La$_{0.4}$Sr$_{0.6}$Ti$_{1-x}$Mn$_x$O$_{3-\delta}$ Perovskites as Anode Materials for Solid Oxide Fuel Cells

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Perovskite oxides, La$_{0.4}$Sr$_{0.6}$Ti$_{1-x}$Mn$_x$O$_{3-\delta}$ ($x = 0, 0.2, 0.4, 0.6$), have been investigated in the search for new solid oxide fuel cell (SOFC) anode materials. La$_{0.4}$Sr$_{0.6}$Ti$_{0.4}$Mn$_{0.6}$O$_{3-\delta}$ (LSTM4646) shows an electrical conductivity of 22.6 S/cm in air and 1.5 S/cm in wet Ar/4% H$_2$ [$p$(O$_2$) $\approx$ $10^{-13}$ bar] at 810°C. It is thermally and chemically compatible with yttria-stabilized zirconia (YSZ) electrolytes. Three processes govern the electrochemical performance of LSTM4646/YSZ anodes in wet Ar/H$_2$ or wet CH$_4$. They are proposed to be charge transfer at the LSTM4646/YSZ interface, dissociative adsorption of hydrogen on the electrode surface, and gas conversion impedance, respectively. Due to the low polarization resistance of the LSTM4646/YSZ anode, 0.32 $\Omega$ cm$^2$, an electrolyte-supported H$_2$/air fuel cell with an LSM/YSZ cathode yields a power density of 365 mW cm$^{-2}$ at 0.7 V at 856°C. In addition, this anode material is stable under a moderately humidified hydrogen atmosphere. It shows insignificant catalytic activity for the direct oxidation of methane however.

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Experimental

Powder synthesis.— The Pechini method$^{23}$ was used to synthesize the powders with the following compositions:

One of the most attractive features of solid oxide fuel cells (SOFCs) is that they can use hydrocarbon fuels (e.g., natural gas) directly to generate electrical energy in a highly efficient way. Carbon monoxide, which is inevitable in the reforming products of hydrocarbons, is rather a fuel than a poison as is the case in proton exchange membrane fuel cells (PEMFCs). To realize this feature, an efficient anode is of particular importance. Currently, corresponding all-ceramic anodes are preferable because the oxidation/reduction of nickel and nickel oxide are materials that may cause cancer or allergies, posing difficulties in handling and processing of these materials. Therefore, it would be advantageous to develop alternative anode materials to overcome problems with Ni/YSZ.

From the viewpoint of volume stability upon redox cycling, an all-ceramic anode is preferable because the oxidation/reduction of metals like Ni or Cu is always accompanied by a large volume change. In recent years, many ceramic oxides with various crystal structures, such as rutile, fluorite, perovskite, pyrochlore, and tungsten bronze, have been investigated as anode materials.$^{1,14}$ Among them, the perovskite oxides, mainly titanates and chromites, which are chemically stable under anode conditions, have been studied more intensively. For instance, La-substituted SrTiO$_3$ materials show high electrical conductivity in reducing atmosphere as well as good dimensional and chemical stability upon redox cycling, but the electrocatalytic activity for H$_2$ oxidation is very poor.$^{2}$ Further modification of these materials with CeO$_2$ greatly improved the electrocatalytic activity for H$_2$ oxidation.$^{3}$ However, it is actually a two-phase composite containing (Ce,La)O$_2$-$\delta$ and (Sr,La)TiO$_3$-$\delta$, in which the catalytic activity is provided by the ceria phase. It is thus not surprising that this composite material still shows insufficient electrocatalytic activity for CH$_4$ oxidation.$^{4}$ Because doped ceria itself is not a good catalyst for CH$_4$ oxidation.$^{4,5}$ The application of ceria-containing anode on YSZ-based SOFCs may also be limited by the detrimental reaction between ceria and YSZ at elevated temperatures forming a poorly conductive intermediate layer,$^{15}$ especially when a co-firing step of the anode/electrolyte bilayer is required. Y-substituted SrTiO$_3$ also shows high electrical conductivity, but so far no good fuel cell performance has been reported with this material.$^{5}$

