Tailoring the Stability of Ti-Doped Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_6$-$\delta$ Electrode Materials for Solid Oxide Fuel Cells

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Abstract: In this work, the stability of Sr$_2$(FeMo)O$_6$-$\delta$-type perovskites was tailored by the substitution of Mo with Ti. Redox stable Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_6$-$\delta$ ($x = 0.1, 0.2$ and $0.3$) perovskites were successfully obtained and evaluated as potential electrode materials for SOFCs. The crystal structure as a function of temperature, microstructure, redox stability, and thermal expansion properties in reducing and oxidizing atmospheres, oxygen content change, and transport properties in air and reducing conditions, as well as chemical stability and compatibility towards typical electrolytes have been systematically studied. All Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_6$-$\delta$ compounds exhibit a regular crystal structure with $Pm$-3n space group, showing excellent stability in oxidizing and reducing conditions. The increase of Ti-doping content in materials increases the thermal expansion coefficient (TEC), oxygen content change, and electrical conductivity in air, while it decreases the conductivity in reducing condition. All three materials are stable and compatible with studied electrolytes. Interestingly, redox stable Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_6$-$\delta$, possessing 1 μm grain size, low TEC (15.3 $\times$ 10$^{-6}$ K$^{-1}$), large oxygen content change of 0.72 mol·mol$^{-1}$ between 30 and 900°C, satisfactory conductivity of 4.1–7.3 S·cm$^{-1}$ in 5% H$_2$ at 600–800°C, and good transport coefficients $D$ and $k$, could be considered as a potential anode material for SOFCs, and are thus of great interest for further studies.

Keywords: titanium doped Sr$_2$(FeMo)O$_6$-$\delta$ perovskites; redox stability; anode materials; solid oxide fuel cells; crystal structure; thermal expansion; oxygen content; transport properties; compatibility with electrolytes

1. Introduction

Solid oxide fuel cells (SOFCs) with the advantage of high efficiency and fuel flexibility are among the most promising devices for the generation of electrical energy and heat from renewable and traditional energy sources, considerably reducing the emission of CO$_2$ and other harmful gases (NO$_x$, SO$_x$, CO) [1–5]. However, the high operational temperature (above 800°C) of SOFCs leads to a high operational cost, limiting the choice of materials and delaying commercial applications of SOFCs. For practical use, SOFCs need to operate at much lower temperatures than the current range ($\leq$800°C) and still be able to generate a high-power production. Therefore, new anode [6–8] and cathode materials [9,10] with high stability and electrocatalytic activity are required to maintain a reasonable power output at temperature below 800°C [11–14].

One group of the most interesting cathode and anode material candidates for SOFCs is the Sr$_2$(FeMo)O$_6$-type perovskite with Fe- and Mo-cations at B-site [15–21]. The B-site rock
salt-type ordered $\text{Sr}_2-x\text{Ba}_x\text{M}_{1-y}\text{Mo}_y\text{O}_{6}$ ($M = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) double perovskite-type compounds were initially proposed and evaluated as novel anode materials for SOFCs showing promising cell performance in different fuels, including hydrogen [22–26] and methane [27,28]. Generally, the choice of chemical composition in $\text{Sr}_2(\text{Fe},\text{Mo})\text{O}_{6-\delta}$-type materials is governed by several crucial factors. The double perovskite (cations ordering) structure which favors the oxygen ion transport can be ensured by the considerable difference in oxidation state of B-site cations between $\text{Mo}^{6+}$ or $\text{Mo}^{5+}$ (in reducing atmospheres) and larger $\text{M}^{2+/3+}$ cations (3d elements and Mg) [6,29]. The redox couple of $\text{Mo}^{6+}/\text{Mo}^{5+}$ and $\text{Mo}^{5+}/\text{Mo}^{4+}$ suggest that $\text{Sr}_2(\text{Fe},\text{Mo})\text{O}_{6-\delta}$-type materials can not only favour an effective charge transport providing excellent conductivity [24,26], but also facilitate the creation of oxygen vacancies. For instance, $\text{Sr}_2\text{FeMoO}_{6-\delta}$ oxide shows very high metallic conductivity with 1000 S cm$^{-1}$ in reducing condition, while unfortunately the compound is not stable in air at high temperatures [26]. The modification of B-site cations in $\text{Sr}_2(\text{Fe},\text{Mo})\text{O}_{6-\delta}$-type double perovskites can possibly bring good redox stability in both oxidizing and reducing conditions [30–32]. $\text{SrFe}_{0.75}\text{Mo}_{0.25}\text{O}_{3-\delta}$ [30,31], $\text{SrFe}_{0.5}\text{Mn}_{0.25}\text{Mo}_{0.25}\text{O}_{3-\delta}$ [30], $\text{Sr}_{1-x}\text{Ba}_x\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ [33], and $\text{Sr}_2\text{Fe}_{1}\text{Mg}_{0.2}\text{Mo}_{0.2}\text{O}_{6-\delta}$ and $\text{Sr}_2\text{Fe}_{0.9}\text{Mg}_{0.1}\text{Mo}_{0.7}\text{O}_{6-\delta}$ perovskites [34] show good redox stability both in air and reducing conditions and have been studied as both cathode and anode materials for SOFCs. However, $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ compound is sensitive to water, and the reaction of $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ with $\text{H}_2\text{O}$ is a possible shortcoming of this perovskite as cathode and anode materials for SOFCs [35,36]. Mg-doped $\text{Sr}_2\text{FeMo}_{2/3}\text{Mg}_{1/3}\text{O}_{6-\delta}$ double perovskite with a good tolerance to sulfur poisoning and carbon deposition was evaluated as a promising anode material candidate for SOFCs [37]. The $\text{Fe}_9\text{O}_7\text{Fe}_9\text{O}_7$ bonds in materials promote easy creation of oxygen vacancies and their fast migration. However, the low electrical conductivity (4–5 S cm$^{-1}$ at 600–800°C in air) may limit the application of such a material for SOFCs [37]. The copper-substituted $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{Cu}_{0.2}\text{O}_{6-\delta}$ material was investigated as a fuel electrode for the oxidation of $\text{H}_2$ and $\text{CO}_2$-CO reduction, showing improved reaction activity and durability, with an excellent SOFC power yield of 1.51 W cm$^{-2}$ in $\text{H}_2$ and a very good current density in the reduction of $\text{CO}_2$ (with 1.94 A cm$^{-2}$ at 1.4 V) [38]. The effect of Co-doping on the physicochemical and electrochemical properties of $\text{SrFe}_{0.45}\text{Co}_{0.45}\text{Mo}_{0.1}\text{O}_{3-\delta}$ double perovskite has been investigated [39]. The material has been proposed as an air electrode for reversible solid oxide fuel cells, with high mobility of electron holes and oxygen ions. However, the recorded high thermal expansion coefficient is a limiting issue for the potential application of Co-doped oxide [39]. $\text{Sr}_2\text{Mg}_{1-x}\text{Co}_x\text{MoO}_{6-\delta}$ perovskites with Co-doping at Mg-site, were investigated as novel anode materials for SOFCs, showing small anode polarization resistances [40], and the cobalt-doping positively contributes to the sinterability and ionic conductivity of materials [40]. However, the relatively weak bonding between Co-O is ascribed to the instability issue in anode condition, causing the reduction of Co to metallic cobalt. In addition, $\text{PrBa}_{0.95}\text{Fe}_{0.9}\text{Mo}_{0.1}\text{O}_{5+\delta}$ double perovskite with very high conductivity (59.2 S cm$^{-1}$ in 5% H$_2$, and 217 S cm$^{-1}$ in air at 800°C) was evaluated as an anode candidate for SOFCs, presenting excellent cell performance with 1.18 W cm$^{-2}$ at 800°C in $\text{H}_2\text{S}$-containing fuel [8,11]. Therefore, the further modification of $\text{Sr}_2(\text{Fe},\text{Mo})\text{O}_{6-\delta}$-type perovskites will contribute to the development of novel cathode and anode materials with high performance for SOFCs.

