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## **Synthesis and Electrochemical Characterization of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{0.5-x}\text{Al}_x\text{O}_3$ , for IT and HT- SOFCs**

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### **Abstract**

The main emphasis of this work is to create a new perovskite material with three different compositions ( $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{0.5-x}\text{Al}_x\text{O}_3$ ,  $x = 0.1, 0.2, 0.3$ ) applied in both Intermediate and high Temperature - Solid Oxide Fuel Cells (IT & HT-SOFCs). Perovskite-type polycrystalline  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{0.5-x}\text{Al}_x\text{O}_{3-\delta}$  ( $x = 0.1, 0.2, 0.3$ ) powders were synthesized and formed in a single phase structure by a dry chemistry route (standard solid-state reaction method). The effect of Al-doping on physicochemical and surface properties has been discovered.. The compounds were crystallized in single phase rhombohedral symmetry ( $R\bar{3}C$  Space. Group). Total conductivity of Al-doping in wet 5%  $\text{H}_2$  was higher than both dry 5%  $\text{H}_2$  and air. The obtained results enhance the electro-catalytic performance and the material conductivity as well, which will be good for anode materials in IT- HT-SOFCs and the optimum doping is 10%.

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## 1. Introduction

The essential demand for clean/green energy with long-term stability, conversion efficiency and effective economic investment, solid oxide fuel cell (SOFC) is one of the best promising technology to be considered[1]. Thus, researches and investigations of SOFCs are very encouraging especially for new energy conversion devices[2,3].

Mainly, a fuel cell consist of two porous electrodes (an anode and cathode) detached by a highly dense electrolyte material. High electric conductivity, redox stability and chemical adapting with the electrolyte are the primary key requirements for anode materials. Presently, redox stability under H<sub>2</sub> fuel is one of the major concerns in developing new electrode materials. Hence, the state-of-the-art anode material, Ni/YSZ cermets, give poor redox cycling under hydrocarbon fuels and low tolerance to sulfur. La<sub>0.75</sub>Sr<sub>0.25</sub>Cr<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3-δ</sub> (LSCM), a perovskite oxide, has been proved to be potential anode material that can overcome these problems[4,5].

In structural level, the properties of mixed metal oxides are complex. This is more apparent when the oxide contains more than one magnetic species, or when the crystal structure permits some degree of atomic disorder [6,7]. La<sub>0.75</sub>Sr<sub>0.25</sub>Mn<sub>0.5</sub>Cr<sub>0.5</sub>O<sub>3-δ</sub> can be considered as a solid solution of La<sub>1-x</sub>Sr<sub>x</sub>CrO<sub>3</sub> and La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub>. Substitution of Sr at the A-site and Cr at the B-site in LaMnO<sub>3</sub> gives rise to various interesting magnetic[8] and electrical properties [9]. LaMnO<sub>3</sub>-based materials were identified as good anodes in SOFCs fed with hydrocarbon fuels [10]. Often, La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3-δ</sub> is used as cathode materials for its high conductivity and stability in oxidation conditions[11–14]. La<sub>1-x</sub>Sr<sub>x</sub>CrO<sub>3-δ</sub> can be used as interconnects materials for its high stability in anodic conditions. It was found that the introduction of transition metals into the B-site of La<sub>1-x</sub>Sr<sub>x</sub>Mn<sub>1-y</sub>M<sub>y</sub>O<sub>3</sub> (M = Cr, Fe, Co, Ni) can improve the catalytic properties for hydrocarbon reforming [15,16]. The double doped perovskite phases are stable within redox conditions, showing a little volume change chemically and physically compatible with interconnect materials.

Yaremchenko et al.[17] reported the substitution of Fe with Cr and Al in La<sub>0.3</sub>Sr<sub>0.7</sub>Fe<sub>1-x-y</sub>Al<sub>x</sub>Cr<sub>y</sub>O<sub>3-δ</sub> decreased the total conductivity, O<sub>2</sub> permeability and thermal expansion coefficient. However, La<sub>0.3</sub>Sr<sub>0.7</sub>Fe<sub>0.5</sub>Cr<sub>0.5</sub>O<sub>3-δ</sub> was stable under a reducing atmosphere, but its

electrochemical performance in wet CH<sub>4</sub> was noted to be poor [9]. So, considering the catalytic activity and cracking resistance (LaSr)(CrNi)O<sub>3</sub> with 10% Ni doping suggested being more suitable for a CH<sub>4</sub> oxidation reaction [10]. In contrast, to Ni/YSZ cermets, a La<sub>0.75</sub>Sr<sub>0.25</sub>Mn<sub>0.5</sub>Cr<sub>0.5</sub>O<sub>3</sub> electrode is active for the electro-oxidation of CH<sub>4</sub> at higher temperatures in the absence of excess steam. However, the relative contributions of direct oxidation and internal reforming have yet to be determined.

