

SYNTHESIS AND CHARACTERIZATION OF $\text{Sr}_2\text{Fe}_{0.75}\text{Ti}_{0.25}\text{MoO}_{6-\delta}$ AS ANODE FOR SOLID OXIDE FUEL CELL

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ABSTRACT

$\text{Sr}_2\text{Fe}_{0.75}\text{Ti}_{0.25}\text{MoO}_{6-\delta}$ has been synthesized in solid state reaction method and characterised as a potential anode material for solid oxide fuel cells. Rietveld refinement of X-ray powder diffraction data of the composition using Fullprof software shows that the materials crystallize in the tetragonal symmetry in the $I4/m$ space group. The cell parameters are: $a = b = 5.3711 \text{ \AA}$, $c = 11.9823 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$. SEM image indicates a porous but compact morphology. Addition of titanium to the B-site of $\text{Sr}_2\text{Fe}_{0.75}\text{Ti}_{0.25}\text{MoO}_{6-\delta}$ yields a total conductivity $3.78 \times 10^{-5} \text{ S cm}^{-1}$ of in air at 800°C with activation energy of 0.142 eV .

Keywords: Anode; Double Perovskite; Electrical Conductivity; Solid Oxide Fuel Cell; X-ray Diffraction

INTRODUCTION

Solid oxide fuel cell (SOFC) has drawn considerable attentions from worldwide researchers in the past few decades as one of the cleanest and most efficient power generation devices[1-3]. A significant advantage of SOFCs lies in the high flexibility of fuel choices which allows direct utilization of hydrocarbon fuels without any pretreatment. Conventional nickel/electrolyte composite anodes show good performance using pure H_2 fuel. However, such anodes have disadvantages such as poor redox stability, carbon deposition and sulfur poisoning when used on natural gas. The nickel particles also tend to agglomerate after prolonged exposure to the fuel. These factors remain as the motivation of this research [4-5].

Mixed ionic and electronic conductors (MIECs) as anode materials for SOFC have attracted much attention recent years due to their excellent resistance to sulfur poisoning and carbon deposition, high thermochemistry stability and extended triple phase boundary (TPB)[6-8]. The most investigated MIEC anode materials include fluorite-type($\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$), perovskite- type($\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$), tungsten bronze-type ($\text{Sr}_{0.6}\text{Mg}_x\text{Nb}_{1-x}\text{O}_{3-\delta}$) and pyrochlore-type ($\text{Gd}_2\text{Ti}_2\text{O}_7$) materials [9].

In recent years, double perovskite receives much attention due to wide properties they present. The structure of the double perovskite, $A_2B'B''O_{6-\delta}$ is derived from that simple perovskite ABO_3 where B-cation site is occupied by 2 different cation, B' and B'' normally transition metals whereas A is occupied by alkaline earth metals [10-11]. One of the most popular perovskite electrode is $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ since it can be used both as anode and a cathode for SOFCs in a symmetrical configuration owing to its good redox stability and catalytic activity both in a reducing and oxidizing environment. It has also been investigated as a ferromagnetic material and is stable in reducing atmospheres due to the protection of the Mo^{4+}/Mo^{5+} redox couple that prevents Fe^{3+} from being reduced to Fe^{2+} . Generally, substituting fully or partially at the A or B site can be an effective way to improve the performance of the anode. Studies has been done on $Sr_{2-x}Sm_xMgMoO_{6-\delta}$ [12], $Sr_2MMoO_{6-\delta}$ (M=Mg, Mn, Fe, Co & Ni) [13], $Sr_2FeTiO_{6-\delta}$ [14] and Al-doped $SrMgMoO_{6-\delta}$ all have shown significant increase in electrical conductivity and power density.

In this study, we will look into the structural and electrical characterization of Ti doped $Sr_2FeMoO_{6-\delta}$ by altering the ratio of iron and titanium on the B site.