$\text{SrTiO}_3$-derived perovskites are also of great interest as novel electrode materials for SOFCs, characterized by high redox stability in oxidizing and reducing conditions, and by a low economic and environmental impact [41–43]. Perovskites with mixed Fe- and Ti-at B-sites can favour the oxygen reduction reaction for SOFCs [44]. Ti- and Mo-containing $\text{Sr}_2\text{TiMoO}_{6-\delta}$ double perovskite oxide was studied as novel anode material for SOFC, and it demonstrates excellent stability, sulphur poisoning resistance, and coking tolerance, as well as a good power output of 275 mW cm$^{-2}$ in $\text{H}_2\text{S}$-containing syngas at 850°C [45]. $\text{Ba}_x\text{Sr}_{1-x}\text{Ti}_{1-y}\text{Mo}_y\text{O}_3$ materials were synthesised and investigated as potential catalysts for the oxidation of CO and methane reforming [46]. In addition, the electrical conductivity and sintering properties of Ti-containing $\text{La}_{0.5}\text{Sr}_{1.5}\text{Ti}_{1.5}\text{M}_{0.5}\text{O}_{6-\delta}$ ($M = \text{Fe}, \text{Co}$ and Ni) double
perovskites were evaluated in terms of their application as new anode material candidates for [47]. Sr$_2$ScTi$_{1-x}$Mo$_6$O$_{12} \ (x = 0.1$ and $0.5)$ double perovskites were studied as both cathode and anode materials for symmetrical solid oxide fuel cells, exhibiting a good power output of 218 mW cm$^{-2}$ at 800 °C in humidified CH$_4$ [48]. Ti-containing Sr$_2$TiN$_{1.5}$Mo$_{0.5}$O$_6$–$\delta$ perovskite was also proposed and systematically evaluated as a new anode material for SOFCs, generating a power density of 335 mW cm$^{-2}$ at 800 °C in humidified H$_2$ [49].

It has been reported that the electrocatalytic activity In the series of Sr$_2$Fe$_{2-x}$Mo$_6$O$_{12}$–$\delta$ double perovskites enhances with the increase of Mo-doping content, which contributes to the improved performance of SOFCs cells in different fuels (H$_2$ and methanol) [32], and SOFC with Sr$_2$Fe$_{1.4}$Mo$_{0.6}$O$_{6}$–$\delta$ anode material shows much better electrochemical performance than the SOFC cell with redox stable Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_6$–$\delta$ electrode [32]. Sr$_2$Fe$_{1.4}$Mo$_{0.6}$O$_6$–$\delta$ double perovskite possess very high electrical conductivity with 330 S cm$^{-1}$ at 500 °C, nonetheless unfortunately it decomposes in air above 500 °C [50]. Interestingly, the Ti-doping at Fe-site in Sr$_2$Fe$_{1.4-x}$Ti$_x$Mo$_{0.6}$O$_{6}$–$\delta$ double perovskites significantly improves the structural stability of materials, which were systematically investigated as new anode material candidates for SOFCs [50]. Sr$_2$Fe$_{1.3}$Ti$_{0.1}$Mo$_{0.6}$O$_6$–$\delta$ anode-based SOFC cell delivers a promising power output with >0.64 W cm$^2$ in wet hydrogen at 900 °C [50]. However, such a material is still not stable in air at a high temperature range. Therefore, in this work, the stability of Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6}$O$_{6}$–$\delta$ ($x = 0.1$, 0.2 and 0.3) perovskites was tailored by the substitution of Mo with Ti at B-site. Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6}$–$\delta$ materials with excellent stability in both reducing and oxidizing atmospheres have been obtained. The crystal structure as a function of temperature, microstructure, redox stability, and thermal expansion properties in reducing and oxidizing atmospheres, oxygen content change and transport properties in air and reducing condition, as well as the chemical stability and compatibility towards typical solid electrolytes have been evaluated for the studied materials in terms of their application as electrode material candidates for SOFCs.

2. Materials and Methods

The synthesis of Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6}$O$_{6}$–$\delta$ ($x = 0.1$, 0.2 and 0.3) materials was conducted using the high temperature method (solid state reaction), with the calculated amounts of SrCO$_3$, Fe$_2$O$_3$, TiO$_2$, and MoO$_3$ (all compounds with $\geq 99.9\%$ purity) chemicals. All required chemicals after milling in the high efficiency planetary ball mill (Spex Sample-Prep 8000 M, Spex Sampleprep, Metuchen, UK) were pressed into pellets and fired in air for 10 h at 1200 °C. The crystal structure properties of all obtained materials were investigated by the XRD measurements within 10–110 deg. 2 Theta range using the Panalytical Empyrean diffractometer (CuK$\alpha$ radiation, Malvern, UK).

The chemical stability of Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6}$O$_{6}$–$\delta$ compounds was studied by the reduction of oxides in 5 vol.% H$_2$ in argon for 10 h at 1200 °C. The XRD data refinement was applied applying the Rietveld method using GSAS/EXPGUI software [51,52]. Scanning electron microscopy (SEM) studies of reduced powders were conducted using FEI Nova NanoSEM 200 apparatus. The high temperature XRD studies were performed for the in-situ oxidation in air of reduced Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6}$–$\delta$ ($x = 0.1$, 0.2 and 0.3) samples using Panalytical Empyrean apparatus with Anton Paar HTK 1200N oven-chamber. The in-situ oxidation of Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6}$–$\delta$ sinters was also investigated with the thermal expansion measurements in air from room temperature to 900 °C using the Linseis L75 Platinum Series dilatometer (Selb, Germany).