J.M. Porras-Vázquez et al [18] have reported the Al-doped Sr<sub>2</sub>SiO<sub>4</sub> as electrolyte materials in SOFCs devices and showing that Al doping content increases the amount of holes resulting in higher p-type electronic conductivity. In addition to highest value of 3.0 x 10<sup>-5</sup> S cm<sup>-1</sup> in wet N<sub>2</sub> at IT of 800 °C. While Nicoleta Cioatera et al [19] have shown a great enhancement of the Al doped material {Sm<sub>2</sub>Ti<sub>2-x</sub>Al<sub>x</sub>O<sub>7-d</sub> (x = 0, 0.1, 0.2)} in the electrical conductivity with lower activation energy of 0.64 eV at temperature lower than 700 °C.

The addition of Cr have been reported by Agnieszka Ła<sub>c</sub> cz et al [20] in formula SrTi<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub> (where x = 0, 1, 4, 6 mol%) by wet chemistry route, showing a good enhancement in the conductivity properties with a minimum value of activation energy 0.44 ± 0.01eV. But Yinghua Niu et al [21] have shown in their investigation, that applying Cr in SOFCs electrodes is impacted by many factors and the electrochemical performance is mainly related to the microstructure and doping percentages of Cr.

XPS enables the study of changes in chemistry as well as in electrostatic potentials of atoms in materials. Ions of an oxide may exhibit modified chemical surface states e.g. different oxidation numbers or neighbouring atoms because the chemical environment of surface ions is different from the bulk. Electrochemical polarization and atmosphere effects on the BEs along with surface species requires to be investigated for a mechanistic interpretation of oxygen exchange kinetics. Less information about surface chemistry of perovskite-type anodes and cathodes other than La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3-d</sub> [ 22-23].

In the current research, three new compositions La<sub>0.75</sub>Sr<sub>0.25</sub>Mn<sub>0.5</sub>Cr<sub>0.5-x</sub>Al<sub>x</sub>O<sub>3-δ</sub> (x = 0.1, 0.2, 0.3) were synthesised to discover the effect of Al-doping on physicochemical and surface properties. Substitution of Al, a trivalent cation, with Cr resulted in an interesting changes in electrical properties, magnetic properties and the cation valence state [24]. Structural, electrical and surface characterisations of these materials are useful for fundamental understanding and applications of electrode materials in SOFCs devices. These

characterisations will help to identify the practical applications of these compounds, particularly applications in both IT & HT-SOFCs.

## 2. Experimental

Single perovskite-type polycrystalline  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{0.5-x}\text{Al}_x\text{O}_{3-\delta}$  ( $x = 0.1, 0.2, 0.3$ ) (later mentioned as LSCMA1, LSCMA2 and LSCMA3) powders were formed in a single phase by standard solid-state reaction method. Stoichiometric amounts of high-purity  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{MnO}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  powders were ground under acetone. The samples were mixed together and first dried at 350 for preliminary heating and humidity releasing. After weighting the chemicals and it has been mixed again with acetone in agate mortar pestle before sonication process for 1 hour. Later on powders were collected and well dried in fume hood. The treatment of the compounds started by first calcination at 1100 °C for 6 hours. The next step was firing the samples at 1300 C for 12 hours then followed by an X-Ray Diffraction (XRD) checking. The synthesized materials were not pure yet so the final sintering step was achieved at 1500 °C for 24 hours in 5 °C/min as a heating and cooling rate in air and pure single phase structures were obtained.

XRD data were obtained using a transmission type Stoe Stadi-P diffractometer ( $\text{CuK}\alpha_1=1.540598 \text{ \AA}$ ) to determine phase purity and measure crystal structure parameters. XRD data were collected in the  $2\theta$  range from 10 to 90° with a 0.01° step size and count time of 70 s/step. XRD patterns were indexed using the automatic indexing program TREOR90 [21-25]. SPuDS [22-26] software was used to find the preliminary atomic positions and unit cell parameters. Rietveld analysis of the obtained XRD data was done through FullProf program [23- 27]. A pseudo-Voigt function quantified the shapes of diffracted peak, applying angles a symmetry peak correction below 45° in  $2\theta$ .