EXPERIMENTAL

Sample Preparation

Powders of $Sr_2Fe_{0.75}Ti_{0.25}MoO_{6-\delta}$ were synthesized by the solid state sintering method. A total of 16.149 g of $Sr_2Fe_{0.75}Ti_{0.25}MoO_{6-\delta}$ was made by adding the following powders: 7.384 g of SrO (Merck Aldrich, 99.9%), 5.926 g of $(NH_4)_6Mo_7O_{24} \cdot 2H_2O$ (Merck Aldrich, 99.9%), 2.129 g of Fe_2O_3 (Merck Aldrich, 99.9%), 0.710 g of TiO_2 (Merck Aldrich, 99.9%) as according to the stoichiometry. Powders were mixed with ethyl alcohol and ball milled overnight and evaporated. About 2.0 g of the powder was pressed with a Kennedy hydraulic press at 3 tonnes in 20 mm radius die to make a pellet. The pellets were sintered at 1100 °C first by using a Nabertherm furnace. The pellets were again crushed and powders pelletized using the same condition and sintered at 1350 °C until a single phase is achieved.

Characterization

The phase purity and crystal parameter were examined at room temperature by using a Shimadzu 7000 X-ray diffractometer using $CuK\alpha_1$ wavelength $\lambda = 0.15406$ nm at 40 kV and 30 mA and a scan speed of 1.0 deg/min. The experiment data were refined by a Rietveld method using the Fullprof program. Winplotr which is available within the suit was used for powder diffraction data viewing and processing, peak profiling and indexing. The morphology was taken by a scanning electron microscope. SEM images were collected using a JEOL-2011 electron microscope. The SEM data were collected with a voltage of 1.00 kV and with magnification of 1000 times.

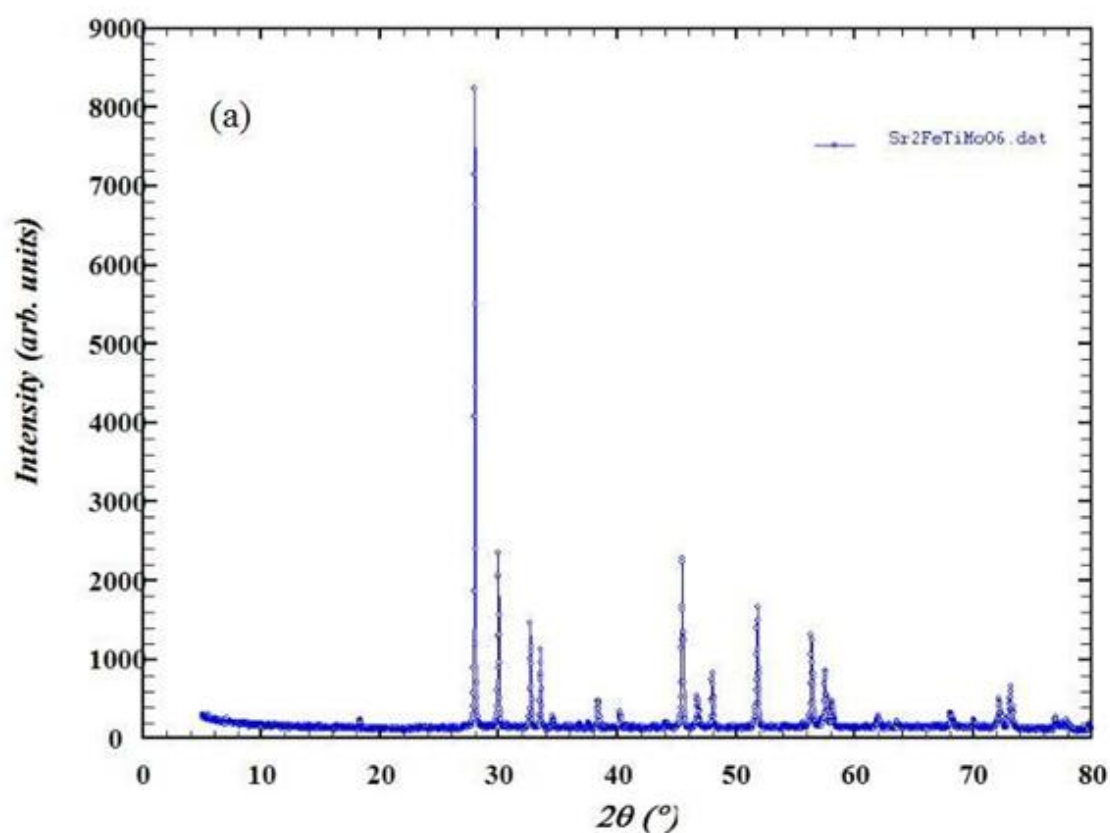
Resistivity and conductivity was measured by a homemade DC four-probe setup in air over the temperature range of 100 °C to 800 °C. Platinum wire and platinum paste were used as a current collector. The electrical resistivity (ρ) was calculated by