Thermogravimetric (TG) studies were carried out on the TA Instruments Q5000IR apparatus (New Castle, DE, USA) and STA PT1600 TG with differential scanning calorimetry (DSC) studies from 30 to 900 °C in different conditions (in air and in 5 vol.% H$_2$/Argon) with the rate of 2°·min$^{-1}$. The buoyancy effect was also taken into account. The electrical conductivity ($\sigma$) of Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6}$–$\delta$ samples was recorded to 900 °C in air and 5 vol.% H$_2$ in argon by a four-probe DC technique, on the dense cuboid shape sinters. The porosity effect of the studied sinters was also considered [53]. The oxygen diffusion coefficient $D$ and surface exchange constant $k$ of Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_6$–$\delta$ compound were studied...
using the mass relaxation technique in TA Instruments Q5000 IR on a very thin-sheet shape sample [54,55]. The mass relaxation measurements were performed with a very fast oxygen partial pressure change between 0.21 atm and 0.01 atm. The determination of coefficients $D$ and $k$ was conducted in custom-made Matlab code, based on Crank's mathematical solutions [56]. The chemical stability and compatibility studies of Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ ($x = 0.1, 0.2$ and $0.3$) materials towards typical electrolytes, such as CGO20–Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ and LSGM–La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mo$_{0.2}$O$_{3-\delta}$ solid electrolytes, were investigated by measuring the XRD data gathered for the respective oxide and solid electrolyte mixtures (with a 50:50 wt.%), fired in air for 10 h at 1200 °C.

3. Results and Discussion

3.1. Crystal Structure and Microstructure

The obtained XRD results with the Rietveld refinement in Figure 1 and Table 1 show that as-synthesized Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ ($x = 0.1, 0.2$ and $0.3$) samples exhibit simple perovskite crystal structure, belonging to the cubic $Pm-3m$ space-group. However, the Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6-\delta}$ material synthesized in air possesses about 3.6% secondary phase (SrMoO$_4$), which can be successfully removed by annealing the compound in reducing condition (see Figure 2a). As evidenced, the substitution of molybdenum by titanium in Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ perovskites does not change the crystal symmetry but leads to a decrease of the unit cell parameter $a$. The doping of Ti$^{4+}$ (with smaller oxidation state) at Mo$^{6+}$ site contributes to the increase of Fe$^{4+}$ (reducing the amount of Fe$^{3+}$) and the content of oxygen vacancies in materials. The larger difference in ionic radius between Fe$^{3+}$ ($r_{Fe^{3+}} = 0.645$ Å) and Fe$^{4+}$ ($r_{Fe^{4+}} = 0.585$ Å) causes the decrease of the unit cell parameter, despite Ti$^{4+}$ ($r_{Ti^{4+}} = 0.605$ Å) presenting a slightly bigger ionic radius than Mo$^{6+}$ ($r_{Mo^{6+}} = 0.59$ Å). The geometric tolerance factor $t_g$ of all studied materials was calculated using the following equation of $t_g = \frac{[A-O]}{\sqrt{2}[B-O]}$, where $[A-O]$ and $[B-O]$ are the refined geometric average values of interatomic distances of Sr-O and M-O (M: Fe, Ti and Mo), respectively [26]. The geometric tolerance factor was calculated to be $t_g = 1.00$ for all measured Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ ($x = 0.1, 0.2$ and $0.3$) samples, which indicates the presence of a regular crystal structure in the studied materials. Similar compositions, such as Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_{6-\delta}$ and SrFe$_{0.5}$Mn$_{0.25}$Mo$_{0.75}$O$_{3-\delta}$ [30], Sr$_2$TiFe$_{0.5}$Mo$_{0.5}$O$_{6-\delta}$ [57], and SrFe$_{0.45}$Co$_{0.45}$Mo$_{0.1}$O$_{3-\delta}$ [39] oxides, also show a $Pm-3m$ simple perovskite structure. Meanwhile, the Ti-doping at Fe-site in Sr$_2$Fe$_{1.4-x}$Ti$_x$Mo$_{0.6}$O$_{6-\delta}$ ($x = 0$ and $0.1$) leads to a double perovskite structure with $Pm-3m$ space group [50].

Table 1. Rietveld refinement results including unit cell parameters for the as-synthesized and reduced Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ ($x = 0.1, 0.2$ and $0.3$) oxides.

| Composition | $x = 0.1$ | $x = 0.2$ | $x = 0.3$ |
|-------------|------------|------------|------------|
| space group | * As Synthesized | Reduced | As Synthesized | Reduced | As Synthesized | Reduced |
| $a$ [Å]     | $3.9190$ (1) | $3.9257$ (1) | $3.9121$ (1) | $3.9277$ (1) | $3.9038$ (1) | $3.9186$ (1) |
| $V$ [Å$^3$] | $60.19$ (1) | $60.50$ (1) | $59.88$ (1) | $60.59$ (1) | $59.49$ (1) | $60.17$ (1) |
| \(\Delta V/\delta\) | 0.52% | 1.19% | 1.14% |
| density [g/cm$^3$] | 5.55 | 5.52 | 5.51 | 5.45 | 5.48 | 5.42 |
| \(CHI^2\) | 3.25 | 3.53 | 2.32 | 2.77 | 2.04 | 4.64 |
| $R_p$ (%) | 1.38 | 1.65 | 1.26 | 1.46 | 1.15 | 1.53 |
| $R_{wp}$ (%) | 1.99 | 2.39 | 1.71 | 2.14 | 1.61 | 2.51 |

* With around 3.6% SrMoO$_4$ phase.
The redox stability of Sr$_{2}$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ (x = 0.1, 0.2 and 0.3) materials was studied by annealing the compounds in 5 vol.% H$_2$ in Argon at 1200 °C for 10h. The collected XRD data (Figure 2) after the reduction measurements show the reduced Sr$_{2}$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ still possess the same crystal structure (Pm-3m), and the reduced B-site cations (Fe, Ti and Mo cations) with larger ionic radius contribute to a larger unit cell parameter $a$ and volume $V$ (see Table 1). Interestingly, among all investigated Sr$_{2}$Fe$_{1.4}$Ti$_{x}$Mo$_{0.6−x}$O$_{6−δ}$ materials, Sr$_{2}$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ oxide presents the smallest relative volume change $\Delta V = 0.52\%$ between the reduced and oxidized samples. This indicates the possible application of such a compound in oxidizing and reducing conditions [54]. For comparison, the relative volume changes between the oxidized and reduced Sr$_{2}$Fe$_{1.5}$Mo$_{0.5}$O$_{6−δ}$ and Sr$_{2}$Fe$_{0.9}$Mg$_{0.4}$Mo$_{0.7}$O$_{6−δ}$ oxides are larger and reach 1.18% [30] and 0.55% [34], respectively. The increase of Ti-doping in Sr$_{2}$Fe$_{1.4}$Ti$_{x}$Mo$_{0.6−x}$O$_{6−δ}$ (x = 0.2 and 0.3) leads to a significantly large volume change $\Delta V$, which can contribute to larger thermal expansion coefficients (TEC) in reducing and oxidizing atmospheres.