Measurements of AC impedance were performed on 13 mm diameter pellets with Pt electrode painted on both sides using a Schlumberger Solartron 1260 electrochemical impedance analyzer in the frequency range of 1Hz to 1MHz in 50 °C steps in air, dry 5%  $\text{H}_2/\text{Ar}$  and wet 5%  $\text{H}_2/\text{Ar}$  in the range 300 to 900 °C.

XPS spectra were collected on powders using an ESCALAB II spectrometer (V.G., UK) using an Al  $\text{K}\alpha$  ( $h\nu = 1486.6 \text{ eV}$ ) X-ray source with 5 sec acquisition time. A hemispherical electron analyser having constant energy mode was used to measure the photoelectrons kinetic energies. In addition to, the characterisation of the surface and several near surface

layers were achieved at a take-off angle of  $45^\circ$ . BEs were calibrated relative to the C 1s peak from carbon contamination of the tested samples at 284.9 eV to correct for charging effects. High resolution spectral envelopes were obtained by curve fitting in XPS peak software. The data were used with no preliminary smoothing. Symmetric Gaussian-Lorentzian peak functions were used to convergent the line shapes of the fitting components. The estimation of Peak intensities were achieved by the integral calculating of each peak after a Shirley background subtraction.

### 3. Results and Discussion

#### A. Structural analysis

Rietveld structure refinements of the obtained XRD data confirm the single-phase with cationic stoichiometry close to the ideal value. Fig. 1 shows the Rietveld fitted XRD profile of  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{0.3}\text{Al}_{0.2}\text{O}_{3-\delta}$ . Small amount of oxygen deficiency was observed which might be due to the divalent Sr substitution with tri-valent La. Oxygen vacancy can also be related to the valence state of Mn and Cr. Since oxygen vacancy has a strong effect on both ionic and electronic conductivities, it is important to study the valence state of the constituting atoms in the composition. All three compositions have showed distorted structure; crystallized in the rhombohedral symmetry in R-3Cs.g (no. 167). The refined cell parameters, atomic positions and R-factors from XRD data refinement are listed in Table 1.

#### B. Electrical Conductivity

Electrochemical impedance measurements in air, dry 5%  $\text{H}_2$  and wet 5%  $\text{H}_2$  shows that the conductivities decreases with the increase of Al-doping in all three environments. In wet 5%  $\text{H}_2$ , the total conductivity for  $x = 0.1$  samples was 0.46 S/cm at  $870^\circ\text{C}$ , which was reduced to 0.32 and 0.30 S/cm for  $x = 0.2$  and 0.3, respectively. The corresponding activation energies were calculated to be 0.087, 0.069 and 0.084 eV. For dry 5%  $\text{H}_2$ , the total conductivities were 0.39, 0.14 and 0.24 S/cm with activation energies of 0.26, 0.22 and 0.31 eV. In air, the total conductivities were 0.25, 0.16, 0.17 S/cm and the activation energies were 0.34, 0.33 and 0.41 eV. The doping of both Cr and Al have shown a good enhancement and stability of electrical conductivities especially for  $x = 0.1$  with lower activation energy value of 0.087 eV. Meanwhile, the doping of Cr is lowering [20] the oxidation state but doping of Al increases the oxygen vacancy concentration [19] which gives more stability in electrochemical transportation of ions. Fig. 2 shows the Arrhenius plots for all samples and

table 2 lists the summarized conductivity results and how its varying with doping percentage of Cr and Al.

### *C. Isothermal conductivity measurements*

Fig.3 is showing the change in isothermal conductivity according to Brouwer diagram, which the LSCMA perovskite was investigated and measured. The logarithmic plots of the equilibrium total conductivity versus the logarithm of pO<sub>2</sub> for x = 0.1 and x = 0.2 at 900 °C, The pO<sub>2</sub> test temperature was selected to be within the structural stability limit of the LSCM doped materials. The Slope of linear fitting in the high pO<sub>2</sub> corresponds to slope of 1/12m where isothermal conductivity changes in the concentration of the various charge collated to pO<sub>2</sub>. The obtained data have shown a steady state/stable equilibration with a higher value of the measured conductivity for x= 0.1, basically, this is happened due to the reduction of Mn 4+ to Mn 3+ and atomic oxygens from the unit cell as made by Irvine et al [24]. However, the tested specimens showed a small change in the isothermal conductivity along the same variation with pO<sub>2</sub> for x=0.1 and x = 0.2 at higher temperature, But it leads to an equal concentrations of electron- and hole-like carriers in the material.