Due to their good stability and high electrical conductivity, it is actually anticipated that LaCrO$_3$-based interconnect materials$^{16}$ can be modified to anode materials through appropriate elemental substitution. Therefore, various transition metal elements (e.g., Ru, V, Mn, Fe, Co, Ni) with 3–10 atom % concentration were inserted into the Cr site of the perovskite lattice, and the Ni substitution seemed most promising.$^{6,7}$ However, further investigations revealed nickel segregation from the perovskite lattice upon reduction.$^{8}$ Thus, the observed good electrocatalytic activity of 10 atom % Ni-substituted (La,Sr)CrO$_3$ could be ascribed to the well-dispersed metallic Ni because the catalytic effect of only a small fraction of Ni in an anode has been demonstrated by other investigations.$^{17,19}$ Recently, a high-level Mn-substituted lanthanum strontium chromite, La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_3$ (LSCM), was reported to display rather good electrochemical performance.$^{12,13}$ The electrode polarization resistance at 900°C was 0.26 and 0.87 $\Omega$ cm$^2$ in wet H$_2$ and wet CH$_4$, respectively. The observed good performance of this material could be linked to its possibly improved ionic conductivity by the 50 atom % Mn substitution for Cr because the ionic conductivity was found to be crucial for a mixed ionic/electronic conductor to have good electrocatalytic activity for fuel oxidation.$^1$ In reducing atmosphere and at high temperatures, the reduction of Mn leads to an oxygen loss of as much as 0.25 mol O$^2-$ per mol of LSCM,$^{14}$ giving rise to a high concentration of oxygen vacancies. The strong ability of oxygen incorporation/lease of LSCM upon redox cycling is essentially due to the presence of 50 atom % Mn, which is capable of adjusting its valence (+4, +3, and +2) according to the ambient oxygen partial pressure ($p$(O$_2$)). As in (La,Sr)MnO$_3$,$^{20,22}$

As stated above, despite its high electrical conductivity, La-substituted SrTiO$_3$ itself has little electrocatalytic activity for fuel oxidation. It is possible, however, to improve its activity through a high level of Mn substitution on the Ti site. Due to the good chemical stability of (La,Sr)TiO$_3$ perovskites in reducing atmosphere, Mn is expected to be stabilized in the perovskite lattice in a way similar to that in LSCM. In this work, La$_{0.4}$Sr$_{0.6}$Ti$_{1-x}$Mn$_x$O$_{3-\delta}$ ($x = 0, 0.2, 0.4, 0.6$) perovskites were synthesized and evaluated as potential anode materials in terms of crystal structure, chemical stability, thermal and chemical expansion, as well as electrical and electrochemical properties.

Experimental

Powder synthesis.— The Pechini method$^{23}$ was used to synthesize the powders with the following compositions:
(La_{0.4}Sr_{0.6})TiO_{3−δ} (LST), La_{0.8}Sr_{0.2}MnO_{3−δ}, (LSTM4682), La_{0.8}Sr_{0.2}TiO_{3−δ}, La_{0.4}Sr_{0.6}Mn_{0.4}O_{3−δ}, (LSTM4664), and La_{0.8}Sr_{0.2}Ti_{0.8}Mn_{0.2}O_{3−δ} (LSTM4666). The Mn-containing compositions are generally designated as LSTM throughout this paper. Nitrates of La, Sr, Mn, and titanium isopropoxide were used as the starting chemicals. To control the final compositions as precisely as possible, the hygroscopic nitrates were first dissolved in water and then assayed by the thermogravimetric method. Titanium isopropoxide was dissolved in ethylene glycol and citric acid to form a stable solution that can be mixed with other nitrate aqueous solutions without causing precipitation. The Ti content in the as-prepared Ti solution was also assayed by the thermogravimetric method. During the concentrating process of the precursor solution, no precipitate or turbidity was observed, indicating the near-molecular-level cation mixing through the whole process. The resulting resins were then calcined at 900°C for 5 h to completely burn out the organic substances and to form the expected crystalline phases. The as-prepared powders may be mixed directly for the preparation of electrode pastes or subjected to further calcination at higher temperatures to achieve better crystallization, e.g., for structural stability studies.

Characterization.—Powder X-ray diffraction (XRD) with Cu Kα radiation (Siemens D5000) was used to characterize the phase purity of air-sintered samples as well as those subjected to various subsequent heat-treatments in reducing atmospheres. The XRD patterns were analyzed with related softwares including PowderX24 and DicoVol91.25 The structural stability to reduction was studied by exposing the air-calcined (at 1300°C) powders at different O_{2} pressure and temperatures and examining the resulting phases by XRD. To study the reactivity with YSZ, LSTM powders were mixed with commercial YSZ (Tosoh, TZ-8Y) in a 1:1 weight ratio and then calcined at 1400°C for 5 h in air.

Powders were uniaxially pressed into bars and then sintered in air. LSTM samples were densified to over 95% of theoretical density by sintering in air at 1300°C for 5 h. However, the LSTM powder was difficult to sinter, with only 70% theoretical density achieved under the same sintering conditions. The as-obtained rectangular-shaped samples with dimensions of 3 × 4 × 40 cm were subjected directly to electrical conductivity measurements, or cut to a length of 25 mm before dilatometric measurements. As the electrical conductivity of LST was found to be very sensitive to the sintering atmosphere, one LSTM sample was prereduced at 1320°C for 20 h in Ar/4% H_{2} before the electrical conductivity measurements. The thermal expansion measurements (25–1100°C in air) and chemical expansion upon reduct cycling were carried out using a push-round dilatometer (Netzsch DIL 402C) with heating and cooling rates of 3 K/min. The standard de fabrication method was used to measure the electrical conductivity in air and reducing atmosphere (wet Ar/4% H_{2}) at 100–910°C. Unless specified, gas humidification was performed by passing the gases through a water container at ambient temperatures (20–28°C). A zirconia oxygen sensor (Metrotec) was used to monitor the P(O_2) at 700°C, and the P(O_2) at other temperatures was then deduced by thermodynamic calculations of the H_{2}O–O_{2}–H_{2} system.