Figure 1. XRD patterns of the as-synthesized (a) Sr$_{2}$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$; (b) Sr$_{2}$Fe$_{1.4}$Ti$_{0.2}$Mo$_{0.4}$O$_{6−δ}$ and (c) Sr$_{2}$Fe$_{1.4}$Ti$_{0.3}$Mo$_{0.3}$O$_{6−δ}$ oxides in 5 vol.% H$_2$/Argon at 1200 °C for 10h.
Figure 1. XRD patterns of the as-synthesized (a) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$; (b) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.2}\text{Mo}_{0.4}\text{O}_{6-\delta}$ and (c) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$ samples.

Figure 2. XRD patterns recorded for reduced (a) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$; (b) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.2}\text{Mo}_{0.4}\text{O}_{6-\delta}$ and (c) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$ oxides in 5 vol.% H$_2$/Argon at 1200 °C for 10h.

SEM microphotographs of reduced $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{x}\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ (x = 0.1, 0.2 and 0.3) powders are shown in Figure 3. No substantial differences were observed in the microstructure for all studied materials, and the grain size is approximately 1 µm. Interestingly, the Ti-doping at Fe-site in $\text{Sr}_2\text{Fe}_{1.4-x}\text{Ti}_x\text{Mo}_{0.6}\text{O}_{6-\delta}$ materials (x = 0–0.2) introduces a totally different microstructure with well-sintered aggregates (primary grains/crystallites are not visible) reported in the work [50].
The redox stability of Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ (x = 0.1, 0.2 and 0.3) materials was studied by annealing the compounds in 5 vol.% H$_2$ in Argon at 1200 °C for 10h. The collected XRD materials are stable to 850 °C in air (Figure 5), possessing the same simple crystal structure. While Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6}$ presents a rather high TEC value of 22.1 × 10$^{-6}$ K$^{-1}$, which can be a shortcoming for applications as electrode materials for SOFCs. No phase transition was observed in the HT-XRD studies for all samples, and all Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ materials are stable to 850 °C in air (Figure 5), possessing the same simple Pm-3m perovskite structure.
3.2. Redox Stability and Thermal Expansion Properties

In-situ XRD measurements of oxidizing reduced Sr$_2$Fe$_{1.4}$TixMo$_{0.6}$O$_{6-\delta}$ (x = 0.1, 0.2 and 0.3) compounds was also investigated by dilatometry measurements in air (see Figure 6a). As in the case of HT-XRD measurements (Figure 4), the oxidation of reduced samples in dilatometry (Figure 6a) occurs between 250 and 400 °C. A linear thermal expansion occurs in the range of 400–900 °C. Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6-\delta}$ sinter shows the smallest TEC value of Sr$_2$Fe$_{1.4}$TixMo$_{0.6}$O$_{6-\delta}$ (x = 0.1, 0.2 and 0.3) leads to an increase of TEC values. Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6-\delta}$ sinter shows the smallest TEC value of 22.1 × 10$^{-6}$ K$^{-1}$ within the temperature range of 400–900 °C. Sr$_2$Fe$_{1.4}$TixMo$_{0.6}$O$_{6-\delta}$ materials are stable to 850 °C in air (Figure 5), possessing the same simple Pm-3m perovskite structure.

Figure 4. In-situ XRD measurements of oxidizing reduced (a) Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6-\delta}$; (b) Sr$_2$Fe$_{1.4}$Ti$_{0.2}$Mo$_{0.4}$O$_{6-\delta}$ and (c) Sr$_2$Fe$_{1.4}$Ti$_{0.3}$Mo$_{0.3}$O$_{6-\delta}$ materials.

Figure 5. XRD patterns recorded at 30 °C and 850 °C in air for reduced (a) Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6-\delta}$; (b) Sr$_2$Fe$_{1.4}$Ti$_{0.2}$Mo$_{0.4}$O$_{6-\delta}$ and (c) Sr$_2$Fe$_{1.4}$Ti$_{0.3}$Mo$_{0.3}$O$_{6-\delta}$.
est TEC with $16.4 \times 10^{-6}$ K$^{-1}$ among all studied samples, and the value is comparable with the TEC measured by HT-XRD studies (Figure 6a). Data presented in Figure 6a show that the TEC value of Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ (x = 0.1, 0.2 and 0.3) increases with the increased content of Ti in materials.

![Figure 6](image_url)

**Figure 6.** Thermal expansion behaviour of (a) oxidizing reduced Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ sintered in air; (b) oxidized Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ (x = 0.1, 0.2 and 0.3) samples in air; (c) reducing oxidized Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ and the reduced sample in 5 vol. % H$_2$/argon.

In addition, the thermal expansion behavior of oxidized Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ (x = 0.1, 0.2 and 0.3) was studied in air (Figure 6b). For all three samples, two slopes with an obvious bending at 400 °C can be observed. The slope in the range of 400–900 °C, corresponding to a higher TEC, is related with the chemical expansion, caused by the reduction of B-site cations and loss of lattice oxygen, which was observed in the TG studies (Figure 7a). Sr$_2$Fe$_{1.4}$Ti$_{0.3}$Mo$_{0.5}$O$_6$ possesses the largest TEC value ($22.1 \times 10^{-6}$ K$^{-1}$), while the TEC of Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_6$ is the smallest ($15.3 \times 10^{-6}$ K$^{-1}$), which is close to the TEC values of typical solid electrolytes for SOFCs, such as: La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mo$_{0.2}$O$_{3-\delta}$ (TEC = $12.17 \times 10^{-6}$ K$^{-1}$), Zr$_{0.86}$Y$_{0.15}$O$_{2-\delta}$ (TEC = $10.8 \times 10^{-6}$ K$^{-1}$), and Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ (TEC = $12.5 \times 10^{-6}$ K$^{-1}$) [26]. Moreover, the in-situ reduction of oxidized Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6-\delta}$ sample was conducted in 5 vol. % H$_2$/argon (Figure 6c), and a considerable nonlinear change due to the reduction of B-site cations occurs above 400 °C, which corresponds well with the significant mass reduction of Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6-\delta}$ recorded in the TG measurement in Figure 7b. Meanwhile, a linear thermal expansion of reduced material was observed above 575 °C and it presents a relatively low TEC of $15.0 \times 10^{-6}$ K$^{-1}$. For the reduced Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6-\delta}$ sample in 5 vol. % H$_2$/argon, it exhibits a linear thermal expansion, with a small TEC value of $13.7 \times 10^{-6}$ K$^{-1}$, which favours the application of such a material in reducing conditions. Therefore, in the case of the application of redox sta-
ble Sr$_{2}$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6-\delta}$ perovskite as electrode material for SOFCs, the TEC mismatch (causing delamination) problem is alleviated, possibly providing stable cell performance.