### *D. XPS analysis:*

The chemical state of the elements and the surface properties of La<sub>0.75</sub>Sr<sub>0.25</sub>Mn<sub>0.5</sub>Cr<sub>0.5-x</sub>Al<sub>x</sub>O<sub>3-δ</sub> (x = 0.1, 0.2, 0.3) were determined by XPS. BEs were determined from the fittings of the main peaks of C1s, Sr 2p, Cr 2p, Mn 2p, Al 2p and O 1s levels for as-prepared and pre-reduced samples. To illustrate the wide spectral features of the samples, the C 1s, Sr 3d, Mn 2p and Cr 2p core level spectra are shown in Fig.4.

Fig.4 illustrates that La, Sr, Mn, Cr, Al, C and O elements were detected on the surface of the powders. The calibration process of the BE resulted in carbon (C-H) on the surface which occurred due to the atmospheric contamination and was used as the standard reference for the XPS results. It gave a strong peak near 284.6 eV. The evidence of segregated carbonate presence with inorganic substances located near the 288.86 eV is responsible for the surface state of the reforming catalyst powders [28]. BEs of the selected elements is summarized in Table 3. BEs were determined from the fitting of the main peaks in the lanthanide 3d core level spectra and decomposed peaks of La<sub>0.75</sub>Sr<sub>0.25</sub>Mn<sub>0.5</sub>Cr<sub>1-x</sub>Al<sub>x</sub>O<sub>3-δ</sub>. The core level 3d<sub>5/2</sub> for La<sub>2</sub>O<sub>3</sub> is conventionally observed near 834.4 eV. La<sub>0.75</sub>Sr<sub>0.25</sub>Mn<sub>0.5</sub>Cr<sub>1-x</sub>Al<sub>x</sub>O<sub>3-δ</sub> (x = 0.1,

0.2,0.3) samples shown in Fig.4 are consistent with normal oxidations  $\text{La}^{3+}$ . They were well substituted into the A site of the precursors and sustained a charge state of  $3+$ .

The Chemical state of La is generally well-known from XPS spectra[28,29]. La 3d states splits into two lines. Both of  $3d_{5/2}$  and  $3d_{3/2}$  split because of the released electron from  $\text{O}_2$  ligands of La 4f. This phenomenon results from defected crystals[30]. Also, La in perovskites shows low BEs than that of La in  $\text{La}_2\text{O}_3$  because of a low interaction between Location and the transition metal element in perovskites [29].

Fig.5 shows the measured XPS spectra and the deconvolution results of Mn, Cr  $2p_{1/2}$  and  $2p_{3/2}$  in the LSCMA that was heat-treated under the oxidizing conditions (in air) and were found to include 3 peaks for  $x = 0.1$ , 2 peaks for  $x= 0.2$  and 2 peaks for  $x= 0.3$  for Mn. For Cr, we observed 2 peaks for  $x = 0.1$ , 4 peaks for  $x= 0.2$  and 3 peaks for  $x= 0.3$ . The split of the Mn peaks 2d level spectrum is due to spin-orbit splitting. The Full Width at Half Maximum (FWHM) values of the Mn peaks were increased with Al doping and became maximum at  $x=0.3$ . BEs of 641.90 eV, 641.39 eV and 644.22 eV represent the  $2p_{3/2}$  of  $\text{Mn}^{+2}$ ,  $\text{Mn}^{+3}$  and  $\text{Mn}^{+4}$ , respectively, according to the literature[28],[31-34]. BEs at 653.60 eV, 651.92 eV and 655.57 eV represent the  $2p_{1/2}$  of  $\text{Mn}^{+2}$ ,  $\text{Mn}^{+3}$  and  $\text{Mn}^{+4}$ , respectively. For the Cr 2d level spectrum, there were similar values of exchange splitting [35] due to many of the valence/spin-state regions in the studied samples [36]. In the XPS spectra the pure oxides  $\text{Cr}^{+3}$  and  $\text{Cr}^{+4}$  are quite difficult to distinguish [16]. BEs at 576.07 eV, 575.51 eV and 578.43 eV represents the  $2p_{3/2}$  of  $\text{Cr}^{+3}$ ,  $\text{Cr}^{+4}$  and  $\text{Cr}^{+6}$ , respectively. The BEs at 585.20 eV and 587.86 eV represent the  $2p_{1/2}$  of  $\text{Cr}^{+4}$  and  $\text{Cr}^{+6}$ . The increase of satellite peaks in the  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{1-x}\text{Al}_x\text{O}_{3-\delta}$  with the dopant percentages with Mn and Cr indicates high electrochemical, electronic and electro-catalytic performance [31,36].