The electrode polarization resistances were characterized by electrochemical impedance spectroscopy (EIS) with a symmetric cell configuration. TZ-SY powder was first pressed into pellets and then sintered at 1500°C for 10 h to obtain dense YSZ electrolyte substrates (Ø 12 mm and 1–2 mm thick). LSTM or LST/YSZ composite electrodes were applied onto both surfaces of the YSZ substrates by screen printing and then calcined in air at 1200°C for 3 h. A content of 35 vol % YSZ in the composite electrodes was chosen in order to supply an additional percolating ionic transport path while retaining as much as possible the electronic conduction path provided by the LSTM phase. Furthermore, the YSZ in the composite electrode was added to improve the adhesion to the electrolyte. The thickness and diameter of the electrodes are 15–30 μm and 10 mm, respectively. Before the EIS measurements, Au paste (Ferro, 64101003) was applied onto the electrodes by screen printing and then calcined at 800°C for 1 h to obtain a current collection layer with a thickness of 3–5 μm. The impedance spectra of the electrochemical cells were obtained with a Solartron 1260 frequency response analyzer working in a galvanostatic mode. The ac current amplitude was 3 mA and the frequency range was 10^5–0.05 Hz. The reducing atmosphere used in this measurement is wet Ar/H_{2} or wet CH_{4} with a normal flow rate of 100 mL/min. The impedance spectra were analyzed with Zview software (Scribner Associates, Inc.). The microstructure of the electrodes was investigated by scanning electron microscopy (SEM, Zeiss Ultra25).

Fuel cell performance with LSTM/YSZ anodes was also measured in wet H_{2} or wet CH_{4} vs air. YSZ sheets (Ø 20 mm and 0.2 mm thick, Kerafol GmbH) were used as the electrolyte supports. Anodes were applied by screen printing and calcined in air at 1200°C for 3 h, then the LSM (La_{0.4}Sr_{0.6}MnO_{3−δ})-based double-layer cathodes [LSM–YSZ (1:1 wt %)/LSM] were applied by the same method and calcined in air at 1100°C for 3 h. Finally, Au current collectors were applied onto both sides in the same way as for the symmetric cells. The diameter of both electrodes was 12 mm. The gas flow rate of H_{2}, CH_{4} or air was controlled at 200 mL/min. The humidification of the fuel gases was also performed at room temperature. Both the I-V curves and impedance spectra of the two-electrode asymmetric cells were measured at 750–860°C.

Results and Discussion

Crystal structure and electrical conductivity.—As determined by XRD, all four compositions show single-phase perovskite-type structures after sintering in air at 1300°C for 5 h. While LST exhib-
its cubic structure, the structures of LSTM can be best refined as hexagonal perovskites. Because LST is stable in highly reducing atmospheres, only LSTMs were subjected to reduction under selected conditions to study the structural stability to reduction. After reduction in wet Ar/4% H₂ at 950°C (p(O₂) = 2.3 × 10⁻¹⁶ bar) for 12 h, all three compositions retained their perovskite structure. However, after reduction in nonhumidified Ar/4% H₂ at 850°C (p(O₂) = 10⁻²³ bar) for 12 h, the perovskite structures of LSTM4682 and LSTM4664 were still retained, whereas a slight decomposition of LSTM4646 was observed (Fig. 1). The decomposition products were identified as MnO and (La,Sr)₂MnO₄ with K₂NiF₄-type structure, both being previously reported as the decomposition products of (La,Sr)₂MnO₄. The practical p(O₂) in an SOFC anode chamber depends on the fuel cell working conditions, e.g., the inlet fuel composition, fuel utilization, anode polarization. The anode materials experience the lowest p(O₂) when the fuel cell is under open-circuit conditions. In practice, humidification is usually carried out before H₂ or CH₄ is fed into the anode chamber to avoid extreme low p(O₂). The present results indicate that LSTM4646 can only be used in a moderately humidified atmosphere. It seems stable at 800°C in an atmosphere with a H₂O/H₂ ratio of 3:20, as shown later.

