

Article

Tailoring the Stability of Ti-Doped $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ Electrode Materials for Solid Oxide Fuel Cells

Kun Zheng ^{1,2,*} , Maciej Albrycht ³, Min Chen ⁴, Kezhen Qi ⁵  and Paweł Czaja ⁶

¹ Department of Hydrogen Energy, Faculty of Energy and Fuels, AGH University of Science and Technology, al. A. Mickiewicza 30, 30-059 Krakow, Poland

² AGH Centre of Energy, AGH University of Science and Technology, ul. Czarnowiejska 36, 30-054 Krakow, Poland

³ Decentralised Hydrogen—Maciej Albrycht, ul. Wały Dzwernickiego 21/23a, lok. 8, 42-200 Częstochowa, Poland

⁴ School of Materials Science and Energy Engineering, Foshan University, Foshan 528000, China

⁵ College of Pharmacy, Dali University, Dali 671000, China

⁶ Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 25 Reymonta Str., 30-059 Krakow, Poland

* Correspondence: zheng@agh.edu.pl

Abstract: In this work, the stability of $\text{Sr}_2(\text{FeMo})\text{O}_{6-\delta}$ -type perovskites was tailored by the substitution of Mo with Ti. Redox stable $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ compounds exhibit a regular crystal structure with $Pm-3m$ 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$, possessing $1\ \mu\text{m}$ grain size, low TEC ($15.3 \times 10^{-6}\ \text{K}^{-1}$), large oxygen content change of $0.72\ \text{mol}\cdot\text{mol}^{-1}$ between 30 and $900\ ^\circ\text{C}$, satisfactory conductivity of $4.1\text{--}7.3\ \text{S}\cdot\text{cm}^{-1}$ in 5% H_2 at $600\text{--}800\ ^\circ\text{C}$, 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 $\text{Sr}_2(\text{FeMo})\text{O}_{6-\delta}$ perovskites; redox stability; anode materials; solid oxide fuel cells; crystal structure; thermal expansion; oxygen content; transport properties; compatibility with electrolytes



Citation: Zheng, K.; Albrycht, M.; Chen, M.; Qi, K.; Czaja, P. Tailoring the Stability of Ti-Doped $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ Electrode Materials for Solid Oxide Fuel Cells. *Materials* **2022**, *15*, 8268. <https://doi.org/10.3390/ma15228268>

Academic Editor: Ana Belen Munoz Garcia

Received: 22 October 2022

Accepted: 16 November 2022

Published: 21 November 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

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 $800\ ^\circ\text{C}$) 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 ($\leq 800\ ^\circ\text{C}$) 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 $800\ ^\circ\text{C}$ [11–14].

One group of the most interesting cathode and anode material candidates for SOFCs is the $\text{Sr}_2(\text{FeMo})\text{O}_6$ -type perovskite with Fe- and Mo-cations at B-site [15–21]. The B-site rock

salt-type ordered $\text{Sr}_{2-x}\text{Ba}_x\text{M}_{1-y}\text{Mo}_y\text{O}_6$ ($\text{M} = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) 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 Mo^{6+} or Mo^{5+} (in reducing atmospheres) and larger $\text{M}^{2+/3+}$ cations (3d elements and Mg) [6,29]. The redox couple of $\text{M}^{2+}/\text{M}^{3+}$ and $\text{Mo}^{6+}/\text{Mo}^{5+}$ present in $\text{Sr}_2(\text{Fe},\text{Mo})\text{O}_{6-\delta}$ -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 $\text{Sr}_2\text{Fe}_{1.2}\text{Mg}_{0.2}\text{Mo}_{0.6}\text{O}_{6-\delta}$ and $\text{Sr}_2\text{Fe}_{0.9}\text{Mg}_{0.4}\text{Mo}_{0.7}\text{O}_{6-\delta}$ 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 H_2O 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 $\text{Fe}_\text{B}\text{-O-Fe}_\text{B'}$ bonds in materials promote easy creation of oxygen vacancies and their fast migration. However, the low electrical conductivity ($4\text{--}5 \text{ S cm}^{-1}$ at $600\text{--}800^\circ\text{C}$ in air) may limit the application of such a material for SOFCs [37]. The copper-substituted $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.3}\text{Cu}_{0.2}\text{O}_{6-\delta}$ material was investigated as a fuel electrode for the oxidation of H_2 and $\text{CO}_2\text{-CO}$ reduction, showing improved reaction activity and durability, with an excellent SOFC power yield of 1.51 W cm^{-2} in H_2 and a very good current density in the reduction of CO_2 (with 1.94 A cm^{-2} at 1.4 V) [38]. The effect of Co-doping on the physico-chemical 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, $(\text{PrBa})_{0.95}(\text{Fe}_{0.9}\text{Mo}_{0.1})_2\text{O}_{5+\delta}$ 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 H_2S -containing fuel [8,11]. Therefore, the further modification of $\text{Sr}_2(\text{Fe},\text{Mo})\text{O}_6$ -type perovskites will contribute to the development of novel cathode and anode materials with high performance for SOFCs.

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 H_2S -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 $\text{La}_{0.5}\text{Sr}_{1.5}\text{Ti}_{1.5}\text{M}_{0.5}\text{O}_{6-\delta}$ ($\text{M} = \text{Fe}, \text{Co}$ and Ni) double

perovskites were evaluated in terms of their application as new anode material candidates for [47]. $\text{Sr}_2\text{ScTi}_{1-x}\text{Mo}_x\text{O}_6$ ($x = 0.1$ 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 $\text{Sr}_2\text{TiNi}_{0.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ 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 $\text{Sr}_2\text{Fe}_{2-x}\text{Mo}_x\text{O}_{6-\delta}$ 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Mo}_{0.6}\text{O}_{6-\delta}$ anode material shows much better electrochemical performance than the SOFC cell with redox stable $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ electrode [32]. $\text{Sr}_2\text{Fe}_{1.4}\text{Mo}_{0.6}\text{O}_{6-\delta}$ 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 $\text{Sr}_2\text{Fe}_{1.4-x}\text{Ti}_x\text{Mo}_{0.6}\text{O}_{6-\delta}$ double perovskites significantly improves the structural stability of materials, which were systematically investigated as new anode material candidates for SOFCs [50]. $\text{Sr}_2\text{Fe}_{1.3}\text{Ti}_{0.1}\text{Mo}_{0.6}\text{O}_{6-\delta}$ anode-based SOFC cell delivers a promising power output with $>0.64 \text{ W cm}^2$ 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) perovskites was tailored by the substitution of Mo with Ti at B-site. $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) materials was conducted using the high temperature method (solid state reaction), with the calculated amounts of SrCO_3 , Fe_2O_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 $10\text{--}110^\circ$ 2 Theta range using the Panalytical Empyrean diffractometer ($\text{CuK}\alpha$ radiation, Malvern, UK).

The chemical stability of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) samples using Panalytical Empyrean apparatus with Anton Paar HTK 1200N oven-chamber. The in-situ oxidation of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ 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 (σ) of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) materials towards typical electrolytes, such as CGO20– $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ and LSGM– $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ solid electrolytes, were investigated by examining 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) samples exhibit simple perovskite crystal structure, belonging to the cubic $Pm-3m$ space-group. However, the $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ 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+} ($r_{\text{Fe}^{3+}} = 0.645 \text{ \AA}$) and Fe^{4+} ($r_{\text{Fe}^{4+}} = 0.585 \text{ \AA}$) causes the decrease of the unit cell parameter, despite Ti^{4+} ($r_{\text{Ti}^{4+}} = 0.605 \text{ \AA}$) presenting a slightly bigger ionic radius than Mo^{6+} ($r_{\text{Mo}^{6+}} = 0.59 \text{ \AA}$). 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) samples, which indicates the presence of a regular crystal structure in the studied materials. Similar compositions, such as $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ and $\text{SrFe}_{0.5}\text{Mn}_{0.25}\text{Mo}_{0.25}\text{O}_{3-\delta}$ [30], $\text{Sr}_2\text{TiFe}_{0.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ [57], and $\text{SrFe}_{0.45}\text{Co}_{0.45}\text{Mo}_{0.1}\text{O}_{3-\delta}$ [39] oxides, also show a $Pm-3m$ simple perovskite structure. Meanwhile, the Ti-doping at Fe-site in $\text{Sr}_2\text{Fe}_{1.4-x}\text{Ti}_x\text{Mo}_{0.6}\text{O}_{6-\delta}$ ($x = 0$ and 0.1) leads to a double perovskite structure with $Fm-3m$ space group [50].

Table 1. Rietveld refinement results including unit cell parameters for the as-synthesized and 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) oxides.

Composition	x = 0.1		x = 0.2		x = 0.3	
	* As Synthesized	Reduced	As Synthesized	Reduced	As Synthesized	Reduced
space group	$Pm-3m$	$Pm-3m$	$Pm-3m$	$Pm-3m$	$Pm-3m$	$Pm-3m$
$a [\text{\AA}]$	3.9190 (1)	3.9257 (1)	3.9121 (1)	3.9277 (1)	3.9038 (1)	3.9186 (1)
$V [\text{\AA}^3]$	60.19 (1)	60.50 (1)	59.88 (1)	60.59 (1)	59.49 (1)	60.17 (1)
relative volume change ΔV	0.52%		1.19%		1.14%	
density $[\text{g}/\text{cm}^3]$	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.