$$\rho = RS/L \quad (1)$$

where S is the cross-sectional area and L is the length of the measured section. The conductivity (σ) was obtained by the reciprocal of the resistivity. An Arrhenius plot is obtained to determine the activation energy.

RESULTS AND DISCUSSION

Phase and Structural Characterization



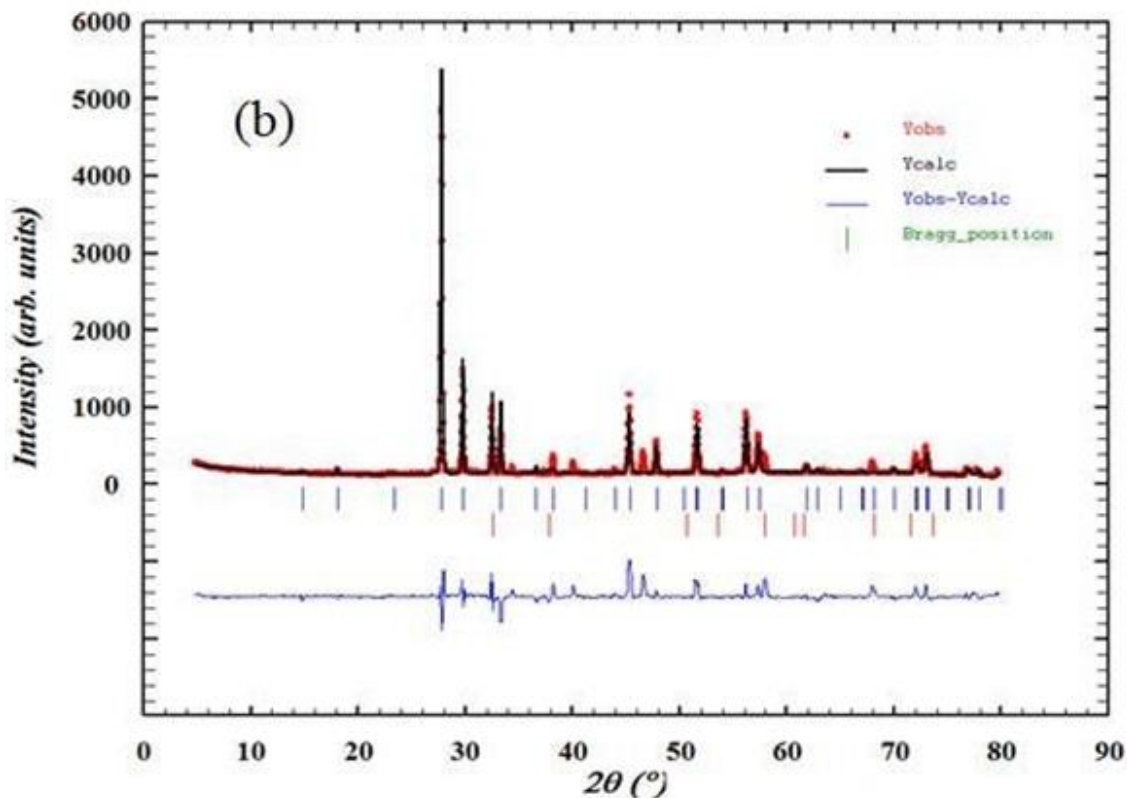


Figure 1(a): Room temperature XRD of $\text{Sr}_2\text{Fe}_{0.75}\text{Ti}_{0.25}\text{MoO}_{6-\delta}$ and (b). XRD Rietveld plot of $\text{Sr}_2\text{Fe}_{0.75}\text{Ti}_{0.25}\text{MoO}_{6-\delta}$. Observed line (red) and calculated (black) XRD intensity profiles for SFTM.

The room temperature XRD powder patterns were indexed to know the single phase nature of the samples and to find the symmetry and cell parameters. Figure 1(a) shows the X-ray powder diffraction patterns and Figure 1(b). shows the Rietveld refinement profile on the SFTM sample. The compound has a tetragonal crystal structure with $I4/m$ spacegroup, which corresponds to a $\sqrt{2}ap \times \sqrt{2}ap \times 2ap$ superstructure. Structure parameters and cell volume are obtained from the Rietveld analyses. The cell parameters was found to be $5.3711 \text{ \AA}$, $c = 11.9823 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$, cell volume, $v = 345.6816 \text{ \AA}^3$ and $\chi^2 = 5.97$. The extra observed peaks can be indexed as TiO_2 and is less than 5%. Since χ^2 value is very reasonable and profile matching is good, therefore we accept the refinement.

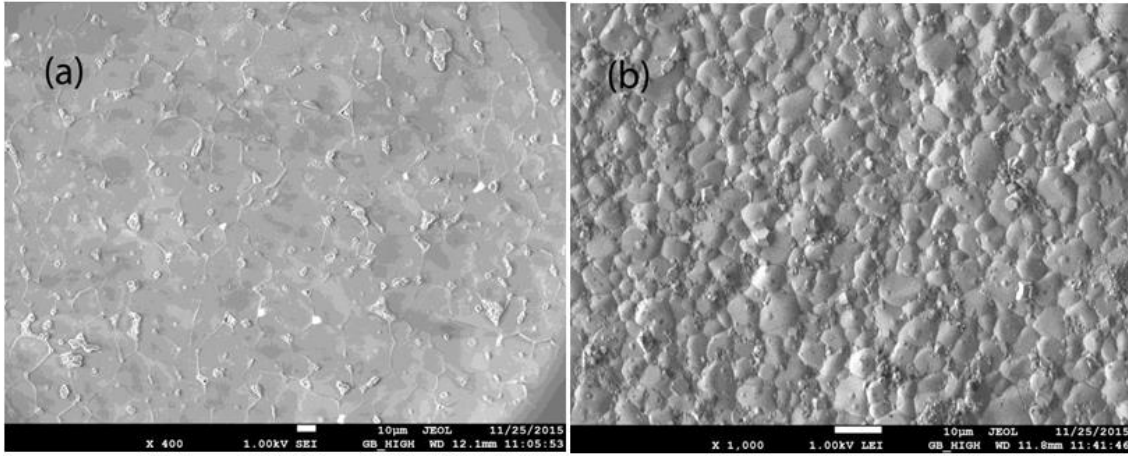


Figure 2: SEM image of (a) undoped $\text{Sr}_2\text{FeMoO}_{6-\delta}$ and (b) $\text{Sr}_2\text{Fe}_{0.75}\text{Ti}_{0.25}\text{MoO}_{6-\delta}$

Figure 2(a) and (b) shows the SEM top-view of surface morphology of the as-prepared SFM and SFTM material. Both surface was rough and cracks could be observed. No trace of liquid or secondary phases were found at the grain boundary region. The SEM data were collected with a voltage of 1.00 kV and with magnification of 1000 times. These results suggest that introducing Ti leads to a compactness of the grain size.