The calculated lattice parameters of LST and LSTM in the oxidized as well as reduced state are listed in Table I. For comparison, the pseudo-cubic lattice parameters are plotted in Fig. 2. The reduced state of LST was obtained by a high-temperature (1320°C) reduction process in Ar/4% H₂, while LSTMs were only reduced at 950°C in wet Ar/4% H₂ to assure the phase integrity. These reduction conditions were chosen because LST shows strongly improved electrical conductivity after a high-temperature reduction process. In this work, such a process leads to a lowered crystal symmetry refined as tetragonal for LST. In addition, it seems that LSTM4646 also changes its structure from hexagonal to tetragonal after reduction. Under oxidizing conditions, substitution of Mn for Ti leads to a gradual lattice expansion until x = 0.4, and further substitution to 60 atom % causes an apparent lattice shrinkage. Upon reduction, while all compositions show lattice expansions, the linear expansion of LSTM4646 (0.20%) is significantly smaller than that of LSTM4682 (0.69%) and LSTM4664 (0.39%).

The electrical conductivity in both air and humidified Ar/4% H₂ of air-sintered L₀.₄Sr₀.₆T₁₋ₓMnO₃₋₄ as a function of temperature and Mn content is shown in Fig. 3 and 4. For a better comparison, the electrical conductivity data were corrected with the sample density according to an empirical equation proposed by Tagawa et al.: $\sigma_{app}/\sigma_{corr} = 2(d_{app}/100 - 0.5)$

where $\sigma_{corr}$ is the corrected electrical conductivity, $\sigma_{app}$ the measured apparent conductivity, and $d_{app}$ the relative density (%).

In oxidizing atmosphere, the electrical conductivity increases monotonically with Mn content. However, the behavior in reducing atmosphere is quite different. In fact, both the electrical property and the crystal structure can be linked to the inherent charge compensa-

### Table I. Unit cell parameters of L₀.₄Sr₀.₆T₁₋ₓMnO₃₋₄ subjected to different firing conditions.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Firing conditions</th>
<th>Lattice setting</th>
<th>Lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>LST</td>
<td>1300°C/5 h/air</td>
<td>Cubic</td>
<td>a = 3.892(1) Å, V = 58.93(4) Å³, Z = 1</td>
</tr>
<tr>
<td>LSTM4682</td>
<td>1300°C/5 h/air</td>
<td>Tetragonal</td>
<td>a = 7.811(3) Å, c = 2.964(1) Å, V = 180.9(2) Å³, Z = 3</td>
</tr>
<tr>
<td>LSTM4682</td>
<td>1300°C/5 h/air, then 950°C/12 h/ wet Ar/4%H₂</td>
<td>Hexagonal</td>
<td>a = 5.522(2) Å, c = 13.48(2) Å, V = 356.0(8) Å³, Z = 6</td>
</tr>
<tr>
<td>LSTM4664</td>
<td>1300°C/5 h/air</td>
<td>Hexagonal</td>
<td>a = 5.559(1) Å, c = 13.57(1) Å, V = 363.3(4) Å³, Z = 6</td>
</tr>
<tr>
<td>LSTM4646</td>
<td>1300°C/5 h/air, then 950°C/12 h/ wet Ar/4%H₂</td>
<td>Hexagonal</td>
<td>a = 5.528(1) Å, c = 13.483(4) Å, V = 356.8(2) Å³, Z = 6</td>
</tr>
<tr>
<td>LSTM4646</td>
<td>1300°C/5 h/air, then 950°C/12 h/ wet Ar/4%H₂</td>
<td>Hexagonal</td>
<td>a = 5.540(2) Å, c = 13.505(6) Å, V = 359.0(4) Å³, Z = 6</td>
</tr>
<tr>
<td>LSTM4646</td>
<td>1300°C/5 h/air, then 950°C/12 h/ wet Ar/4%H₂</td>
<td>Hexagonal</td>
<td>a = 5.497(2) Å, c = 13.40(2) Å, V = 350.7(8) Å³, Z = 6</td>
</tr>
<tr>
<td>LSTM4646</td>
<td>1300°C/5 h/air, then 950°C/12 h/ wet Ar/4%H₂</td>
<td>Tetragonal</td>
<td>a = 3.9015(6) Å, c = 15.552(4) Å, V = 236.7(1) Å³, Z = 4</td>
</tr>
</tbody>
</table>

**Figure 2.** Pseudo-cubic lattice parameters of L₀.₄Sr₀.₆T₁₋ₓMnO₃₋₄ as a function of Mn content in both oxidized (closed symbols) and reduced (open symbols) states. The pseudo-cubic lattice parameter is defined as the cubic root of the primitive cell volume, i.e., a = $\sqrt[3]{V}$. Squares are results of this work. Detailed firing conditions and calculated lattice parameters are listed in Table I. Even the structure of oxidized LST is not really cubic due to the appearance of the diffusive “background” (see the text). Triangles are results from the literature for LST. (▲) Annealed at 1400°C for 17 h in air; (▼) annealed at 1400°C for 17 h in N₂/10% H₂; (▲) annealed at 1350°C in air (note: the parameter remains unchanged after reduction at 1050°C in CO/CO₂).³²
tion mechanisms, which vary with the atmosphere (or $p(\text{O}_2)$) and the Mn content in $\text{La}_{0.4}\text{Sr}_{0.6}\text{Ti}_{0.5}\text{Mn}_{0.5}\text{O}_3$. This is discussed from the viewpoint of defect chemistry.