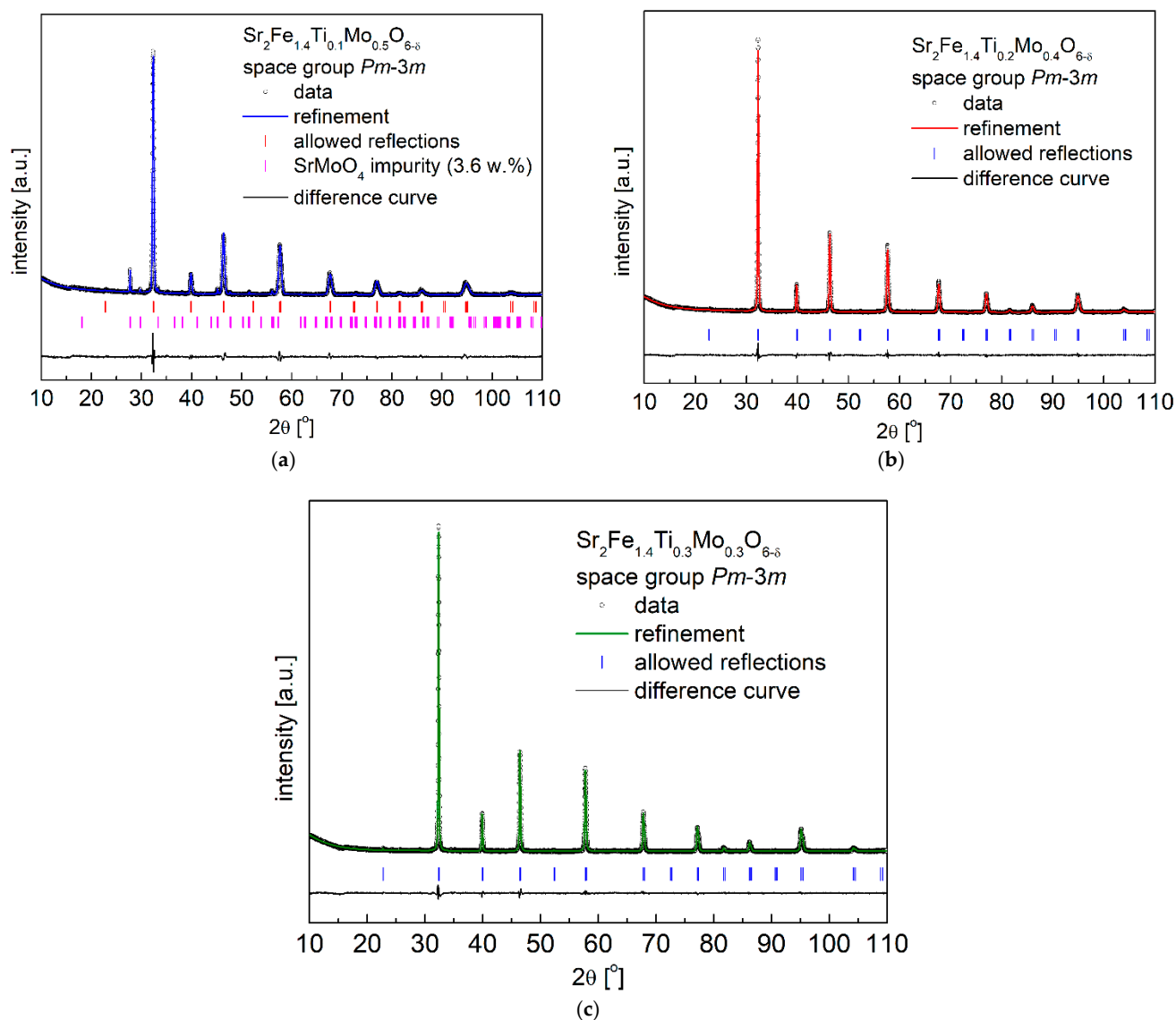


Figure 1. XRD patterns of the as-synthesized (a) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$; (b) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.2}\text{Mo}_{0.4}\text{O}_{6-\delta}$ and (c) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$ samples.

The redox stability of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ materials, $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ 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 $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ and $\text{Sr}_2\text{Fe}_{0.9}\text{Mg}_{0.4}\text{Mo}_{0.7}\text{O}_{6-\delta}$ oxides are larger and reach 1.18% [30] and 0.55% [34], respectively. The increase of Ti-doping in $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.2$ and 0.3) leads to a significantly large volume change ΔV , which can contribute to larger thermal expansion coefficients (TEC) in reducing and oxidizing atmospheres.

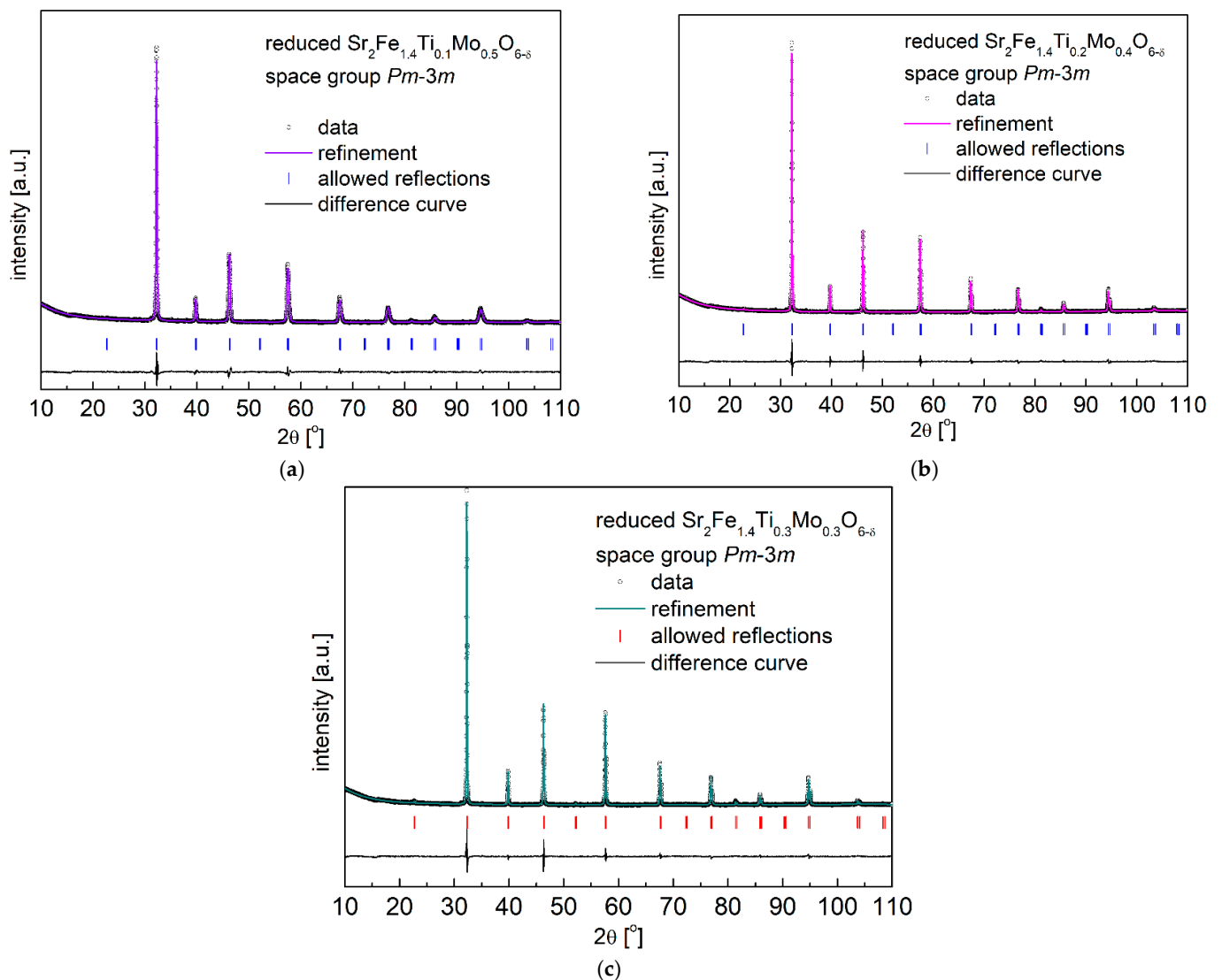


Figure 2. XRD patterns recorded for reduced (a) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$; (b) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.2}\text{Mo}_{0.4}\text{O}_{6-\delta}$ and (c) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$ oxides 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].

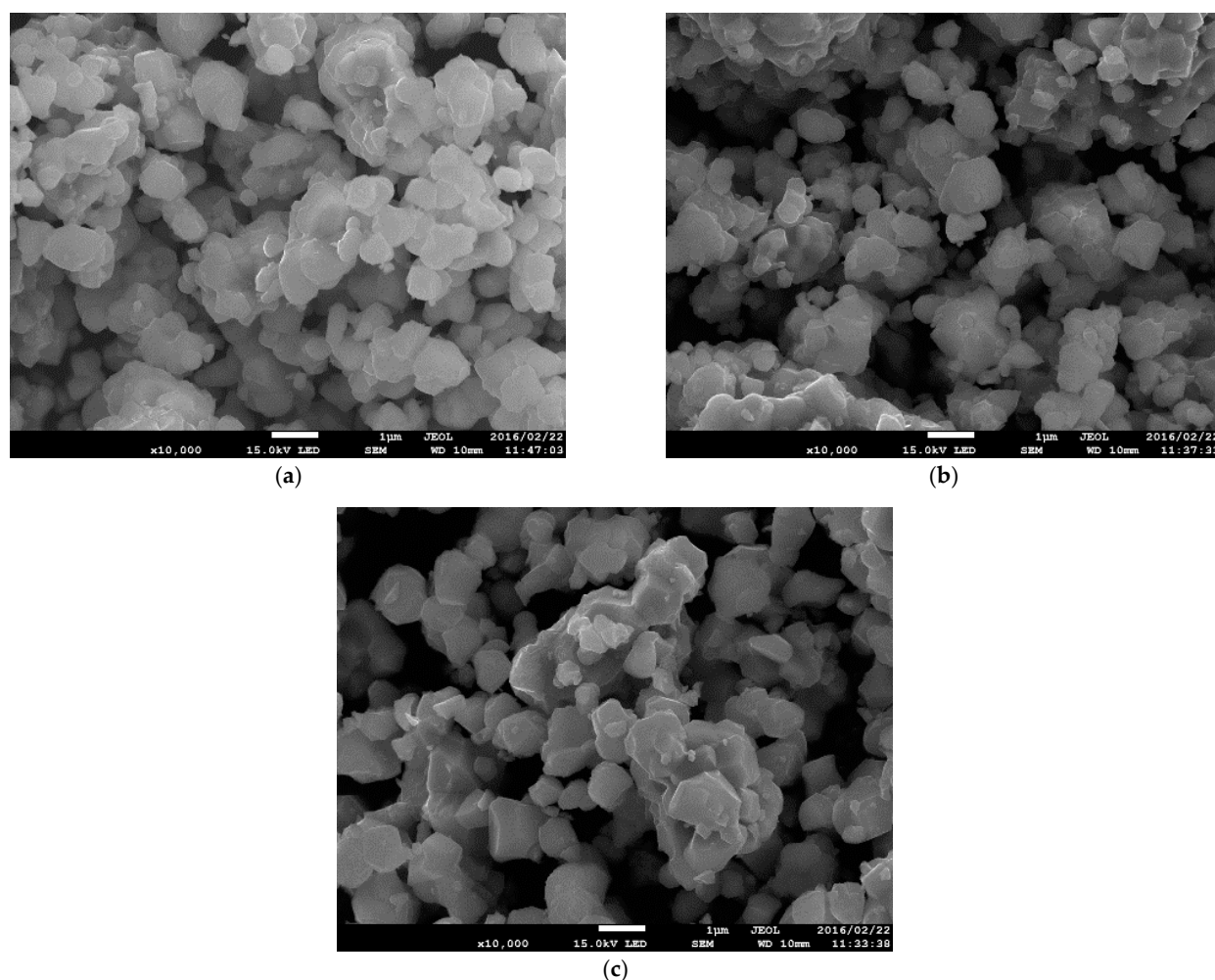


Figure 3. SEM micrographs of reduced (a) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$; (b) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.2}\text{Mo}_{0.4}\text{O}_{6-\delta}$ and (c) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$ powder.