Fig.6 illustrates the XPS plots for Mn and Cr on reduced samples for  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{1-x}\text{Al}_x\text{O}_{3-\delta}$  ( $x = 0.1, 0.2, 0.3$ ). The BEs shown in Table 2 represent a distinct increase after pre-reduced condition for composition  $x= 0.1$  and  $0.2$  and there is a small decrease for  $x=0.3$  in both cases for Mn and Cr. This decrease is due to  $\text{La}_2\text{O}_3$  which was highly dispersed on the surface[37]. In addition to the formation of  $\text{Mn}_2\text{O}_3$  in as-prepared and pre-reduced samples, shown by Mn  $2p_{3/2}$  considering the depth analysis by XPS, the photoemitted electrons increased with increasing kinetic energy [38]. Hence, the Mn  $2p_{1/2}$  is more sensitive than  $2p_{3/2}$  to the surface of  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{1-x}\text{Al}_x\text{O}_{3-\delta}$  specifically for  $x=0.3$ . Subsequently, the

oxidation conditions affect the valence state of  $Mn^{+2}$ ,  $Mn^{+3}$  and  $Mn^{+4}$ . However, the findings in  $Cr^{+3}$  and  $Cr^{+6}$  agree with literature data [39] and the reference spectrum. The occurred deviation is due to the depth distribution in the analysed samples [38,39].

$Al_2O_3$  is a highly attractive material from thermal and chemical stability perspective [40]. It is able to increase the total BEs while doped with  $La^{3+}$  precursors [41]. The XPS spectra of Al 2p of  $La_{0.75}Sr_{0.25}Mn_{0.5}Cr_{1-x}Al_xO_{3-\delta}$  are shown in Fig.7 and were plotted for as-prepared and pre-reduced samples.

Previous studies complemented that the occurrence of  $La^{3+}$  is near to the Al surface [42-44]. The La dopant may form  $La_2O_3$  or  $LaAlO_3$  layer on the Al surface [44,45]. The BEs of the Al 2p line is listed in Table 2 after fitting of the mean peaks. BEs of 71.90 eV and 76.93 eV for  $x=0.1$  and the BEs of 72.94 eV and 72.01 eV for  $x=0.2$  and 0.3, of the as-prepared samples represent Al as a metallic state with closely spaced spin-orbit components. BEs of 75.93 eV for  $x=0.2$  and 74.64 eV for  $x=0.3$  in the pre-reduced samples acquire an oxide peak position. The spectra demonstrate BEs changes with and without reduction state which is due to exhibit energy loss features on the  $Al_2O_3$  surface. According to the obtained results it is emphasized that the  $La^{3+}$  dopant remains dispersed as isolated atoms on the Al surface [46].