For the Mn-free composition, LST, the replacement of $\text{Sr}^{2+}$ by $\text{La}^{3+}$ requires charge compensation to ensure charge neutrality in the lattice. In moderately reducing atmospheres, e.g., water-saturated $\text{Ar}/\text{H}_2$, the formation of oxygen vacancies can be neglected. The charge compensation is then realized by the reduction of $\text{Ti}^{4+}$ to $\text{Ti}^{3+}$, i.e., $[\text{La}_{0.4}] + 2[V_{\text{O}}] = [\text{Ti}^{3+}]$. In atmospheres with high $p(\text{O}_2)$, however, $\text{Ti}^{4+}$ is unlikely to exist in the material; thus, the charge neutrality dictates the presence of additional oxygen beyond the $\text{ABO}_3$ stoichiometry ($\text{La}_0.4\text{Sr}_{0.6}\text{Ti}_0.2\text{O}_3$). One way to accommodate the extra oxygen is the formation of A-site cation vacancies coupled with planar defects similar to those in the Ruddlesden–Popper phases ($\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$), $^{33,34}$ where SrO layers are interleaved within perovskite layers. Assuming this compensation mechanism, the composition LST may be represented by $(\text{La}_0.4\text{Sr}_0.6\text{Ti}_0.2\text{O}_3)$, $^{33,34}$ where Sr vacancies compensate the positive charge from $\text{La}_{0.4}$. The formation of Ruddlesden–Popper phases to accommodate SrO layers structurally in an ordered manner, $^{33,34,35}$ therefore, wide agreement on this issue was reached in the literature, $^{2,3,8-11}$ although no strong evidence was reported.

With the help of high-resolution transmission electron microscopy (HRTEM), Bowden et al. $^{22}$ and later Canales-Vázquez et al. $^{34}$ showed that the extra oxygen in La-substituted $\text{SrTiO}_3$ is actually accommodated by the creation of planar defects similar to those of $\text{La}_2\text{Ti}_2\text{O}_7$. $^{44}$ No cation vacancy is required in this mechanism. Thus, La-substituted $\text{SrTiO}_3$ (Sr$_{1-x}\text{La}_x\text{Ti}_2\text{O}_7$, $0.5 < x < 1$) can be described as a structural solid solution of $\text{La}_2\text{Ti}_2\text{O}_7$-type layers in $\text{SrTiO}_3$. This solution occurs across the entire $\text{Sr}_1\text{La}_x\text{Ti}_2\text{O}_{7.5}$ composition range ($0 < x < 1$). At higher levels of substitution ($x \approx 0.67$), such layers are ordered into new compounds, which are clearly visible by HRTEM and also detectable by diffraction methods. These compounds are represented by the general formula $\text{La}_2\text{Sr}_{x-4/3}\text{Ti}_{x+5/3}\text{O}_{2x+2}$, and the members with $x = 4.5, 5.6$ have been investigated recently by Bowden et al. $^{42}$ and Canales-Vázquez et al. $^{33}$ With lower levels of substitution, the concentration of $\text{La}_2\text{Ti}_2\text{O}_7$-type layers becomes smaller and they are randomly distributed throughout the perovskite host. XRD patterns may only show a broadened perovskite signal.

The lanthanum content of $x = 0.4$ is equivalent to the member with $n = 10$ of $\text{La}_2\text{Sr}_{x-4/3}\text{Ti}_{x+5/3}\text{O}_{2x+2}$. With this composition, Bowden et al. $^{33}$ found the $\text{La}_2\text{Ti}_2\text{O}_7$-type layers either in clusters or in isolation, and accordingly, some weak impurity peaks in the XRD pattern. Although in our present work the XRD diffraction pattern of LST sintered in air can be fitted with a cubic symmetry, a diffusive “background” that is significantly higher than in other samples is also clearly visible (Fig. 1a). It is considered that higher annealing temperatures or longer annealing times would lead to better ordering of those $\text{La}_2\text{Ti}_2\text{O}_7$-type layers, and hence, transform the “background” to sharp impurity peaks, as observed previously. $^{32,33}$ In their work, Bowden et al. annealed the sample at 1350°C for 16 h, and Canales-Vázquez et al. did this at 1400–1600°C for 96 h. In comparison, the LST sample in this work was only sintered at 1300°C for 5 h.