3.2. Redox Stability and Thermal Expansion Properties

The in-situ oxidation 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) samples was examined by the high temperature XRD (HT-XRD) measurements in air. As can be observed in Figure 4, the oxidation of the reduced materials starts around 250°C and finishes below 400°C , accompanied by the significant change of unit cell parameter a . This is associated with the oxidation of reduced B-site cations (Fe, Ti, and Mo). The introduction of a higher content of titanium in $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.2$ and 0.3) leads to a more considerable unit cell parameter change. The initial linear increase of unit cell parameter recorded below 250°C is attributed to the thermal expansion of reduced samples. Above 400°C , the oxidized materials present a linear increase of unit cell parameter (indicating a linear thermal expansion behavior) to 850°C in air, and the HT-XRD data allow to calculate the thermal expansion coefficient (TEC). The increase of Ti content in $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ leads to an increase of TEC values. $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ sample shows the lowest TEC among all studied materials, with $\text{TEC} = 17.4 \times 10^{-6} \text{ K}^{-1}$. While $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$ presents a rather high TEC value of $22.1 \times 10^{-6} \text{ K}^{-1}$, 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ materials are stable to 850°C in air (Figure 5), possessing the same simple $Pm\text{-}3m$ perovskite structure.

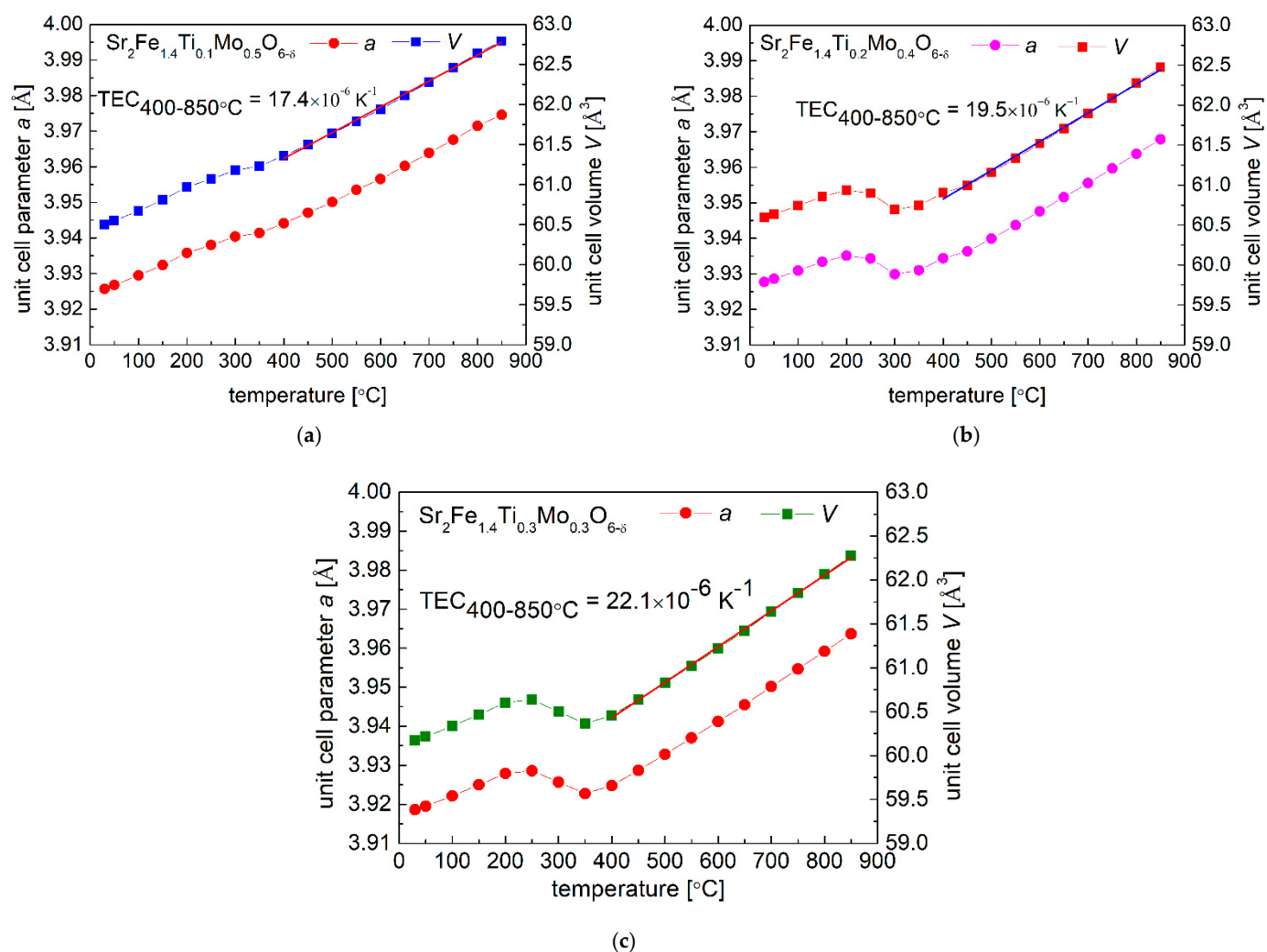


Figure 4. In-situ XRD measurements of oxidizing reduced (a) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$; (b) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.2}\text{Mo}_{0.4}\text{O}_{6-\delta}$ and (c) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$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

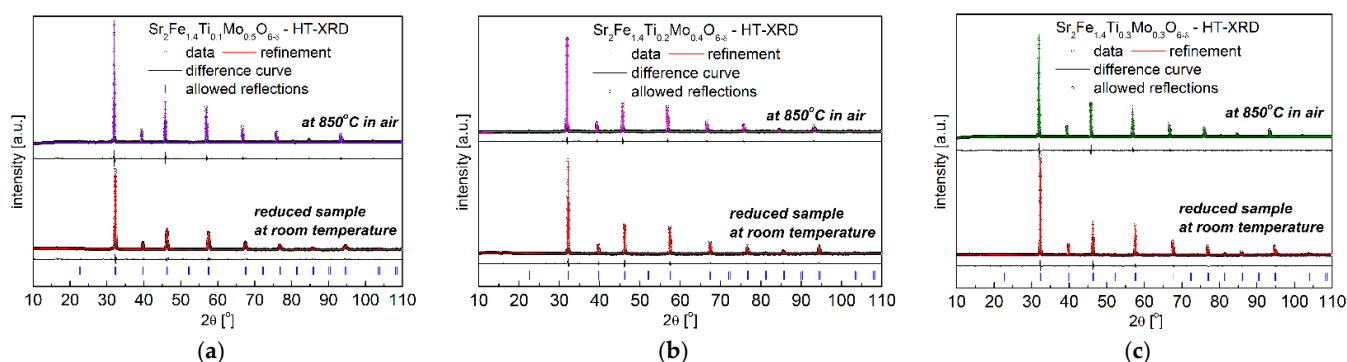


Figure 5. XRD patterns recorded at 30 °C and 850 °C in air for reduced (a) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$; (b) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.2}\text{Mo}_{0.4}\text{O}_{6-\delta}$ and (c) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$.

The in-situ oxidation 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) 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 measurements (Figure 6a) occurs between 250 and 400 °C. A linear thermal expansion of reduced samples was recorded below 250 °C, and for oxidized materials a linear thermal expansion occurs in the range of 400–900 °C. $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ sinter shows the small-

est TEC with $16.4 \times 10^{-6} \text{ K}^{-1}$ 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) increases with the increased content of Ti in materials.

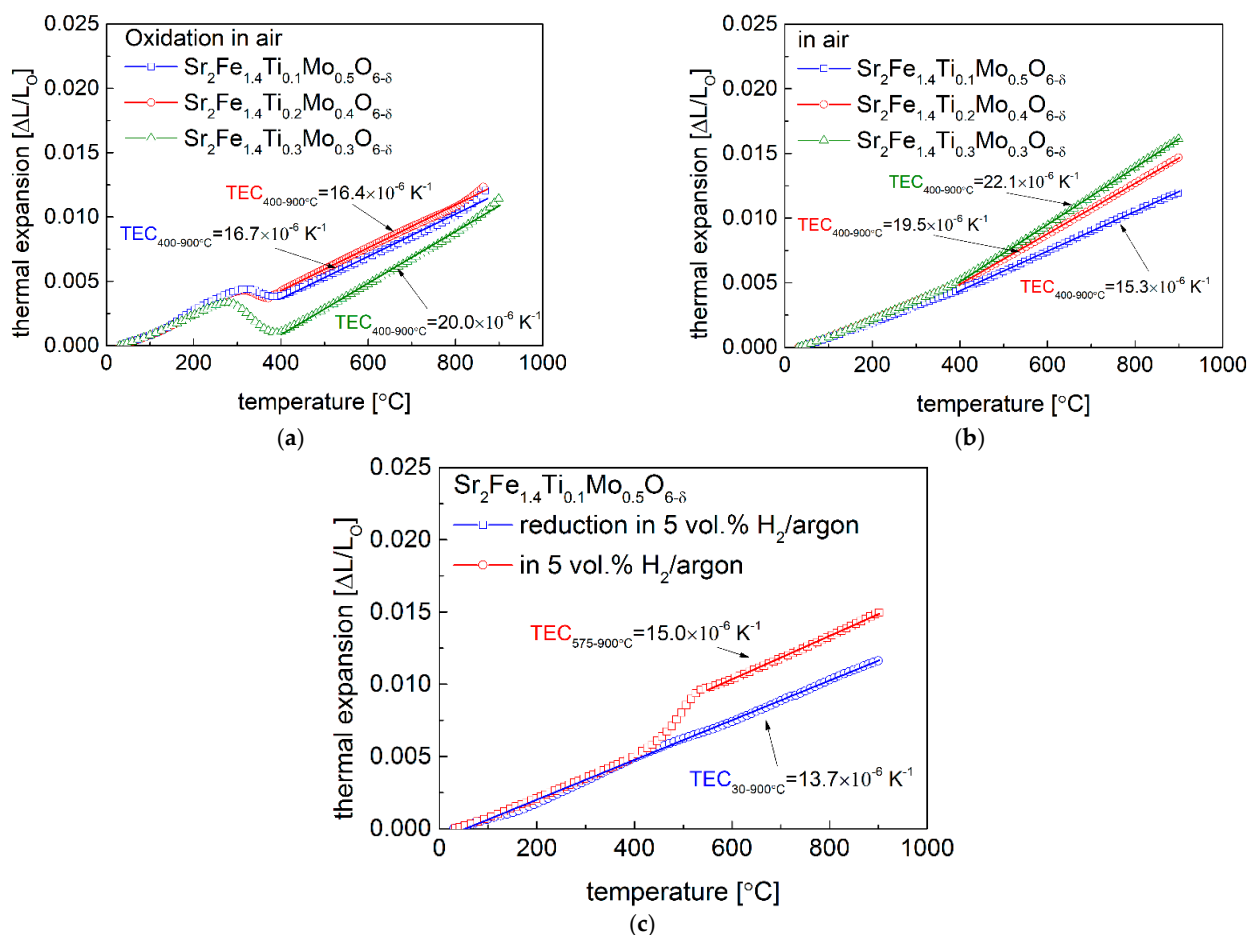


Figure 6. Thermal expansion behaviour of (a) oxidizing reduced $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ sinters in air; (b) oxidized $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) samples in air; (c) reducing oxidized $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ and the reduced sample in 5 vol. % H_2/argon .