In the XPS spectra of O 1s, the BEs can be separated into two groups of perovskites containing  $O_2$ : Low BE and High BE [29]. The XPS spectra of O 1s for the  $La_{0.75}Sr_{0.25}Mn_{0.5}Cr_{1-x}Al_xO_{3-\delta}$  ( $x = 0.1, 0.2, 0.3$ ) are shown in Fig.7. Two main peaks are clearly observed and their values were found to be higher than 530.02 eV. In Fig.8 and Table 2 about O 1s peak, LBE of 530.62 eV ( $x=0.1$ ), 532.52 eV ( $x=0.2$ ) and 531.01 eV ( $x=0.3$ ) correspond to the  $O_2$  in the lattice and HBE of 534.14 eV ( $x=0.1$ ), 535.85 eV ( $x=0.2$ ) and 533.7 eV ( $x=0.3$ ) indicate adsorbed oxygen-containing species near the surface. The value of percentage area of the  $O_2$  peaks reduced with the Al-doping i.e. 25.49, 14.63 and 11.93 for  $x = 0.1, 0.2$  and 0.3, respectively. When the value of percentage area of the  $O_2$  peaks with respect to the LBE shows lower value than other compositions, less  $O_2$  vacancies are generated on the surfaces of LSCMA. The maximum BE was observed to be 532.52 eV at  $x=0.2$  which attributed to a broader peak and assigned to surface adsorbed  $O_2$  species [16, 28,47]. The overall composition is mainly  $O^{2-}$  because of the lattice  $O_2$  on the surface. XPS spectra of O 1s reveal a different propensity of BEs due to the  $O_2$  penetration path of each composition in the precursor being largely different in  $La_{0.75}Sr_{0.25}Mn_{0.5}Cr_{1-x}Al_xO_{3-\delta}$ .



#### 4. Conclusions

- Rietveld structure refinements of the obtained XRD data confirmed the single-phase with cationic stoichiometry close to the ideal value. Small amount of oxygen deficiency was observed. In addition to, all three compositions showed distorted structure; crystallized in the rhombohedral symmetry in R-3C s.g (no. 167).
- Electrochemical impedance analysis showed that the proposed perovskite materials  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{1-x}\text{Al}_x\text{O}_{3-\delta}$  ( $x = 0.1, 0.2, 0.3$ ) are highly conductive. The conductivities decreases with the increase of Al-doping in all three environments (wet  $\text{H}_2$ , dry  $\text{H}_2$  and air). The total conductivities are higher in wet  $\text{H}_2$  than in dry  $\text{H}_2$  or air.
- A steady state/stable equilibration with a higher value of the measured conductivity for  $x=0.1$  was obtained. However, the tested specimens showed a small change in the isothermal conductivity along the same variation with  $p\text{O}_2$  for  $x=0.1$  and  $x=0.2$  at higher temperature, But it leads to an equal concentrations of electron- and hole-like carriers in the material.
- Binding energies of nonredox active elements (La, Sr, O, Al) showed a pronounced dependence on the atmosphere and the electrochemical polarization. Fermi level shift resulted from defect chemical models of oxygen has a strong influence on the binding energy shift.. Only the transition metals manganese and chromium appear to undergo valence changes. However, in oxidizing atmosphere near surface manganese is present as  $\text{Mn}^{3+}$ , irrespective of polarization. In reducing atmosphere, manganese is present in the oxidation states as  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$ .
- Promising enhancement in the electro-catalytic performance and the material conductivity were achieved, which will be good for anode materials in IT- HT-SOFCs and the optimum doping is 10% (i.e.  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{1-x}\text{Al}_x\text{O}_{3-\delta}$  with  $x=0.1$ ).

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**Figure and Table Caption List:**

**Figure 1: Rietveld refinement profile of XRD data of La<sub>0.75</sub>Sr<sub>0.25</sub>Mn<sub>0.5</sub>Cr<sub>0.3</sub>Al<sub>0.2</sub>O<sub>3- $\delta$</sub>  in the rhombohedral symmetry.**

**Figure 2: Total conductivity of La<sub>0.75</sub>Sr<sub>0.25</sub>Mn<sub>0.5</sub>Cr<sub>0.3</sub>Al<sub>0.2</sub>O<sub>3- $\delta$</sub>  (x = 0.1, 0.2, 0.3) in (a) wet 5%H<sub>2</sub>, (b) dry 5%H<sub>2</sub> and (c) air at different temperatures.**

**Figure 3: Change of isothermal conductivity with oxygen partial pressure for x = 0.1 (a) and x = 0.2 (b) at 900 oC, dotted line corresponds to slope of 1/12.**

**Figure 4: Wide spectra of La<sub>0.75</sub>Sr<sub>0.25</sub>Mn<sub>0.5</sub>Cr<sub>0.3</sub>Al<sub>0.2</sub>O<sub>3- $\delta$</sub>  (x = 0.1, 0.2, 0.3) oxide in air and H<sub>2</sub>.**

**Figure 5: XPS measurement plots for Mn and Cr on as-prepared samples for different percentage of Al doping. For Mn (a to c) and for Cr (d to f) for x = 0.1, 0.2, and 0.3, respectively.**