As can be observed in Table 2, the substitution of Mo by Ti at B-site in Sr$_{2}$Fe$_{1.4}$Ti$_{x}$Mo$_{0.6-x}$O$_{6-\delta}$ (x = 0.1, 0.2 and 0.3) materials leads to an increase of TEC values. Hence, the Ti-doping in Sr$_{2}$Fe$_{1.4}$Ti$_{x}$Mo$_{0.6-x}$O$_{6-\delta}$ does not benefit the thermal expansion properties and the titanium content in those materials should be restricted to a rather small level (such as x = 0.1).

Table 2. Thermal expansion coefficients TEC [10$^{-6}$ K$^{-1}$] of Sr$_{2}$Fe$_{1.4}$Ti$_{x}$Mo$_{0.6-x}$O$_{6-\delta}$ (x = 0.1, 0.2 and 0.3) sinters from dilatometry studies and HT-XRD studies in air.

|          | HT-XRD (400–850 °C) | Dilatometer (400–900 °C, Oxidation in Air) | Dilatometer (400–900 °C, in Air for Oxidized Sinters) | Dilatometer (30–900 °C in 5 vol. % H$_2$/Ar for Reduced Sinters) |
|----------|---------------------|------------------------------------------|--------------------------------------------------------|---------------------------------------------------------------|
| Sr$_{2}$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6-\delta}$ | 17.4                 | 16.4                                      | 15.3                                                    | -                                                             |
| Sr$_{2}$Fe$_{1.4}$Ti$_{0.2}$Mo$_{0.4}$O$_{6-\delta}$ | 19.5                 | 16.7                                      | 19.5                                                    | 13.7                                                          |
| Sr$_{2}$Fe$_{1.4}$Ti$_{0.3}$Mo$_{0.3}$O$_{6-\delta}$ | 22.1                 | 20.0                                      | 22.1                                                    | -                                                             |

Figure 7. Oxygen content change of Sr$_{2}$Fe$_{1.4}$Ti$_{x}$Mo$_{0.6-x}$O$_{6-\delta}$ materials (a) in air and (b) in 5 vol.% H$_2$ in argon; (c) results of DSC measurements for Sr$_{2}$Fe$_{1.4}$Ti$_{x}$Mo$_{0.6-x}$O$_{6-\delta}$ (x = 0.1, 0.2 and 0.3) oxides in 5 vol.% H$_2$/Ar.
3.3. Oxygen Content and Transport Properties

The oxygen content change of Sr$_{2}$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ ($x = 0.1$, 0.2 and 0.3) was recorded by TG measurements in air and in 5 vol.% H$_2$ in argon (see Figure 7a,b), respectively. For the TG studies in air, a significant mass loss of all three samples occurs above 300 °C, indicating the generation of additional oxygen vacancies in the studied perovskites, according to the following reaction: $O_{3}^{O} \leftrightarrow 1/2O_{2} + V^{**}_{O} + 2e^{-}$, which corresponds well with the chemical expansion of materials observed in Figure 6b. The substitution of Mo$^{6+}$ by Ti$^{4+}$ in the studied Sr$_{2}$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ materials leads to the increase of oxygen vacancies. The data presented in Figure 7a indicate oxygen content decrease of ca. 0.1 mol·mol$^{-1}$ for $x = 0.1$ sample up to 900 °C, ca. 0.17 mol·mol$^{-1}$ for $x = 0.2$, and the largest change of ca. 0.20 mol·mol$^{-1}$ for $x = 0.3$ material, respectively. In the reducing condition (Figure 7b), more oxygen vacancies were created in the materials, related with the reduction of B-site cations (Fe, Ti, Mo) to lower oxygen states (Fe$^{2+}$/Fe$^{3+}$, Ti$^{3+}$ and Mo$^{5+}$/Mo$^{4+}$). The largest oxygen content change of ca. 0.86 mol·mol$^{-1}$ was recorded for Sr$_{2}$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6-\delta}$ sample. In the case of Sr$_{2}$Fe$_{1.4}$Ti$_{0.2}$Mo$_{0.4}$O$_{6-\delta}$, the oxygen content decrease of ca. 0.84 mol·mol$^{-1}$ was documented, while for Sr$_{2}$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6-\delta}$ it presents a relatively smaller change of 0.72 mol·mol$^{-1}$.

In the supplementary DSC studies (Figure 7c), no endothermic or exothermic effects were observed for the investigated compounds, confirming no phase transition recorded, which was also documented in the in-situ HT-XRD studies (see Figure 4).

The electrical conductivity $\sigma$ data measured for Sr$_{2}$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ ($x = 0.1$, 0.2 and 0.3) oxides in air (Figure 8a) show a maximum value of $\sigma$ with the increase of temperature: it increases firstly and then decreases. All three materials initially exhibit a linear relationship below 400 °C with quite similar activation energy (0.22-0.23 eV), indicating small polaron conduction behavior. Similar behavior was also observed for Sr$_{2}$Fe$_{1.2}$Mo$_{0.6}$O$_{6-\delta}$ and Sr$_{2}$Fe$_{0.9}$Mo$_{0.4}$O$_{6-\delta}$ perovskites [34]. In Sr$_{2}$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ materials, the electrons are transmitted via Fe$^{3+}$-$O^{2-}$/Fe$^{4+}$ network in air. The Ti$^{4+}$ substitution of Mo$^{6+}$ at B-site leads to the increase of Fe$^{4+}$ content, thus favouring the electrical conductivities in air. Sr$_{2}$Fe$_{1.4}$Ti$_{0.3}$Mo$_{0.3}$O$_{6-\delta}$ sample shows the highest conductivity in air among all studied materials, with a peak value of 17.8 S·cm$^{-1}$ at 500 °C. Meanwhile, in the case of Sr$_{2}$Fe$_{1.4}$Ti$_{0.2}$Mo$_{0.4}$O$_{6-\delta}$ compound, the maximum conductivity value of 11.5 S·cm$^{-1}$ was observed at around 600 °C. For Sr$_{2}$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6-\delta}$, the maximum value (9.4 S·cm$^{-1}$) was documented at 700 °C. The electrical conductivity decreases with a further increase of temperature, which is related with the release of oxygen from the lattice ($O_{3}^{O} \leftrightarrow 1/2O_{2} + V^{**}_{O} + 2e^{-}$) at high temperature range breaking the Fe$^{3+}$-$O^{2-}$/Fe$^{4+}$ network, causing the decrease of electrical conductivity. Similar behaviour was also observed in SrFeO$_3$-based materials [21,30].