In addition, the thermal expansion behavior of oxidized $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) 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). $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$ possesses the largest TEC value ($22.1 \times 10^{-6} \text{ K}^{-1}$), while the TEC of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ is the smallest ($15.3 \times 10^{-6} \text{ K}^{-1}$), which is close to the TEC values of typical solid electrolytes for SOFCs, such as: $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (TEC = $12.17 \times 10^{-6} \text{ K}^{-1}$), $\text{Zr}_{0.85}\text{Y}_{0.15}\text{O}_{2-\delta}$ (TEC = $10.8 \times 10^{-6} \text{ K}^{-1}$), and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (TEC = $12.5 \times 10^{-6} \text{ K}^{-1}$) [26]. Moreover, the in-situ reduction of oxidized $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ 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 $15.0 \times 10^{-6} \text{ K}^{-1}$. For the reduced $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ sample in 5 vol. % H_2/argon , it exhibits a linear thermal expansion, with a small TEC value of $13.7 \times 10^{-6} \text{ K}^{-1}$, which favours the application of such a material in reducing conditions. Therefore, in the case of the application of redox sta-

ble $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ perovskite as electrode material for SOFCs, the TEC mismatch (causing delamination) problem is alleviated, possibly providing stable cell performance.

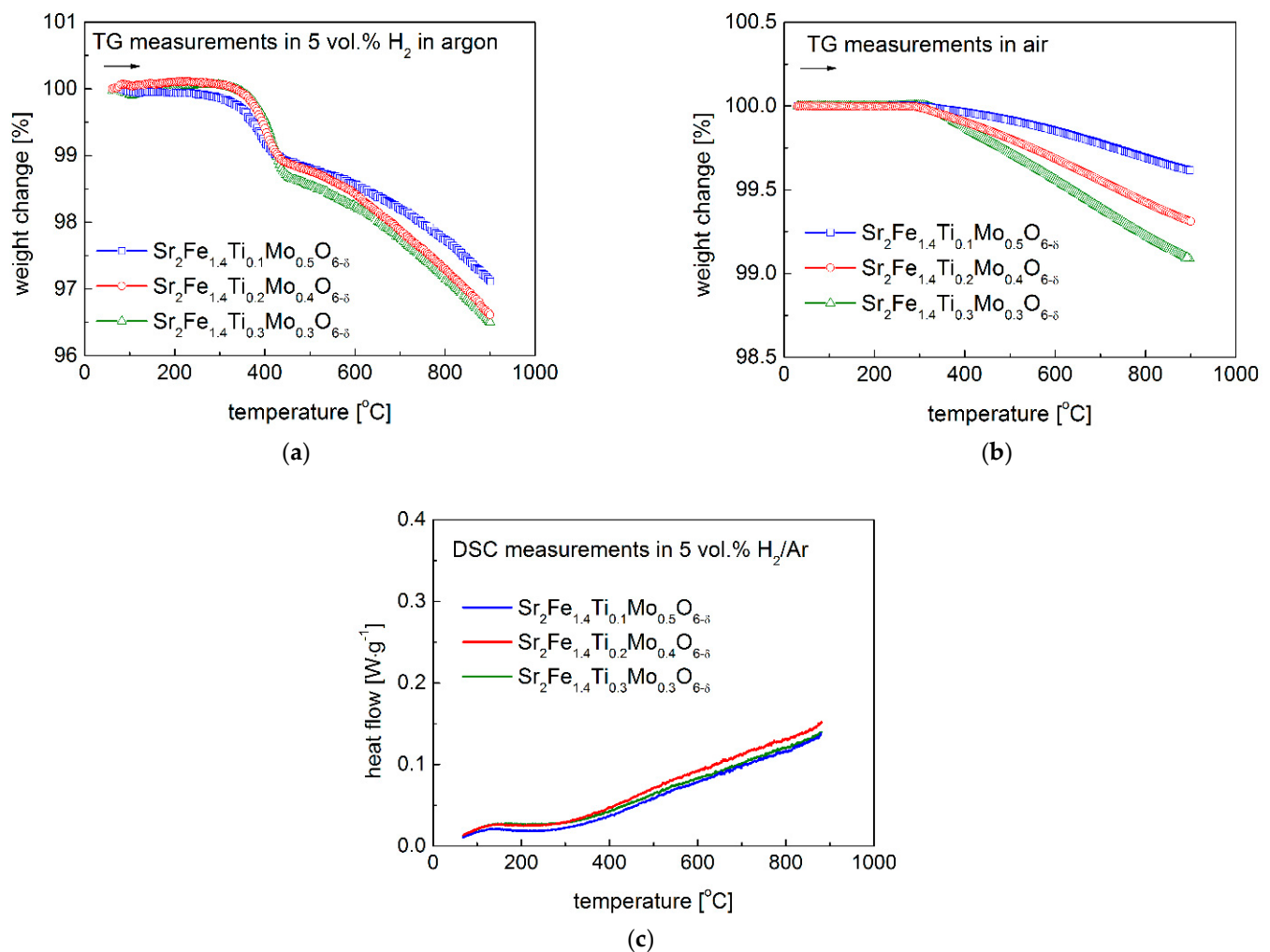


Figure 7. Oxygen content change of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ materials (a) in air and (b) in 5 vol.% H_2 in argon; (c) results of DSC measurements for $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) oxides in 5 vol.% H_2/Ar .

As can be observed in Table 2, the substitution of Mo by Ti at B-site in $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) materials leads to an increase of TEC values. Hence, the Ti-doping in $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) 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 Sintors)	Dilatometer (30–900 °C in 5 vol. % H_2/Argon for Reduced Sintors)
$\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$	17.4	16.4	15.3	-
$\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.2}\text{Mo}_{0.4}\text{O}_{6-\delta}$	19.5	16.7	19.5	13.7
$\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$	22.1	20.0	22.1	-

3.3. Oxygen Content and Transport Properties

The oxygen content change of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) 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: $\text{O}_\text{O}^\times \leftrightarrow 1/2\text{O}_2 + \text{V}_\text{O}^{\bullet\bullet} + 2\text{e}^-$, which corresponds well with the chemical expansion of materials observed in Figure 6b. The substitution of Mo^{6+} by Ti^{4+} in the studied $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ materials leads to the increase of oxygen vacancies. The data presented in Figure 7a indicate oxygen content decrease of ca. $0.1 \text{ mol}\cdot\text{mol}^{-1}$ for $x = 0.1$ sample up to 900°C , ca. $0.17 \text{ mol}\cdot\text{mol}^{-1}$ for $x = 0.2$, and the largest change of ca. $0.20 \text{ mol}\cdot\text{mol}^{-1}$ 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 ($\text{Fe}^{2+}/\text{Fe}^{3+}$, Ti^{3+} and $\text{Mo}^{5+}/\text{Mo}^{4+}$). The largest oxygen content change of ca. $0.86 \text{ mol}\cdot\text{mol}^{-1}$ was recorded for $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$ sample. In the case of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.2}\text{Mo}_{0.4}\text{O}_{6-\delta}$, the oxygen content decrease of ca. $0.84 \text{ mol}\cdot\text{mol}^{-1}$ was documented, while for $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ it presents a relatively smaller change of $0.72 \text{ mol}\cdot\text{mol}^{-1}$.

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 σ data measured for $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) oxides in air (Figure 8a) show a maximum value of σ 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 ($0.22\text{--}0.23 \text{ eV}$), indicating small polaron conduction behavior. Similar behavior was also observed for $\text{Sr}_2\text{Fe}_{1.2}\text{Mg}_{0.2}\text{Mo}_{0.6}\text{O}_{6-\delta}$ and $\text{Sr}_2\text{Fe}_{0.9}\text{Mg}_{0.4}\text{Mo}_{0.7}\text{O}_{6-\delta}$ perovskites [34]. In $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ materials, the electrons are transmitted via $\text{Fe}^{3+}\text{--O}^{2-}/\text{Fe}^{4+}$ 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. $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$ sample shows the highest conductivity in air among all studied materials, with a peak value of $17.8 \text{ S}\cdot\text{cm}^{-1}$ at 500°C . Meanwhile, in the case of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.2}\text{Mo}_{0.4}\text{O}_{6-\delta}$ compound, the maximum conductivity value of $11.5 \text{ S}\cdot\text{cm}^{-1}$ was observed at around 600°C . For $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$, the maximum value ($9.4 \text{ S}\cdot\text{cm}^{-1}$) 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 ($\text{O}_\text{O}^\times \leftrightarrow 1/2\text{O}_2 + \text{V}_\text{O}^{\bullet\bullet} + 2\text{e}^-$) at high temperature range breaking the $\text{Fe}^{3+}\text{--O}^{2-}\text{--Fe}^{4+}$ 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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$, and 0.3) samples exhibit lower conductivity. In the reducing condition, the electrical conductivity of Fe- and Mo-containing perovskites is strongly related with the content of $\text{Fe}^{2+}/\text{Fe}^{3+}\text{--Mo}^{6+}/\text{Mo}^{5+}$ redox couples [24,26,30,38,50]. The Ti-doping in $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ leads to the decrease of $\text{Fe}^{2+}/\text{Fe}^{3+}\text{--Mo}^{6+}/\text{Mo}^{5+}$ redox pairs, thus resulting in the decrease of electrical conductivity. Among all three investigated samples, $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$ oxide possesses the lowest conductivity ($1.2\text{--}2.9$ in 5% H_2/Ar $600\text{--}800^\circ\text{C}$) with the largest activation energy ($E_a = 0.39 \text{ eV}$). In the case of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ perovskite, it shows relatively satisfactory conductivity value ($4.1\text{--}7.3 \text{ S}\cdot\text{cm}^{-1}$ at $600\text{--}800^\circ\text{C}$) with a small activation energy $E_a = 0.25 \text{ eV}$. The measured electrical conductivity σ for $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ is higher than the conductivity values (see Table 3) of $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.3}\text{Cu}_{0.2}\text{O}_{6-\delta}$ [38], $\text{Sr}_2\text{MgMoO}_{6-\delta}$ [58], $\text{Sr}_2\text{Fe}_{0.9}\text{Mg}_{0.4}\text{Mo}_{0.7}\text{O}_{6-\delta}$ [34], $\text{Sr}_{2-x}\text{Ba}_x\text{MgMoO}_{6-\delta}$, and $\text{Sr}_{2-x}\text{Ba}_x\text{MnMoO}_{6-\delta}$ [24,26], but smaller than the values of $\text{Sr}_2\text{Fe}_{1.2}\text{Mg}_{0.2}\text{Mo}_{0.6}\text{O}_{6-\delta}$ [34] and $\text{Sr}_2\text{Fe}_{1.3}\text{Ti}_{0.1}\text{Mo}_{0.6}\text{O}_{6-\delta}$ [50].