In summary, under oxidizing conditions, the substitution of $\text{La}^{3+}$ for $\text{Sr}^{2+}$ in $\text{SrTiO}_3$ does not lead to electronic (via $\text{Ti}^{4+}$) or ionic (via $\text{V}_{\text{O}}$) compensation but only to excess oxygen accommodated by $\text{La}_2\text{Ti}_2\text{O}_7$-type layers in the structure. Due to the excess of oxygen in this material, oxygen vacancies are unlikely to exist. The lack of both electronic charge carrier ($\text{Ti}^{4+}$) and ionic charge carrier ($\text{V}_{\text{O}}$) results in very low electrical conductivity (cf. Fig. 3). Upon reduction, the excess oxygen in LST can be removed, as confirmed by thermogravimetric experiments, $^{38,40,43}$ transferring LST to a reduced state. The concentration of electronic charge carriers ($\text{Ti}^{4+}$) is then significantly increased, resulting in a jump of electrical conductivity by at least 4 orders of magnitude (Fig. 3 and 4). Higher reduction temperatures or longer reduction times would remove more excess oxygen and create a higher concentration of $\text{Ti}^{3+}$. In the present work, reduction of air-sintered LST at 910°C for 15 h in humidified Ar/4% $\text{H}_2$ only yields a conductivity of 1.8 S/cm at 910°C, whereas the sample annealed in Ar/4% $\text{H}_2$ at 1320°C for 20 h shows a conductivity of 50 S/cm under the same experimental conditions (not shown in Fig. 3 and 4). Similar results were reported by Marina et al. $^5$ As discussed above, the removal of excess oxygen tends to integrate the $\text{La}_2\text{Ti}_2\text{O}_7$-type layers into the structure, which is con-
La\textsuperscript{3+} would lead to excess oxygen in the structure under oxidizing conditions; the authors and Eror and Balachandran\textsuperscript{38,45} performed this annealing under relatively moderate conditions, 1300–1350°C for 5–10 h in air, which might cause incomplete ordering and smaller lattice parameters. With respect to the reduced states, samples were reduced either at 1000–1050°C \textsuperscript{38,43} or at 1320–1400°C (this work and Ref. 41). Canales-Vázquez et al.\textsuperscript{43} showed that reduction of \( \text{La}_{0.33}\text{Sr}_{0.67}\text{TiO}_3 \) at 1000°C for 48 h in Ar/\( \text{H}_2 \) produced only 8–10 atom % \( \text{Ti}^{4+} \) (the fully reduced state should have 33 atom % \( \text{Ti}^{4+} \)). Eror and Balachandran\textsuperscript{38} also pointed out that the redox kinetics at 1050°C became very slow when the La\textsuperscript{3+} concentration exceeded 20 atom %. In comparison, full reduction/oxidation of 20 atom % La-substituted \( \text{SrTiO}_3 \) was realized at 1300°C within a reasonable period of time.\textsuperscript{40} Therefore, it can be concluded that a fully reduced state of LST might have been achieved in Ref. 41 and in our work, which in turn led to significantly increased lattice parameters.

The replacement of LST by Mn at the B-site supplies an additional compensation mechanism. While the replacement of \( \text{Sr}^{2+} \) by \( \text{La}^{3+} \) would lead to excess oxygen in the structure under oxidizing conditions, the replacement of \( \text{Ti}^{4+} \) by \( \text{Mn}^{4+} \) would have a counter-effect, presumably leading to fewer \( \text{La}_2\text{Ti}_2\text{O}_7 \)-type layers in the structure. The effect, together with the difference in ionic radius between Mn and Ti, may lead to the observed gradual increase of the lattice parameters with Mn content up to 40 atom %. At a Mn content of 40 atom %, i.e., for LSTM\textsubscript{4646}, complete neutralization (between \( \text{La}_{0.67} \) and \( \text{Mn}_{0.33} \)) is expected, and excess oxygen is then not required anymore. In this sense, LSTM\textsubscript{4646} might be simply regarded as a solid solution of \( \text{LaMnO}_3 \) and \( \text{SrTiO}_3 \), i.e., \( \text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{0.33}\text{Ti}_{0.67}\text{O}_3 \). Further substitution of Mn either creates oxygen vacancies or increases the valence of Mn itself. Due to the smaller ionic radius of Mn\textsuperscript{4+}, the latter might result in a smaller lattice parameter, as shown in Fig. 2.