In the atmosphere of 5 vol.% H$_2$/Ar, all Sr$_{2}$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ ($x = 0.1$, 0.2, and 0.3) samples exhibit lower conductivity. In the reducing condition, the electrical conductivity of Fe- and Mo-containing perovskites is strongly related with the content of Fe$^{2+}$/Fe$^{3+}$-Mo$^{6+}$/Mo$^{5+}$ redox couples [24,26,30,38,50]. The Ti-doping in Sr$_{2}$Fe$_{1.4}$Ti$_x$Mo$_{0.6-x}$O$_{6-\delta}$ leads to the decrease of Fe$^{2+}$/Fe$^{3+}$-Mo$^{6+}$/Mo$^{5+}$ redox pairs, thus resulting in the decrease of electrical conductivity. Among all three investigated samples, Sr$_{2}$Fe$_{1.4}$Ti$_{0.3}$Mo$_{0.3}$O$_{6-\delta}$ oxide possesses the lowest conductivity (1.2–2.9 in 5% H$_2$/Ar 600–800 °C) with the largest activation energy ($E_a = 0.39$ eV). In the case of Sr$_{2}$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6-\delta}$ perovskite, it shows relatively satisfactory conductivity value (4.1–7.3 S·cm$^{-1}$ at 600–800 °C) with a small activation energy $E_a = 0.25$ eV. The measured electrical conductivity $\sigma$ for Sr$_{2}$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6-\delta}$ is higher than the conductivity values (see Table 3) of Sr$_{2}$Fe$_{1.5}$Mo$_{0.1}$Cu$_{0.2}$O$_{6-\delta}$ [38], Sr$_3$Mg$_2$MoO$_{6-\delta}$ [58], Sr$_2$Fe$_{0.9}$Mo$_{0.4}$Mo$_{0.7}$O$_{6-\delta}$ [34], Sr$_2$-Ba$_2$Mg$_2$MoO$_{6-\delta}$, and Sr$_2$-Ba$_2$Mn$_2$MoO$_{6-\delta}$ [24,26], but smaller than the values of Sr$_{2}$Fe$_{1.2}$Mo$_{0.2}$O$_{6-\delta}$ [34] and Sr$_{2}$Fe$_{1.3}$Ti$_{0.1}$Mo$_{0.6}$O$_{6-\delta}$ [50].
For Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.8}$O$_{6−δ}$ sample, the chemical diffusion coefficient $D$ and surface exchange constant $k$ were evaluated by the mass relaxation study (see Figure 8b,c). The chemical diffusion coefficient $D$ is in the range of $5.7 \times 10^{-5}$ to $7.4 \times 10^{-5}$ cm$^2$ s$^{-1}$ at 600–800 °C, with an activation energy $E_{a,D} = 0.1$ eV. While the surface exchange $k$ is within the scope of $1.5 \times 10^{-3}$–$1.8 \times 10^{-3}$ cm s$^{-1}$, with a very small activation energy $E_{a,k} = 0.08$ eV. The determined chemical diffusion coefficient values are comparable with the $D$ values measured for Sr$_2$TiNi$_{0.5}$Mo$_{0.5}$O$_{6−δ}$ [49], Sr$_2$Fe$_{1.2}$Mg$_{0.2}$Mo$_{0.6}$O$_{6−δ}$ sample [34] and Sr$_2$Fe$_{1.4}$Mn$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ [59] materials. While the $k$ values of Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ are bigger than $k$ values of Sr$_2$Fe$_{1.2}$Mg$_{0.2}$Mo$_{0.6}$O$_{6−δ}$ sample [34] and Sr$_2$Fe$_{1.4}$Mn$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ [59]. The relatively good transport coefficients $D$ and $k$ evaluated for Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ compound indicate good ionic transport properties in such a material.
### Table 3. The crystal structure, electrical conductivity, thermal expansion coefficient (TEC), redox stability and compatibility with electrolytes, as well as the application of Sr$_2$(Fe,Mo)O$_{6-δ}$-based compounds.