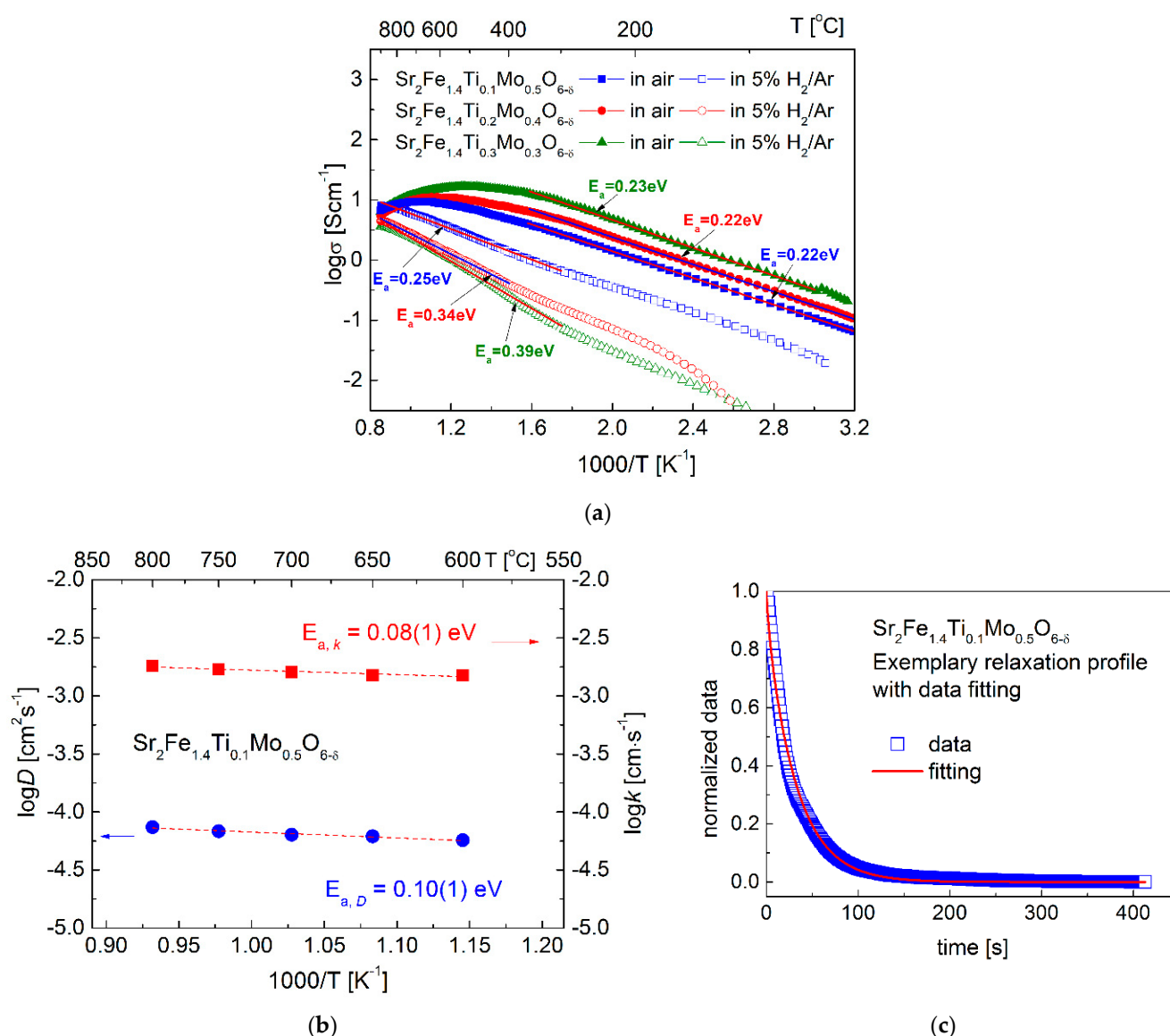


Figure 8. (a) Electrical conductivity of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) oxides in air and 5 vol.% H_2/Ar ; (b) transport coefficients D and k determined as a function of temperature for $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ sample; (c) an exemplary normalized relaxation profile with fitting for $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ sinter.

For $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ 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 5.7×10^{-5} to $7.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 600–800 °C, with an activation energy $E_{a,D} = 0.1$ eV. While the surface exchange k is within the scope of 1.5×10^{-3} – $1.8 \times 10^{-3} \text{ cm s}^{-1}$, 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 $\text{Sr}_2\text{TiNi}_{0.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ [49], $\text{Sr}_2\text{Fe}_{1.2}\text{Mg}_{0.2}\text{Mo}_{0.6}\text{O}_{6-\delta}$ sample [34] and $\text{Sr}_2\text{Fe}_{1.4}\text{Mn}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ [59] materials. While the k values of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ are bigger than k values of $\text{Sr}_2\text{Fe}_{1.2}\text{Mg}_{0.2}\text{Mo}_{0.6}\text{O}_{6-\delta}$ sample [34] and $\text{Sr}_2\text{Fe}_{1.4}\text{Mn}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ [59]. The relatively good transport coefficients D and k evaluated for $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ 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 $\text{Sr}_2(\text{Fe},\text{Mo})\text{O}_{6-\delta}$ -based compounds.

Material	Structure	Electrical Conductivity [$\text{S}\cdot\text{cm}^{-1}$]	TEC Value [$\times 10^{-6}\text{ K}^{-1}$]	Stability	Towards Electrolyte	Application	Ref.
$\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$	<i>Pm-3m</i>	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
$\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.2}\text{Mo}_{0.4}\text{O}_{6-\delta}$	<i>Pm-3m</i>	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
$\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$	<i>Pm-3m</i>	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
$\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.3}\text{Cu}_{0.2}\text{O}_{6-\delta}$	<i>Fm-3m</i>	0.06–0.36 in 5% H_2 at 600–850 °C	-	decomposed in H_2	-	fuel electrode	[38]
$\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$	<i>Fm-3m</i> or <i>Pm-3m</i>	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]
$\text{Sr}_2\text{MgMoO}_{6-\delta}$	<i>I-1</i>	0.8 in 5% H_2 at 800 °C; 0.003 at 800 °C in air	-	stable in 5% H_2	-	anode candidate	[58]
$\text{Sr}_{2-x}\text{Ba}_x\text{MnMoO}_{6-\delta}$	<i>P2₁/n</i> and <i>Fm-3m</i>	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]
$\text{Sr}_{2-x}\text{Ba}_x\text{MgMoO}_{6-\delta}$	<i>I4/m</i> and <i>Fm-3m</i>	0.14 to 1.38 in 5% H_2	13.8 to 18.2 ($x = 0$) in air	redox stable	-	anode candidate	[24,26]
$\text{Sr}_2\text{Mg}_{0.95}\text{Al}_{0.05}\text{MoO}_{6-\delta}$	-	5.4 in 5% H_2 at 800 °C	-	redox stable	Stable with LSGM and CGO, reacts with YSZ	anode candidate	[60]
$\text{SrFe}_{0.5}\text{Mn}_{0.25}\text{Mo}_{0.25}\text{O}_{3-\delta}$	<i>Pm-3m</i>	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	[30]
$\text{Sr}_2\text{Fe}_{1.2}\text{Mg}_{0.2}\text{Mo}_{0.6}\text{O}_{6-\delta}$	<i>Fm-3m</i>	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]
$\text{Sr}_2\text{Fe}_{0.9}\text{Mg}_{0.4}\text{Mo}_{0.7}\text{O}_{6-\delta}$	<i>Fm-3m</i>	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]
$\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.4}\text{Nb}_{0.1}\text{O}_{6-\delta}$	<i>Pnma</i>	30 in air at 550 °C	16.1 in air	stable in air	stable with LSGM	cathode candidate	[61]
$\text{Sr}_{1.9}\text{Fe}_{1.5}\text{Mo}_{0.3}\text{Cu}_{0.2}\text{O}_{6-\delta}$	-	54.8 in air at 630 °C	19.4 in air	decomposed in H_2	-	anode candidate	[62]
$\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.9}\text{Mo}_{0.1}\text{O}_{3-\delta}$	<i>Pm-3m</i>	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]
$\text{Sr}_2\text{FeMo}_{2/3}\text{Mg}_{1/3}\text{O}_{6-\delta}$	<i>Fm-3m</i>	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]
$\text{Sr}_2\text{FeMo}_{0.65}\text{Ni}_{0.35}\text{O}_{6-\delta}$	<i>I4/m</i>	55.4 in 5% H_2 at 800 °C	-	decomposed in H_2	stable with LDC	anode candidate	[18]
$\text{Sr}_2\text{Fe}_{1.3}\text{Ti}_{0.1}\text{Mo}_{0.6}\text{O}_{6-\delta}$	<i>Fm-3m</i>	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]
$\text{Sr}_2\text{TiFe}_{0.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$	<i>Pm-3m</i>	22.3 in H_2 at 800 °C	11.2 in H_2	stable in H_2	stable with LSGM91 and CSO	anode candidate	[57]
$\text{Sr}_2\text{TiNi}_{0.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$	-	17.5 at 800 °C in hydrogen	12.8 in air	stable in H_2	stable with LSGM	anode candidate	[49]
$\text{Sr}_{2-x}\text{Ba}_x\text{FeMoO}_{6-\delta}$	<i>I4/m</i> and <i>Fm-3m</i>	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]
$\text{SrFe}_{0.45}\text{Co}_{0.45}\text{Mo}_{0.1}\text{O}_{3-\delta}$	<i>Pm-3m</i>	298 at 300 °C in air	14.8 to 30.8 in air	stable in air	-	air electrode candidate	[39]
$\text{Sr}_2\text{Mg}_{0.3}\text{Co}_{0.7}\text{MoO}_{6-\delta}$	<i>I-1</i>	9 to 7 at 600–800 °C in 5% H_2	13.9 in air	-	-	anode candidate	[40]

CGO: $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, LSGM: $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\text{d}}$, YSZ: $\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_{1.96}$, LDC: $\text{La}_{0.4}\text{Ce}_{0.6}\text{O}_{2-\text{d}}$, LSGM91: $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\text{d}}$, CSO: $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$.

