$ $Y_{0.1}$ $Ti_{0.9}$ $V_{0.1}$ O_3 (YVST-1) and $Sr_{0.9}$ $Y_{0.1}$ $Ti_{0.8}$ $V_{0.2}$ O_3 (YVST-2)

The percentage weight change was investigated to understand the stability of YVST-1 and YVST-2 anode materials at 20 – 1000 ℃. Thermogravimetric analysis of both samples is illustrated in Figure 5. YVST-1 showed a total weight loss of 18.81%. The decrease in weight at around 100 ℃ could be

attributed to the evaporation of moisture from the sample, and further weight loss beyond this temperature is related to the formation of oxygen vacancy in the samples. For YVST-2, a noticeable weight gain of around 2.28% was observed beyond 95 ℃, this could be attributed to the redox-active component in the sample. As temperature rises, this causes the YVST-2 to undergo reversible oxidation and reduction reactions, leading to the evident weight gain.

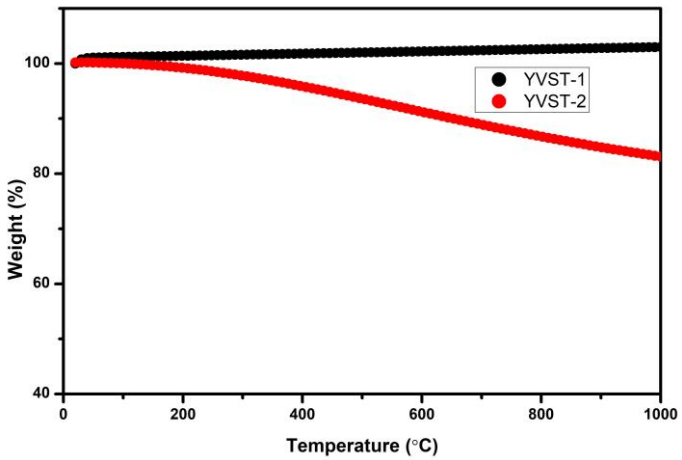

Fig. 5. Percentage weight change in YVST-1 and YVST-2 as a function of temperature

The electrical conductivity of the samples was measured in air with the aid of the traditional DC four-probe technique at 500 to 1000 ℃. As shown in Figure 6, the electrical conductivity of both materials increased with an increase in temperature. This behaviour is consistent with other reported electrical conductivities for anode materials in SOFC. At 900 ℃, YVST-1 and YVST-2 have an electrical conductivity of 0.32 Scm^{-1} and 0.2042 Scm^{-1}. The obtained electrical conductivity for both samples agree with those reported in the literature, as anode materials generally exhibit lower electrical conductivity in the air compared to their cathode counterparts [22].

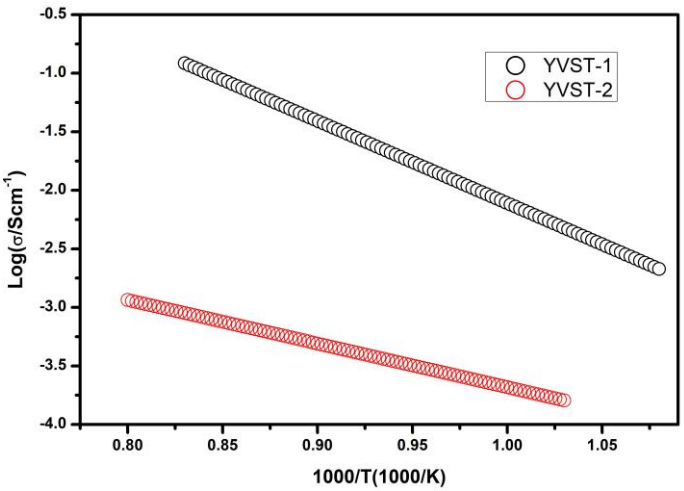

Fig. 6. Log of conductivity versus temperature graph for YVST-1 and YVST-2

4. Conclusions

The experimental investigations of YVST-1 and YVST-2 have revealed a good average linear thermal expansion coefficient of 10.09 $*10^{-6}K^{-1}$ and $9.45*10^{-6}K^{-1}$, respectively. This matches that of the commonly used electrolyte (YSZ) in SOFC, which stands at 10.8 x 10^{-6} K^{-1}. The good coefficient of linear thermal expansion of these materials will minimize thermal stress and prevent cracking or delamination during thermal cycling. YVST-1 and YVST-2 also possess adequate porosity and permeability, which will allow the efficient diffusion of fuel molecules to the catalytically active sites within the anode, promoting the fuel oxidation reaction in SOFC. Based on the findings from these experiments, we can conclude that YVST-1 and YVST-2 are potential anode materials for SOFC.

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