| Material | Structure | Electrical Conductivity [S cm$^{-1}$] | TEC Value [×10$^{-6}$ K$^{-1}$] | Stability | Towards Electrolyte | Application | Ref. |
|----------|-----------|---------------------------------------|----------------------------------|----------|---------------------|-------------|------|
| Sr$_2$Fe$_1.4$Ti$_0.6$Mo$_{2.5}$O$_{6-δ}$ | Pm-3m | 9.4 at 700 °C in air; 4.1–7.3 in 5% H$_2$ at 600–800 °C | 15.3 in air | redox stable | stable with CGO and LSGM | cathode and anode candidate | this work |
| Sr$_2$Fe$_1.4$Ti$_0.6$Mo$_{2.5}$O$_{6-δ}$ | Pm-3m | 11.5 at 600 °C in air; 1.6–3.5 in 5% H$_2$ at 600–800 °C | 19.5 in air | redox stable | stable with CGO and LSGM | cathode and anode candidate | this work |
| Sr$_2$Fe$_1.4$Ti$_0.6$Mo$_{2.5}$O$_{6-δ}$ | Pm-3m | 17.8 at 500 °C in air; 1.2–2.9 in 5% H$_2$ at 600–800 °C | 22.1 in air | redox stable | stable with CGO and LSGM | cathode and anode candidate | this work |
| Sr$_2$Fe$_1.1$Mo$_{3.6}$C$_{0.2}$O$_{6-δ}$ | Fm-3m | 0.06–0.36 in 5% H$_2$ at 600–850°C | - | decomposed in H$_2$ | - | fuel electrode | [38] |
| Sr$_2$Fe$_1.5$Mo$_{0.5}$O$_{6-δ}$ | Fm-3m or Pm-3m | 2.89–5.55 in 5% H$_2$ at 600–850°C; 13 in air at 400–600°C | 13.5–18.3 in air | redox stable | stable with CGO | cathode and anode candidate | [30,38] |
| Sr$_2$Mo$_{0.6}$Mo$_{5.4}$O$_{6-δ}$ | - | 0.8 in 5% H$_2$ at 800 °C; 0.003 at 800°C in air | - | stable in 5%H$_2$ | - | anode candidate | [58] |
| Sr$_2$Fe$_1.5$Ba$_{0.5}$Mo$_{0.5}$O$_{6-δ}$ | P2$_1$/n and Fm-3m | 0.24 to 1.41 in 5% H$_2$; 11.5 to 14.8 (x = 0) in air | stable in 5% H$_2$/Ar | - | - | anode candidate | [24,26] |
| Sr$_2$Fe$_1.5$Ba$_{0.5}$Mo$_{0.5}$O$_{6-δ}$ | 14/m and Fm-3m | 0.14 to 1.38 in 5% H$_2$; 13.8 to 18.2 (x = 0) in air | redox stable | - | - | anode candidate | [24,26] |
| Sr$_2$Fe$_{1.6}$Ag$_{0.4}$Mo$_{0.5}$O$_{6-δ}$ | - | 5.4 in 5% H$_2$ at 800 °C | redox stable | Stable with LSGM and CGO, reacts with YSZ | anode candidate | [60] |
| Sr$_2$Fe$_{1.6}$Ag$_{0.4}$Mo$_{0.5}$O$_{6-δ}$ | Pm-3m | 3 at 850 °C in air; 10 at 850 °C in 5% H$_2$ | 12.9 to 14.5 in air | redox stable | stable with CGO | cathode and anode candidate | [36] |
| Sr$_2$Fe$_{1.6}$Ag$_{0.4}$Mo$_{0.5}$O$_{6-δ}$ | Fm-3m | 56.2 to 42.7 at 600–800°C in air; 7.9 to 10.3 at 600–800°C in 5% H$_2$ | 14.6 to 16.7 in 5%H$_2$; 12.9 to 14.6 in air | redox stable | stable with CGO, reacts with LSGM | cathode and anode candidate | [34] |
| Sr$_2$Fe$_{1.6}$Ag$_{0.4}$Mo$_{0.5}$O$_{6-δ}$ | Fm-3m | 7.9 to 7.5 at 600–800°C in air; 0.3 at 600–800°C in 5% H$_2$ | 14.2 to 15.1 in 5%H$_2$; 13.5 to 15.7 in air | redox stable | stable with CGO, reacts with LSGM | cathode and anode candidate | [34] |
| Sr$_2$Fe$_{1.6}$Ag$_{0.4}$Mo$_{0.5}$O$_{6-δ}$ | Pnma | 30 in air at 550 °C | 16.1 in air | stable with LSGM | stable with LSGM | cathode and anode candidate | [61] |
| Sr$_2$Fe$_{1.6}$Ag$_{0.4}$Mo$_{0.5}$O$_{6-δ}$ | - | 54.8 in air at 630 °C | 19.4 in air | decomposed in H$_2$ | - | anode candidate | [62] |
| Sr$_2$Fe$_{1.6}$Ag$_{0.4}$Mo$_{0.5}$O$_{6-δ}$ | Pm-3m | 2.7 to 6.7 at 600–800°C in H$_2$ | 15.1 in 5% H$_2$; 13.4 in air | stable <750 °C in H$_2$ | stable with LSGM | cathode and anode candidate | [63] |
| Sr$_2$Fe$_{1.6}$Ag$_{0.4}$Mo$_{0.5}$O$_{6-δ}$ | Fm-3m | 4–5 in air at 600–800 °C; 9–13 in H$_2$ at 600–800 °C | 16.9 in air | redox stable | stable with LDC | anode candidate | [37] |
| Sr$_2$Fe$_{1.6}$Ag$_{0.4}$Mo$_{0.5}$O$_{6-δ}$ | 14/m | 55.4 in 5% H$_2$ at 800 °C | - | decomposed in H$_2$ | - | anode candidate | [18] |
| Sr$_2$Fe$_{1.6}$Ag$_{0.4}$Mo$_{0.5}$O$_{6-δ}$ | Fm-3m | 220 to 160 at 500–800 °C in 5% H$_2$ | 13.5 at 550 °C in air | stable in H$_2$ | stable with CGO | anode candidate | [50] |
| Sr$_2$TiFe$_{1.6}$Ag$_{0.4}$Mo$_{0.5}$O$_{6-δ}$ | Pm-3m | 22.3 in H$_2$ at 800 °C | 11.2 in H$_2$ | stable with LSGM91 and CSO | anode candidate | [57] |
| Sr$_2$TiFe$_{1.6}$Ag$_{0.4}$Mo$_{0.5}$O$_{6-δ}$ | - | 17.5 at 800 °C in hydrogen | 12.8 in air | stable in H$_2$ | stable with LSGM | anode candidate | [49] |
| Sr$_2$Fe$_{1.6}$Ba$_{0.5}$Mo$_{0.5}$O$_{6-δ}$ | 14/m and Fm-3m | 100 to 1000 in 5% H$_2$ | 13.8 for x = 0 in air | stable in 5%H$_2$ | stable with CGO | anode candidate | [24,26] |
| SrFe$_{0.48}$Co$_{0.4}$Mo$_{0.5}$O$_{6-δ}$ | Pm-3m | 298 at 300 °C in air | 14.8 to 30.8 in air | stable in air | - | electrode candidate | [39] |
| Sr$_2$Mo$_{0.5}$Co$_{0.5}$Mo$_{0.5}$O$_{6-δ}$ | 1-1 | 9 to 7 at 600–800 °C in 5% H$_2$ | 13.9 in air | - | - | anode candidate | [40] |

CGO: Ca$_{0.6}$Gd$_{0.2}$O$_{1.9}$, LSGM: La$_{0.6}$Sr$_{0.4}$Ga$_{0.8}$Mg$_{0.2}$O$_{3-δ}$, YSZ: Zr$_{0.92}$Ti$_{0.08}$O$_{1.96}$, LDC: La$_{0.4}$Ce$_{0.6}$O$_{2-δ}$, LSGM91: La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{3-δ}$, CSO: Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$. 
3.4. Chemical Stability and Compatibility with Electrolytes

The stability of cathode and anode oxides and their compatibility towards applied electrolytes at high temperature range are very critical for the electrode layer preparation (sintering) and a stable performance of cells. Therefore, the chemical stability of Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6}$O$_{6-\delta}$ ($x = 0.1$, 0.2 and 0.3) oxides and their compatibility with typical solid electrolyte/buffer layer materials, such as Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$–CGO20 and La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3-\delta}$–LSGM, were evaluated by analyzing XRD data gathered for the respective materials and solid electrolyte powders (50:50 wt.%), which were fired in air for 10 h at 1200 °C. The Rietveld refined XRD patterns of Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6}$O$_{6-\delta}$ electrolytes (CGO20 and LSGM), confirming the good stability and compatibility of electrolytes at high temperature range are very critical for the electrode layer preparation.