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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) oxides and their compatibility with typical solid electrolyte/buffer layer materials, such as $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ –CGO20 and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ –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 $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ with electrolyte (50:50 wt.%) powder mixtures are shown in Figures 9 and 10. The XRD patterns present no chemical reaction occurring between the studied compounds and solid electrolytes (CGO20 and LSGM), confirming the good stability and compatibility of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) materials with used electrolytes.

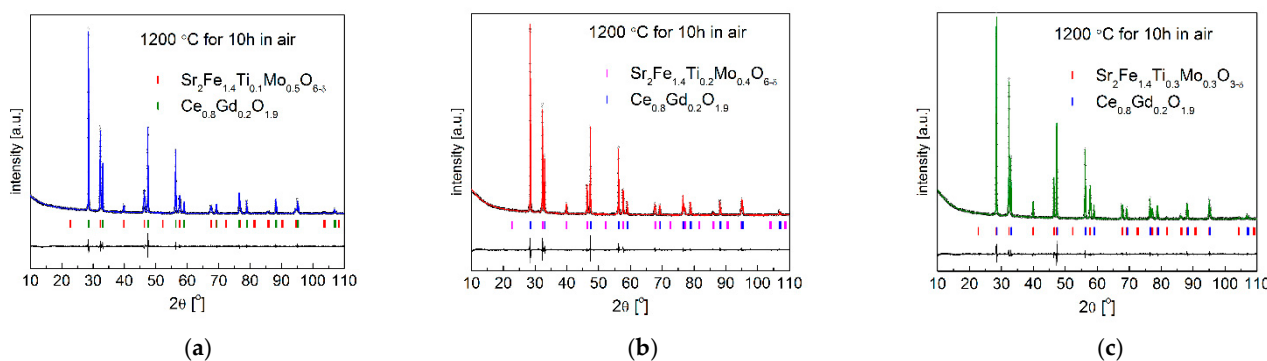


Figure 9. XRD patterns recorded for (a) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$; (b) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.2}\text{Mo}_{0.4}\text{O}_{6-\delta}$ and (c) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$ with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ electrolyte, after firing in air at 1200 °C for 10 h.

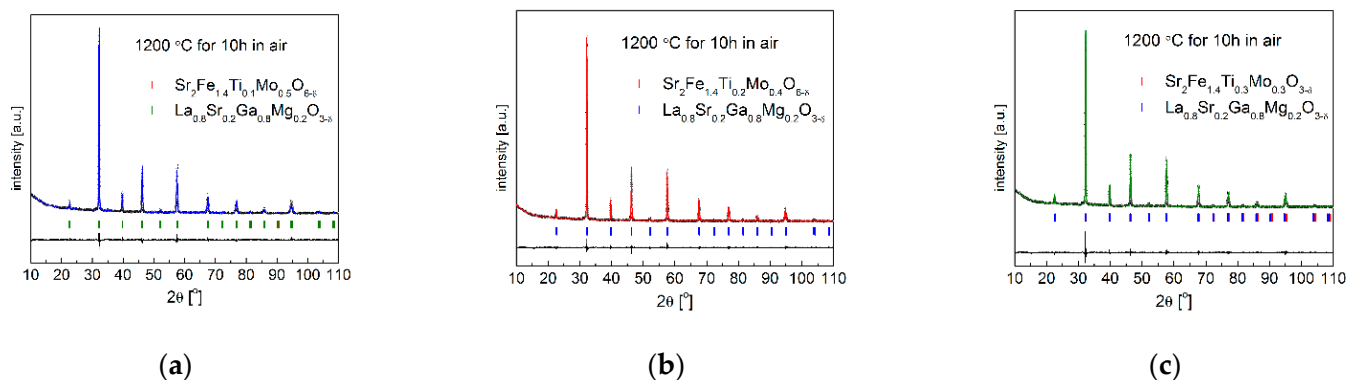


Figure 10. XRD patterns recorded for (a) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$; (b) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.2}\text{Mo}_{0.4}\text{O}_{6-\delta}$ and (c) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$ with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ electrolyte, after sintering at 1200 °C for 10 h in air.

As presented in Table 4, the unit cell parameter of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ from different mixtures is very similar, and the unit cell parameters of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) 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 ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$). Interestingly, similar compositions $\text{Sr}_2\text{Fe}_{1.2}\text{Mg}_{0.2}\text{Mo}_{0.6}\text{O}_{6-\delta}$ and $\text{Sr}_2\text{Fe}_{0.9}\text{Mg}_{0.4}\text{Mo}_{0.7}\text{O}_{6-\delta}$ are compatible with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ electrolyte but react with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ [34]. $\text{Sr}_2\text{Fe}_{1.3}\text{Ti}_{0.1}\text{Mo}_{0.6}\text{O}_{6-\delta}$ (material unstable in air) is also compatible with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ [50].

Table 4. Structural parameters of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) oxides with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ and with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ electrolytes from 50:50 wt.% mixtures fired in air for 10h at 1200 °C.

Composition	x = 0.1	$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$	x = 0.2	$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$	x = 0.3	$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$
space group	<i>Pm-3m</i>	<i>Fm-3m</i>	<i>Pm-3m</i>	<i>Fm-3m</i>	<i>Pm-3m</i>	<i>Fm-3m</i>
a [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
R _p (%)		1.85		1.95		1.76
R _{wp} (%)		2.70		3.09		2.62

Composition	x = 0.1	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	x = 0.2	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	x = 0.3	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$
space group	<i>Pm-3m</i>	<i>Pm-3m</i>	<i>Pm-3m</i>	<i>Pm-3m</i>	<i>Pm-3m</i>	<i>Pm-3m</i>
a [Å]	3.9214 (1)	3.9140 (1)	3.9132 (1)	3.9132 (1)	3.9039 (1)	3.9142 (1)
V [Å ³]	60.30 (1)	59.96 (1)	59.92 (1)	59.92 (1)	59.50 (1)	59.97 (1)
CHI ²		2.03		1.98		2.23
R _p (%)		1.66		1.66		1.70
R _{wp} (%)		2.22		2.24		2.39

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

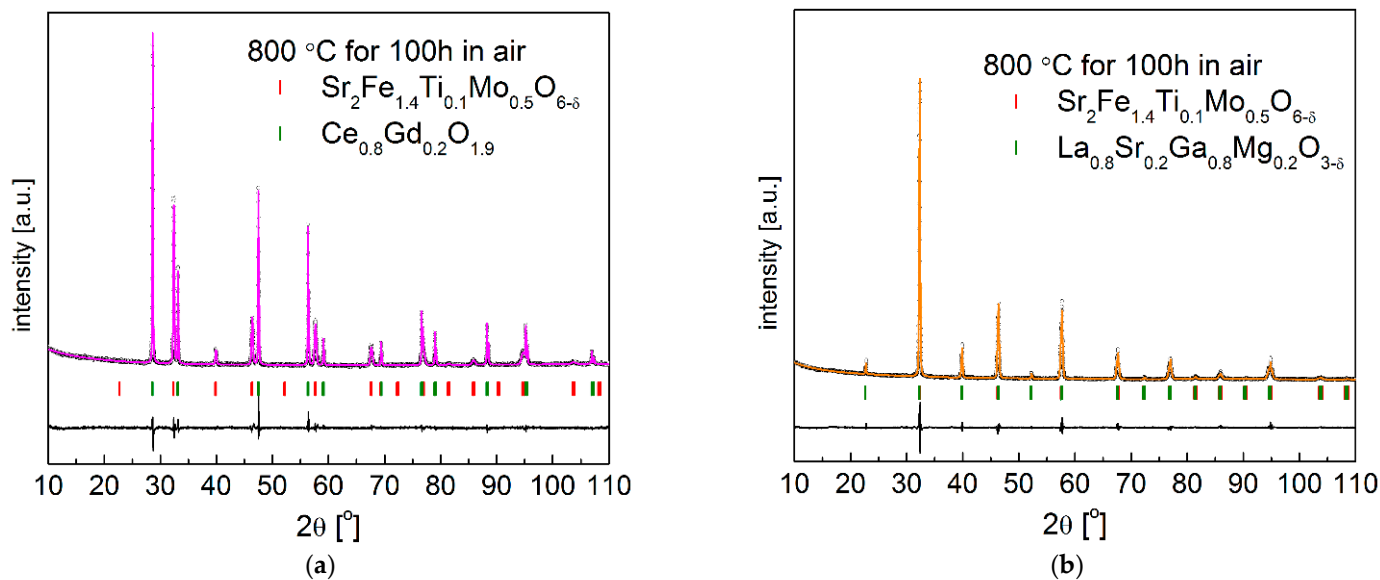


Figure 11. XRD patterns recorded for (a) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$; (b) $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ electrolyte, after firing for 100h at 800 °C in air.

Table 5. Structural parameters of $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ sample with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ and with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ electrolytes after the long-term studies for 100 h at 800 °C in air.

Composition	$\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$	$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$	$\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$
space group	<i>Pm-3m</i>	<i>Fm-3m</i>	<i>Pm-3m</i>	<i>Pm-3m</i>
<i>a</i> [Å]	3.9268 (1)	5.4289 (1)	3.9229 (1)	3.9148 (1)
<i>V</i> [Å ³]	60.55 (1)	160.00 (1)	60.37 (1)	60.00 (1)
CHI ²		2.51		3.62
R _p (%)		2.02		1.93
R _{wp} (%)		2.89		2.82

4. Summary

In this work, the stability of $\text{Sr}_2(\text{FeMo})\text{O}_{6-\delta}$ -type perovskites was successfully tailored by the substitution of Mo with Ti at B-site, and $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ ($x = 0.1, 0.2$ and 0.3) perovskites with excellent redox stability in reducing and oxidizing conditions were obtained. All $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ 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. $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ shows the lowest TEC with $15.3 \times 10^{-6} \text{ K}^{-1}$. In addition, Ti-doping also increases the oxygen content change and electrical conductivity in air, while it decreases the conductivity in reducing condition. $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.3}\text{Mo}_{0.3}\text{O}_{6-\delta}$ sample presents the highest conductivity in air with $17.8 \text{ S}\cdot\text{cm}^{-1}$ at 500 °C, while the high TEC value of $22.1 \times 10^{-6} \text{ K}^{-1}$ can potentially limit the application. All three $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_x\text{Mo}_{0.6-x}\text{O}_{6-\delta}$ materials are stable and compatible with studied electrolytes ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$).