Electrical characterization

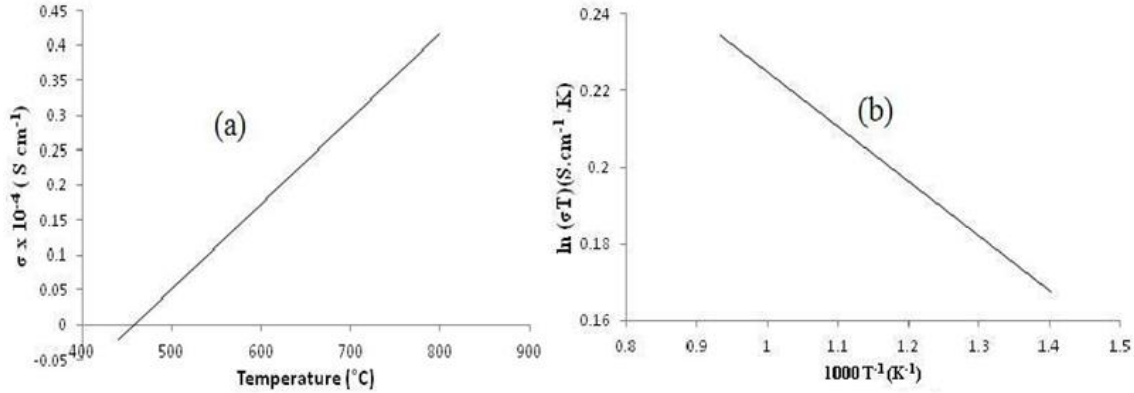


Figure 3: (a). Temperature dependence of electrical conductivity for SFTM in air. (b) The variation of $\log (\sigma T)$ as a function of the reciprocal of absolute temperature for SFTM in air

Figure 3(a). shows the electrical conductivity versus (σ) versus temperature where σ increases continuously as temperature increases. The electrical conductivity is found to be $3.78 \times 10^{-5} \text{ S cm}^{-1}$ at 800°C with an activation energy of 0.142 eV. This value is close to an undoped $\text{Sr}_2\text{FeMoO}_{6-\delta}$ which was reported to be $2.55 \times 10^{-5} \text{ S cm}^{-1}$ [15]. This indicates that doping with Ti increases the electrical conductivity, σ . This conductivity behavior can be described using the small polaron hopping mechanism [16] where electron charge carriers are generated via temperature activated disproportionation

reaction:



The major oxidation state of Mo is +6 with a small portion of +5 hence altering the equilibrium reaction :



The temperature dependence of electrical conductivity through small polaron can be expressed by

$$\sigma = \frac{A}{T} \exp\left(\frac{-E_a}{kT}\right) \quad (5)$$

in which E_a is the activation energy for hopping conduction, k is the Boltzmann temperature, T the absolute temperature and A is the pre-exponential factor independent of temperature. In low temperature range, the disproportionation reaction increases, The charge disproportionation of Fe/Ti increases both n- and p-type carriers further enhances the electrical conductivity.

CONCLUSION

A double perovskite $\text{Sr}_2\text{Fe}_{0.75}\text{Ti}_{0.25}\text{MoO}_{6-\delta}$ has been synthesized by a solid state reaction. The XRD analysis results indicate that a pure phase can be obtained in air at 1350 °C for 8 hours and 10 hours subsequently. The crystal structure has been refined at room temperature and shows a tetragonal symmetry in the $I4/m$ space group. The morphology shows sufficient porosity. Adding Ti in the B-site increases electrical conductivity and improves activation energy making it a potential anode for the SOFC.

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