Regrettably, similar compositions Sr$_2$Fe$_{1.3}$Ti$_0.1$Mo$_{0.6}$O$_{6-\delta}$ and Sr$_2$Fe$_{1.4}$Ti$_0.2$Mo$_{0.4}$O$_{6-\delta}$ with Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ electrolyte, after sintering at 1200 °C for 10 h. As presented in Table 4, the unit cell parameter of Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ from different mixtures is very similar, and the unit cell parameters of Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6}$O$_{6-\delta}$ ($x = 0.1$, 0.2 and 0.3) from CGO20 mixtures are also very close to the values of appropriate materials recorded from LSGM mixtures. In addition, the unit cell parameter for LSGM from various mixtures is almost identical. This shows the good chemical stability of all investigated electrode materials and their compatibility towards electrolytes (Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ and La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3-\delta}$). Interestingly, similar compositions Sr$_2$Fe$_{1.3}$Ga$_{0.2}$Mo$_{0.8}$O$_{6-\delta}$ and Sr$_2$Fe$_{0.9}$Mo$_{0.4}$O$_{6-\delta}$ are compatible with Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ electrolyte but react with La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3-\delta}$ [34]. Sr$_2$Fe$_{1.3}$Ti$_{0.1}$Mo$_{0.6}$O$_{6-\delta}$ (material unstable in air) is also compatible with Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ [50].
In addition, the long-term compatibility of Sr$_2$Fe$_{1.4}$Ti$_{x}$Mo$_{0.5}$O$_{6−δ}$ towards Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ and with La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3−δ}$ solid electrolytes was evaluated, after firing for 100 h at 800 °C in air. As shown in Figure 11, Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ sample has no reaction with Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ and La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3−δ}$ after annealing at 800 °C for 100 h. Moreover, the structural parameters gathered for Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$, Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ and La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3−δ}$ materials in Table 5 are very close to the respective results in Table 4, which indicate that the Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ sample exhibits excellent stability and compatibility towards the used solid electrolytes, potentially providing a stable performance of Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ in the cell.

Table 4. Structural parameters of Sr$_2$Fe$_{1.4}$Ti$_{x}$Mo$_{0.5}$O$_{6−δ}$ (x = 0.1, 0.2 and 0.3) oxides with Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ and with La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3−δ}$ electrolytes from 50:50 wt.% mixtures fired in air for 10 h at 1200 °C.

| Composition | x = 0.1 | Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ | x = 0.2 | Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ | x = 0.3 | Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ |
|-------------|---------|-----------------------------|---------|-----------------------------|---------|-----------------------------|
| space group | Pn-3m   | Pn-3m                       | Pn-3m   | Pn-3m                       | Pn-3m   | Pn-3m                       |
| u [Å]       | 3.9250 (1) | 5.4263 (1)                   | 3.9134 (1) | 5.4259 (1)                   | 3.9049 (1) | 5.4256 (1)                   |
| V [Å$^3$]   | 60.47 (1) | 159.78 (1)                   | 59.93 (1) | 159.74 (1)                   | 59.54 (1) | 159.72 (1)                   |
| CHI$^2$     | 3.29     | 4.35                         |          | 3.08                         |          | 2.70                         |
| Rp (%)      | 1.66     | 1.66                         |          | 1.70                         |          | 1.76                         |
| R$^{e_p}$ (%)| 2.70     | 3.09                         |          | 2.62                         |          | 2.62                         |

In addition, the long-term compatibility of Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ towards Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ and with La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3−δ}$ solid electrolytes was evaluated, after firing for 100 h at 800 °C in air. As shown in Figure 11, Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ sample has no reaction with Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ and La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3−δ}$ after annealing at 800 °C for 100 h. Moreover, the structural parameters gathered for Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$, Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ and La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3−δ}$ materials in Table 5 are very close to the respective results in Table 4, which indicate that the Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ sample exhibits excellent stability and compatibility towards the used solid electrolytes, potentially providing a stable performance of Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ in the cell.

Figure 11. XRD patterns recorded for (a) Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ with Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$; (b) Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_{6−δ}$ with La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3−δ}$ electrolyte, after firing for 100 h at 800 °C in air.
Table 5. Structural parameters of Sr$_{2}$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_6$–δ sample with Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ and with La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3}$–δ electrolytes after the long-term studies for 100 h at 800 °C in air.

| Composition                  | Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_6$–δ | Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ | Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_6$–δ | La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3}$–δ |
|------------------------------|--------------------------------------------|-------------------------------|--------------------------------------------|--------------------------------------------|
| space group                  | Pm-3m                                      | Pm-3m                         | Pm-3m                                      | Pm-3m                                      |
| a [Å]                        | 3.9268 (1)                                 | 5.4289 (1)                    | 3.9229 (1)                                | 3.9148 (1)                                |
| V [Å$^3$]                    | 60.55 (1)                                  | 160.00 (1)                    | 60.37 (1)                                 | 60.00 (1)                                 |
| CHI$^2$                      |                                            |                               |                                            |                                            |
| Rp (%)                       | 2.51                                       | 2.02                          | 1.93                                       | 2.82                                       |
| Rwp (%)                      | 2.89                                       |                               |                                            |                                            |

4. Summary

In this work, the stability of Sr$_2$(FeMo)O$_6$–δ-type perovskites was successfully tailored by the substitution of Mo with Ti at B-site, and Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6}$–xO$_6$–δ (x = 0.1, 0.2 and 0.3) perovskites in reducing and oxidizing conditions were obtained. All Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6}$–xO$_6$–δ materials possess a regular simple perovskite structure with Pm-3m space group, showing excellent stability in both reducing and oxidizing conditions up to 1200 °C. All three materials present a similar microstructure with 1 µm grain size. The in-situ oxidation of reduced samples, observed by HT-XRD measurements and dilatometry studies, shows that the increased content of Ti doping at Mo-site in materials increases the TEC values. Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_6$–δ shows the lowest TEC with 15.3 × 10$^{-6}$ K$^{-1}$. In addition, Ti-doping also increases the oxygen content change and electrical conductivity in air, while it decreases the conductivity in reducing condition. Sr$_2$Fe$_{1.4}$Ti$_{0.3}$Mo$_{0.2}$O$_6$–δ sample presents the highest conductivity in air with 17.8 S·cm$^{-1}$ at 500 °C, while the high TEC value of 22.1 × 10$^{-6}$ K$^{-1}$ can potentially limit the application. All three Sr$_2$Fe$_{1.4}$Ti$_x$Mo$_{0.6}$–xO$_6$–δ materials are stable and compatible with studied electrolytes (Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ and La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3}$–δ).

Redox stable Sr$_2$Fe$_{1.4}$Ti$_{0.1}$Mo$_{0.5}$O$_6$–δ seems to be the most interesting among studied materials, with large oxygen content change of 0.72 mol·mol$^{-1}$ between 30 and 900 °C, satisfactory conductivity of 4.1–7.3 S·cm$^{-1}$ in 5% H$_2$ at 600–800 °C, and good transport coefficients D and k, which indicate that such a material can be considered as a potential anode material for SOFCs and is of great interest for further studies.

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