Upon reduction, both Mn and Ti tend to have lower valence states and larger ionic radii, giving rise to larger lattice parameters. It is not surprising that the fully “neutralized” composition, LSTM\textsubscript{4646}, shows significantly smaller lattice expansion upon reduction compared with its two neighboring compositions, LSTM\textsubscript{4682} and LSTM\textsubscript{4646}. Compared with LSTM\textsubscript{4664}, LSTM\textsubscript{4682} might contain much more excess oxygen that is readily removable and thus would show a larger lattice expansion upon reduction. For LSTM\textsubscript{4646}, if we assume a Mn\textsuperscript{4+} compensation mechanism under oxidizing conditions, i.e., \( \text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{0.33}\)\( \text{SrTiO}_3 \), the existence of a significant amount of Mn\textsuperscript{4+} (\( \text{Mn}^{4+}_e \)) facilitates the reduction of this compound, also resulting in more oxygen release upon reduction than LSTM\textsubscript{4646}. This can be better understood when we consider the oxygen nonstoichiometry of \( \text{La}_2\text{SrTi}_2\text{O}_7 \). Compared with \( \text{LaMnO}_3 \), in which the average valence of Mn is +3, \( \text{La}_{0.33}\text{Sr}_{0.67}\text{Mn}_{0.67}\text{O}_3 \) requires 20 atom % \( \text{Mn}^{4+} \) for charge compensation. \( \text{La}_{0.33}\text{Sr}_{0.67}\text{Mn}_{0.67}\text{O}_3 \) shows much higher oxygen stoichiometry after reduction.\textsuperscript{20,25} It is thus envisaged that the reduced LSTM\textsubscript{4646} might contain a significant amount of oxygen vacancies, which gives rise to a remarkably improved ionic conductivity and therefore good electrocatalytic activity for fuel oxidation.

\( \text{SrTiO}_3 \) or La-substituted \( \text{SrTiO}_3 \) is known as a n-type semiconducting material, in which the electrical conductivity increases with decreasing \( \text{p(O}_2) \).\textsuperscript{39,46} The electrical conductivity is essentially controlled by the concentration of the electronic defect, \( \text{Ti}^{4+} \) or \( \text{Ti}^{3+} \). Instead, \( \text{LaMnO}_3 \) or Sr-substituted \( \text{LaMnO}_3 \) is a p-type conductor, and its electronic conductivity is determined by the mean Mn valence.\textsuperscript{22} It should be noted that even the stoichiometric \( \text{LaMnO}_3 \) exhibits a fairly high electrical conductivity in air (\( \sim 80 \text{ S/cm at 800°C} \)), although the mean Mn valence is +3. After reduction, the electronic conductivity of \( \text{(La, Sr)}\text{MnO}_3 \) is decreased due to the lowered mean Mn valence, but its oxide ionic conductivity is increased due to the significantly increased oxygen vacancy concentration.\textsuperscript{22} Under oxidizing conditions, the electrical conductivity of LST increases monotonically with Mn content and is remarkably higher than that of LST (Fig. 4). Therefore, it can be concluded that the electrical conductivity of LSTM in the oxidizing atmosphere is dominated by the p-type conduction related to Mn. In reducing atmosphere, however, the n-type conductivity related to \( \text{Ti}^{3+} \) is greatly improved, whereas the p-type conductivity related to Mn is decreased. The reduced LSTM\textsubscript{4682} shows lower conductivity than the reduced LSTM, but higher conductivity than the oxidized LSTM\textsubscript{4682}, indicating that the n-type electrical conductivity still predominates in the reduced LSTM\textsubscript{4682}. It seems that 20 atom % Mn substitution partially offsets the n-type contribution from \( \text{Ti}^{3+} \). Due to this shift, the electrical conductivity of the reduced LSTM\textsubscript{4682} is one order of magnitude lower than its oxidized LSTM\textsubscript{4682}, an anode functional layer 15-μm-thick would give rise to an area-specific resistance of about 0.01 Ω cm\textsuperscript{2} at 800°C. Due to the rather low electrical conductivity of the other compositions in reducing atmosphere, only LSTM\textsubscript{4646} was subjected to further dilatometric measurement and electrochemical performance characterization.

Regarding the reactivity of LSTM\textsubscript{4646} with YSZ, the room tem-
The subsequent reoxidation process in Ar/20% O₂ cannot show a chemical expansion of 0.42%, definitely indicating the existence of micro-cracks in the sample. Judging from the shape of the expansion curve, the reoxidation process is much faster than the reduction process. The expansion curve at the reduction stage shows a typical curve, the reoxidation process in Ar/20% O₂ cannot fully restore the sample to its original size, leaving an irreversible expansion of 0.21%, indicating that more micro-cracks were formed. Considering a chemical expansion of 0.5% during redox cycling, this corresponds to a lateral dimensional change of 0.5 mm, or even 1 mm for a 10 × 10 cm²- or a 20 × 20 cm²-sized SOFC. Such large changes may induce strong stresses on the adjacent components, especially on the electrolyte layer in an anode-supported cell. Whereas an electrolyte-supported cell might have enough strength due to the thicker electrolyte layer, the stresses during redox cycling may lead to cracks in the electrolyte of an anode-supported cell. To evaluate more precisely the applicability of LSTM in different types of SOFCs, thermomechanical calculations have to be carried out. On the basis of the results so far, an application of LSTM can only be recommended for electrolyte-supported cells and/or small-sized SOFCs like the integrated planar-type SOFC, in which the dimensions of the cells are kept small in comparison to typical anode-supported cells.