**Figure 6: XPS measurement plots for Mn and Cr on pre-reduced samples for different percentage of Al doping. For Mn (a to c) and for Cr (d to f) for  $x = 0.1, 0.2,$  and  $0.3,$  respectively.**

**Figure 7: XPS plots for Al (a ,b,c for as-prepared samples and d,e is for pre-reduced samples).**

**Figure 8: XPS plots for O 1s for pre-reduced samples of a,b and c for  $x = 0.1, 0.2, 0.3,$  respectively.**

**Table 1: Main crystallographic structure information for  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{0.3}\text{Al}_{0.2}\text{O}_{3-\delta}$  ( $x = 0.1, 0.2, 0.3$ ) in the rhombohedral (space group R-3C) from XRD data refinement.**

**Table 2. Calculated conductivity for AC mode of  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{0.5-x}\text{Al}_x\text{O}_{3-\delta}$  ( $x = 0.1, 0.2, 0.3$ ).**

**Table 3. Binding energies (eV) of core electrons  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{1-x}\text{Al}_x\text{O}_{3-\delta}$  ( $x = 0.1, 0.2, 0.3$ ) on as-prepared and pre-reduced samples.**

**Table 1.** Main crystallographic structure information for  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{0.5-x}\text{Al}_x\text{O}_{3-\delta}$  ( $x = 0.1, 0.2, 0.3$ ) in the rhombohedral (space group R-3C) from XRD data refinement.

	x = 0.1	x = 0.2	x = 0.3
$a = b$ (Å)	5.4897(2)	5.4791(4)	5.4782(6)
$c$ (Å)	13.3086(6)	13.2974(1)	13.3031(5)
$V$ (Å <sup>3</sup> )	347.35(3)	345.70(4)	345.75(7)
La/Sr in $6a$ (0, 0, 0.25)			
B (Å <sup>2</sup> )	0.70(2)	0.74(6)	0.75(3)
Mn/Cr/Al in $6b$ (0, 0, 0)			
B (Å <sup>2</sup> )	0.85(3)	0.90(4)	0.85(6)
O in $18e$ in (x, 0, 0.25)			
$X$	0.453(1)	0.455(2)	0.458(2)
$R_p$ (%)	2.24	3.07	3.17
$R_{wp}$ (%)	2.90	4.03	4.65
$R_{exp}$ (%)	4.45	6.34	5.09
$R_B$ (%)	3.55	6.82	6.27

**Table 2.** Calculated conductivity for AC mode of  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{0.5-x}\text{Al}_x\text{O}_{3-\delta}$  ( $x = 0.1, 0.2, 0.3$ )

		AC conductivity (From Fig. 2)		
		Wet 5% H <sub>2</sub>	Dry 5% H <sub>2</sub>	Air
x = 0.1	Conductivity	0.46	0.39	0.25
	Activation energy	0.087	0.26	0.34
x = 0.2	Conductivity	0.32	0.14	0.16
	Activation energy	0.069	0.22	0.33
x = 0.3	Conductivity	0.30	0.24	0.17
	Activation energy	0.084	0.31	0.41



**Table 3.** Binding energies (eV) of core electrons  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{1-x}\text{Al}_x\text{O}_{3-\delta}$  ( $x = 0.1, 0.2, 0.3$ ) on as-prepared and pre-reduced samples.

Sample	C 1s	Sr 3p <sub>1/2</sub> ; Sr 3p <sub>3/2</sub>	Mn 2p <sub>3/2</sub> ; Mn 2p <sub>1/2</sub>	Cr 2p <sub>3/2</sub> ; Cr 2p <sub>1/2</sub>	Al 2p	O 1s
As-prepared samples						
x = 0.1	284.58	278.57	641.90 653.60	576.07 -	-	-
x = 0.2	284.61	278.39 268.20	641.39 652.91	575.51 585.20	72.935	-
x = 0.3	286.54	278.88 270.78	644.22 655.57	578.43 587.86	75.01	-
Pre-reduced samples						
x = 0.1	285.01	278.75 268.76	643.89 655.24	577.55 587.66	71.90 76.92	530.62
x = 0.2	284.71	275.68 269.09	645.03 656.19	579.08 589.20	75.22	532.52
x = 0.3	284.32	279.60 274.36	643.43 655.00	578.04 588.25	74.64	531.01





