Redox stable $\text{Sr}_2\text{Fe}_{1.4}\text{Ti}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ seems to be the most interesting among studied materials, with large oxygen content change of $0.72 \text{ mol}\cdot\text{mol}^{-1}$ between 30 and 900 °C, satisfactory conductivity of $4.1\text{--}7.3 \text{ S}\cdot\text{cm}^{-1}$ 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.

Author Contributions: Conceptualization, methodology, investigation, validation, formal analysis, resources, data curation, writing—original draft preparation, funding acquisition, supervision, K.Z.; visualization, investigation, M.A.; writing—review and editing, M.C., K.Q. and P.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Science Centre Poland (NCN) on the basis of the decision number UMO-2021/43/D/ST5/00824.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Boldrin, P.; Brandon, N.P. Progress and outlook for solid oxide fuel cells for transportation applications. *Nat. Catal.* **2019**, *2*, 571–577. [CrossRef]
2. Park, S.; Vohs, J.M.; Gorte, R.J. Direct oxidation of hydrocarbons in a solid-oxide fuel cell. *Nature* **2000**, *404*, 265–267. [CrossRef] [PubMed]
3. Develos-Bagarinao, K.; Ishiyama, T.; Kishimoto, H.; Shimada, H.; Yamaji, K. Nanoengineering of cathode layers for solid oxide fuel cells to achieve superior power densities. *Nat. Commun.* **2021**, *12*, 3979. [CrossRef]
4. Irvine, J.T.S.; Neagu, D.; Verbraeken, M.C.; Chatzichristodoulou, C.; Graves, C.R.; Mogensen, M.B. Evolution of the electrochemical interface in high-temperature fuel cells and electrolyzers. *Nat. Energy* **2016**, *1*, 15014. [CrossRef]

5. Myung, J.-H.; Neagu, D.; Miller, D.N.; Irvine, J. Switching on electrocatalytic activity in solid oxide cells. *Nature* **2016**, *537*, 528–531. [[CrossRef](#)] [[PubMed](#)]
6. Huang, Y.-H.; Dass, R.I.; Xing, Z.-L.; Goodenough, J.B.; Goldman, A.S.; Roy, A.H.; Ahuja, R.; Schinski, W.; Brookhart, M. Double Perovskites as Anode Materials for Solid-Oxide Fuel Cells. *Science* **2006**, *312*, 254–257. [[CrossRef](#)]
7. Tao, S.; Irvine, J. A redox-stable efficient anode for solid-oxide fuel cells. *Nat. Mater.* **2003**, *2*, 320–323. [[CrossRef](#)]
8. Ding, H.; Tao, Z.; Liu, S.; Zhang, J. A High-Performing Sulfur-Tolerant and Redox-Stable Layered Perovskite Anode for Direct Hydrocarbon Solid Oxide Fuel Cells. *Sci. Rep.* **2015**, *5*, 18129. [[CrossRef](#)]
9. Graves, C.R.; Ebbesen, S.D.; Jensen, S.H.; Simonsen, S.B.; Mogensen, M.B. Eliminating degradation in solid oxide electrochemical cells by reversible operation. *Nat. Mater.* **2015**, *14*, 239–244. [[CrossRef](#)]
10. Hughes, G.A.; Railsback, J.G.; Yakal-Kremski, K.J.; Butts, D.M.; Barnett, S.A. Degradation of $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_{3-\delta}-\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{2-\gamma}$ composite electrodes during reversing current operation. *Faraday Discuss.* **2015**, *182*, 365–377. [[CrossRef](#)]
11. Ding, H.; Fang, S.; Yang, Y.; Yang, Y.; Wu, W.; Tao, Z. High-performing and stable electricity generation by ceramic fuel cells operating in dry methane over 1000 hours. *J. Power Sources* **2018**, *401*, 322–328. [[CrossRef](#)]
12. Laguna-Bercero, M.A. Recent advances in high temperature electrolysis using solid oxide fuel cells: A review. *J. Power Sources* **2012**, *203*, 4–16. [[CrossRef](#)]
13. Hossain, M.K.; Raihan, G.A.; Akbar, M.A.; Rubel, M.H.K.; Ahmed, M.H.; Khan, M.I.; Hossain, S.; Sen, S.K.; Jalal, M.I.E.; El-Denglawey, A. Current Applications and Future Potential of Rare Earth Oxides in Sustainable Nuclear, Radiation, and Energy Devices: A Review. *ACS Appl. Electron. Mater.* **2022**, *4*, 3327–3353. [[CrossRef](#)]
14. Hossain, M.K.; Chanda, R.; El-Denglawey, A.; Emrose, T.; Rahman, M.T.; Biswas, M.C.; Hashizume, K. Recent progress in barium zirconate proton conductors for electrochemical hydrogen device applications: A review. *Ceram. Int.* **2021**, *47*, 23725–23748. [[CrossRef](#)]
15. Sengodan, S.; Choi, S.; Jun, A.; Shin, T.H.; Ju, Y.-W.; Jeong, H.Y.; Shin, J.; Irvine, J.; Kim, G. Layered oxygen-deficient double perovskite as an efficient and stable anode for direct hydrocarbon solid oxide fuel cells. *Nat. Mater.* **2015**, *14*, 205–209. [[CrossRef](#)] [[PubMed](#)]
16. Skutina, L.; Filonova, E.; Medvedev, D.; Maignan, A. Undoped Sr_2MMoO_6 Double Perovskite Molybdates ($\text{M} = \text{Ni}, \text{Mg}, \text{Fe}$) as Promising Anode Materials for Solid Oxide Fuel Cells. *Materials* **2021**, *14*, 1715. [[CrossRef](#)] [[PubMed](#)]
17. Zamudio-García, J.; Caizán-Juanarena, L.; Porras-Vázquez, J.M.; Losilla, E.R.; Marrero-López, D. A review on recent advances and trends in symmetrical electrodes for solid oxide cells. *J. Power Sources* **2022**, *520*, 230852. [[CrossRef](#)]
18. Du, Z.; Zhao, H.; Yi, S.; Xia, Q.; Gong, Y.; Zhang, Y.; Cheng, X.; Li, Y.; Gu, L.; Świerczek, K. High-Performance Anode Material $\text{Sr}_2\text{FeMo}_{0.65}\text{Ni}_{0.35}\text{O}_{6-\delta}$ with In Situ Exsolved Nanoparticle Catalyst. *ACS Nano* **2016**, *10*, 8660–8669. [[CrossRef](#)]
19. Zhu, K.; Luo, B.; Liu, Z.; Wen, X. Recent advances and prospects of symmetrical solid oxide fuel cells. *Ceram. Int.* **2022**, *48*, 8972–8986. [[CrossRef](#)]
20. Zhang, B.; Wan, Y.; Hua, Z.; Tang, K.; Xia, C. Tungsten-Doped $\text{PrBaFe}_2\text{O}_{5+\delta}$ Double Perovskite as a High-Performance Electrode Material for Symmetrical Solid Oxide Fuel Cells. *ACS Appl. Energy Mater.* **2021**, *4*, 8401–8409. [[CrossRef](#)]
21. Cao, Y.; Zhu, Z.; Zhao, Y.; Zhao, W.; Wei, Z.; Liu, T. Development of tungsten stabilized $\text{SrFe}_{0.8}\text{W}_{0.2}\text{O}_{3-\delta}$ material as novel symmetrical electrode for solid oxide fuel cells. *J. Power Sources* **2020**, *455*, 227951. [[CrossRef](#)]
22. Xiao, G.; Liu, Q.; Zhao, F.; Zhang, L.; Xia, C.; Chen, F. $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6$ as Cathodes for Intermediate -Temperature Solid Oxide Fuel Cells with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.87}\text{Mg}_{0.13}\text{O}_3$ Electrolyte. *J. Electrochem. Soc.* **2011**, *158*, B455. [[CrossRef](#)]
23. Zheng, K.; Świerczek, K.; Bratek, J.; Klimkowicz, A. Cation-ordered perovskite-type anode and cathode materials for solid oxide fuel cells. *Solid State Ion.* **2014**, *262*, 354–358. [[CrossRef](#)]
24. Zheng, K.; Świerczek, K. A- and B-site doping effect on physicochemical properties of $\text{Sr}_{2-x}\text{Ba}_x\text{MMoO}_6$ ($\text{M} = \text{Mg}, \text{Mn}, \text{Fe}$) double perovskites—Candidate anode materials for SOFCs. *Funct. Mater. Lett.* **2016**, *9*, 1641002. [[CrossRef](#)]
25. Zheng, K.; Świerczek, K.; Zając, W.; Klimkowicz, A. Rock salt ordered-type double perovskite anode materials for solid oxide fuel cells. *Solid State Ion.* **2014**, *257*, 9–16. [[CrossRef](#)]
26. Zheng, K.; Świerczek, K. Physicochemical properties of rock salt-type ordered Sr_2MMoO_6 ($\text{M} = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) double perovskites. *J. Eur. Ceram. Soc.* **2014**, *34*, 4273–4284. [[CrossRef](#)]
27. Huang, Y.-H.; Dass, R.I.; Denyszyn, J.C.; Goodenough, J.B. Synthesis and Characterization of $\text{Sr}_2\text{MgMoO}_{6-\delta}$: An Anode Material for the Solid Oxide Fuel Cell. *J. Electrochem. Soc.* **2006**, *153*, A1266. [[CrossRef](#)]
28. Marrero-López, D.; Peña-Martínez, J.; Ruiz-Morales, J.C.; Gabás, M.; Núñez, P.; Aranda, M.A.G.; Ramos-Barrado, J.R. Redox behaviour, chemical compatibility and electrochemical performance of $\text{Sr}_2\text{MgMoO}_{6-\delta}$ as SOFC anode. *Solid State Ion.* **2010**, *180*, 1672–1682. [[CrossRef](#)]
29. Goodenough, J.B.; Huang, Y.-H. Alternative anode materials for solid oxide fuel cells. *J. Power Sources* **2007**, *173*, 1–10. [[CrossRef](#)]
30. Zheng, K.; Świerczek, K.; Polfus, J.M.; Sunding, M.F.; Pishahang, M.; Norby, T. Carbon Deposition and Sulfur Poisoning in $\text{SrFe}_{0.75}\text{Mo}_{0.25}\text{O}_{3-\delta}$ and $\text{SrFe}_{0.5}\text{Mn}_{0.25}\text{Mo}_{0.25}\text{O}_{3-\delta}$ Electrode Materials for Symmetrical SOFCs. *J. Electrochem. Soc.* **2015**, *162*, F1078–F1087. [[CrossRef](#)]
31. Liu, Q.; Dong, X.; Xiao, G.; Zhao, F.; Chen, F. A Novel Electrode Material for Symmetrical SOFCs. *Adv. Mater.* **2010**, *22*, 5478–5482. [[CrossRef](#)] [[PubMed](#)]
32. Li, H.; Zhao, Y.; Wang, Y.; Li, Y. $\text{Sr}_2\text{Fe}_{2-x}\text{Mo}_x\text{O}_{6-\delta}$ perovskite as an anode in a solid oxide fuel cell: Effect of the substitution ratio. *Catal. Today* **2016**, *259*, 417–422. [[CrossRef](#)]

33. Zheng, K.; Świerczek, K. Evaluation of W-containing $\text{Sr}_{1-x}\text{Ba}_x\text{Fe}_{0.75}\text{W}_{0.25}\text{O}_{3-\delta}$ ($x = 0, 0.5, 1$) anode materials for solid oxide fuel cells. *Solid State Ion.* **2016**, *288*, 124–129. [CrossRef]
34. Zheng, K.; Lach, J.; Zhao, H.; Huang, X.; Qi, K. Magnesium-Doped $\text{Sr}_2(\text{Fe},\text{Mo})\text{O}_{6-\delta}$ Double Perovskites with Excellent Redox Stability as Stable Electrode Materials for Symmetrical Solid Oxide Fuel Cells. *Membranes* **2022**, *12*, 1006. [CrossRef]
35. Wright, J.H.; Virkar, A.V.; Liu, Q.; Chen, F. Electrical characterization and water sensitivity of $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ as a possible solid oxide fuel cell electrode. *J. Power Sources* **2013**, *237*, 13–18. [CrossRef]
36. Fang, T.-T.; Ko, T.-F. Factors Affecting the Preparation of $\text{Sr}_2\text{Fe}_{2-x}\text{Mo}_x\text{O}_6$. *J. Am. Ceram. Soc.* **2003**, *86*, 1453–1455. [CrossRef]
37. Du, Z.; Zhao, H.; Li, S.; Zhang, Y.; Chang, X.; Xia, Q.; Chen, N.; Gu, L.; Świerczek, K.; Li, Y.; et al. Exceptionally High Performance Anode Material Based on Lattice Structure Decorated Double Perovskite $\text{Sr}_2\text{FeMo}_{2/3}\text{Mg}_{1/3}\text{O}_{6-\delta}$ for Solid Oxide Fuel Cells. *Adv. Energy Mater.* **2018**, *8*, 1800062. [CrossRef]
38. He, F.; Hou, M.; Zhu, F.; Liu, D.; Zhang, H.; Yu, F.; Zhou, Y.; Ding, Y.; Liu, M.; Chen, Y. Building Efficient and Durable Hetero-Interfaces on a Perovskite-Based Electrode for Electrochemical CO_2 Reduction. *Adv. Energy Mater.* **2022**, 2202175. [CrossRef]
39. Zapata-Ramírez, V.; Mather, G.C.; Azcondo, M.T.; Amador, U.; Perez-Coll, D. Electrical and electrochemical properties of the $\text{Sr}(\text{Fe},\text{Co},\text{Mo})\text{O}_{3-\delta}$ system as air electrode for reversible solid oxide cells. *J. Power Sources* **2019**, *437*, 226895. [CrossRef]
40. Xie, Z.; Zhao, H.; Du, Z.; Chen, T.; Chen, N.; Liu, X.; Skinner, S.J. Effects of Co Doping on the Electrochemical Performance of Double Perovskite Oxide $\text{Sr}_2\text{MgMoO}_{6-\delta}$ as an Anode Material for Solid Oxide Fuel Cells. *J. Phys. Chem. C* **2012**, *116*, 9734–9743. [CrossRef]
41. Zhang, Y.; Yu, Z.; Tao, Y.; Lu, J.; Liu, Y.; Shao, J. Insight into the electrochemical processes of the titanate electrode with in situ Ni exsolution for solid oxide cells. *ACS Appl. Energy Mater.* **2019**, *2*, 4033–4044. [CrossRef]
42. Miller, D.N.; Irvine, J.T.S. B-site doping of lanthanum strontium titanate for solid oxide fuel cell anodes. *J. Power Sources* **2011**, *196*, 7323–7327. [CrossRef]
43. Neagu, D.; Irvine, J.T.S. Enhancing electronic conductivity in strontium titanates through correlated A and B-site doping. *Chem. Mater.* **2011**, *23*, 1607–1617. [CrossRef]
44. Lan, C.; Luo, J.; Dou, M.; Zhao, S. First-principles calculations of the oxygen-diffusion mechanism in mixed Fe/Ti perovskites for solid-oxide fuel cells. *Ceram. Int.* **2019**, *45*, 17646–17652. [CrossRef]
45. Niu, B.; Jin, F.; Liu, J.; Zhang, Y.; Jiang, P.; Feng, T.; Xu, B.; He, T. Highly carbone and sulfuretolerant $\text{Sr}_2\text{TiMoO}_{6-\delta}$ double perovskite anode for solid oxide fuel cells. *Int. J. Hydrogen Energy* **2019**, *44*, 20404–20415. [CrossRef]
46. Carollo, G.; Garbujo, A.; Mauvy, F.; Glisenti, A. Critical Raw Material-Free Catalysts and Electrocatalysts: Complementary Strategies to Activate Economic, Robust, and Ecofriendly SrTiO_3 . *Energy Fuels* **2020**, *34*, 11438–11448. [CrossRef]
47. Ke, M.; Wang, W.; Yang, X.; Li, B.; Li, H. Doped Strontium Titanate Anode for Solid Oxide Fuel Cells: Electrical and Sintering Behavior. *Ceram. Int.* **2022**, *48*, 8709–8714. [CrossRef]
48. Rath, M.K.; Kossenko, A.; Zinigrad, M.; Kalashnikov, A. In-operando gas switching to suppress the degradation of symmetrical solid oxide fuel cells. *J. Power Sources* **2020**, *476*, 228630. [CrossRef]
49. He, B.; Wang, Z.; Zhao, L.; Pan, X.; Wu, X.; Xia, C. Ti-doped molybdenum-based perovskites as anodes for solid oxide fuel cells. *J. Power Sources* **2013**, *241*, 627–633. [CrossRef]
50. Zheng, K. Ti-doped $\text{Sr}_2\text{Fe}_{1.4-x}\text{Ti}_x\text{Mo}_{0.6}\text{O}_{6-\delta}$ double perovskites with improved stability as anode materials for Solid Oxide Fuel Cells. *Mater. Res. Bull.* **2020**, *128*, 110877. [CrossRef]
51. Larson, A.C.; Von Dreele, R.B. General Structure Analysis System (GSAS). Los Alamos National Laboratory Report LAUR 86-748; 2004. Available online: <https://11bm.xray.aps.anl.gov/documents/GSASManual.pdf> (accessed on 10 January 2022).
52. Toby, B.H. EXPGUI, a graphical user interface for GSAS. *J. Appl. Crystallogr.* **2001**, *34*, 210–213. [CrossRef]
53. Stroud, D. Generalized effective-medium approach to the conductivity of an inhomogeneous material. *Phys. Rev. B* **1975**, *12*, 3368–3373. [CrossRef]
54. Zheng, K. Enhanced oxygen mobility by doping Yb in $\text{BaGd}_{1-x}\text{Yb}_x\text{Mn}_2\text{O}_{5+\delta}$ double perovskite-structured oxygen storage materials. *Solid State Ion.* **2019**, *335*, 103–112. [CrossRef]
55. Zheng, K.; Świerczek, K. Possibility of determination of transport coefficients D and k from relaxation experiments for sphere-shaped powder samples. *Solid State Ion.* **2018**, *323*, 157–165. [CrossRef]
56. Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Oxford University Press: New York, NY, USA, 1975.
57. Niu, B.; Jin, F.; Yang, X.; Feng, T.; He, T. Resisting coking and sulfur poisoning of double perovskite $\text{Sr}_2\text{TiFe}_{0.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ anode material for solid oxide fuel cells. *Int. J. Hydrogen Energy* **2018**, *43*, 3280–3290. [CrossRef]
58. Marrero-López, D.; Peña-Martínez, J.; Ruiz-Morales, J.C.; Perez-Coll, D.; Aranda, M.A.G.; Núñez, P. Synthesis, phase stability and electrical conductivity of $\text{Sr}_2\text{MgMoO}_{6-\delta}$ anode. *Mater. Res. Bull.* **2008**, *43*, 2441–2450. [CrossRef]
59. Jiang, Y.; Yang, Y.; Xia, C.; Bouwmeester, H.J.M. $\text{Sr}_2\text{Fe}_{1.4}\text{Mn}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ perovskite cathode for highly efficient CO_2 electrolysis. *J. Mater. Chem.* **2019**, *7*, 22939–22949. [CrossRef]
60. Xie, Z.; Zhao, H.; Chen, T.; Zhou, X.; Du, Z. Synthesis and electrical properties of Al-doped $\text{Sr}_2\text{MgMoO}_{6-\delta}$ as an anode material for solid oxide fuel cells. *Int. J. Hydrogen Energy* **2011**, *36*, 7257–7264. [CrossRef]

61. Hou, M.; Sun, W.; Li, P.; Feng, J.; Yang, G.; Qiao, J.; Wang, Z.; Rooney, D.; Feng, J.; Sun, K. Investigation into the effect of molybdenum-site substitution on the performance of $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ for intermediate temperature solid oxide fuel cells. *J. Power Sources* **2014**, *272*, 759–765. [[CrossRef](#)]
62. Wu, Y.; Wang, S.; Gao, Y.; Yu, X.; Jiang, H.; Wei, B.; Lü, Z. In situ growth of copper-iron bimetallic nanoparticles in A-site deficient $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ as an active anode material for solid oxide fuel cells. *J. Alloys Compd.* **2022**, *926*, 166852. [[CrossRef](#)]
63. Cai, H.; Zhang, L.; Xu, J.; Huang, J.; Wei, X.; Wang, L.; Song, Z.; Long, W. Cobalt-free $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.9}\text{Mo}_{0.1}\text{O}_{3-\delta}$ electrode for symmetrical SOFC running on H_2 and CO fuels. *Electrochim. Acta* **2019**, *320*, 134642. [[CrossRef](#)]