Electrochemical performance and long-term stability.— The electrodes under study show uniform porous structures and good adhesion to the YSZ electrolytes (Fig. 6). In the impedance spectra of the symmetric cells in wet Ar/H₂ or wet CH₄, three arcs are generally observed in the frequency range of 10⁶–0.05 Hz. Only in a few cases are two arcs visible due to the overlap of two adjacent arcs. Examples of the impedance spectra of LSTM4646/YSZ anodes obtained at different temperatures and in different atmospheres are shown in Fig. 7. In general, data are fitted to the equivalent circuit LR₁(RQ₁)(RQ₂). In (a) dotted lines indicate each impedance arc in the fit of one set of as-obtained impedance data of one symmetric cell, which is only corrected for the active electrode area. In (b)–(d) the series resistances R₁ are subtracted and the resulting spectra are then divided by 2 to directly give the polarization resistances (Rₚ) of one electrode. Closed symbols mark the frequency points from 0.1 Hz to 100 kHz at each frequency decade.

Figure 6. SEM picture of the LSTM4646/YSZ anode on YSZ electrolyte. Top layer is Au current collector.

Figure 7. Selected impedance spectra of one LSTM4646/YSZ electrode on YSZ electrolyte at different temperatures in wet CH₄ (squares), wet Ar/20% H₂ (triangles), and wet H₂ (circles). Points are experimental data and solid lines are fit data with the equivalent circuit LR₁(RQ₁)(RQ₂). In (a) dotted lines indicate each impedance arc in the fit of one set of as-obtained impedance data of one symmetric cell, which is only corrected for the active electrode area. In (b)–(d) the series resistances R₁ are subtracted and the resulting spectra are then divided by 2 to directly give the polarization resistances (Rₚ) of one electrode. Closed symbols mark the frequency points from 0.1 Hz to 100 kHz at each frequency decade.
firmed by the comparison of the fitted $R_g$ values with the real electrolyte resistance calculated from the known ionic conductivity of the electrolyte material and the cell geometry. In all cases, they are very close to each other. Figure 7a gives an example of detailed fitting, where three well-distinguished arcs are shown and numbered I, II, and III from high to low frequency.

For each arc represented by a parallel $RQ$, the fitted resistance, $R$, admittance, $Y_o$, and frequency power, $n$, are used to calculate the summit frequency of the arc, $f_{max}$, according to Eq. 2.35

$$f_{max} = \frac{1}{2\pi} (RY_0)^{-1/n}$$

$$C(f) = Y_o(2\pi f)^n-1 \sin\left(\frac{n\pi}{2}\right)$$

Each parallel $RQ$ corresponds physically to one of the processes occurring in the complex electrode reactions. The fitted parameters ($R$, $Y_o$, $n$) and derived parameters [e.g., $f_{max}$, $C(f_{max})$] for each arc help to identify the corresponding process. Under the present experimental conditions, the summit frequency of the high-frequency arc, arc I, is generally over 10 kHz, which is distinctively higher than the low-frequency arcs (1–20 Hz for arc II and 0.2–2 Hz for arc III). Due to such high summit frequencies, part of this arc is often “dragged” down by the inductance to below the real axis on the complex impedance plane ($Z'$ vs $Z$'), as shown in Fig. 7a. In the cases where arc II and III overlap extensively, attempts to fit them with only one ($RQ$) subcircuit, however, often lead to much worse fitting results. Therefore, all the impedance data are fitted to the circuit $LRQ(RQ)_{II}RQ_{III}$, although, in some cases, the fitted parameters for arc II and III contain large uncertainties and hence are not shown in the related graphs. The polarization resistance of the electrode, $R_p$, is defined as $R_1 + R_2 + R_3$.

Under the same experimental conditions, LSTM4646 anodes show larger polarization resistances than LSTM4646/YSZ anodes. As shown in Fig. 8, the main difference of the impedance spectra between LSTM4646 and LSTM4646/YSZ anodes lies in arc I (with peak frequency around 30 kHz). LSTM4646 anodes show a remark-

Figure 8. Comparison of the impedance spectra between LSTM4646 and LSTM4646/YSZ anodes in wet $H_2$ at two temperatures; (a) LSTM, 810°C; (b) LSTM/YSZ, 810°C; (c) LSTM, 760°C; and (d) LSTM/YSZ, 760°C. The original impedance spectra obtained with the symmetric cells were processed in the same way as in Fig. 7b-d to show directly the polarization resistances ($R_p$) of one electrode. Closed symbols as well as numbers beside them indicate the frequency decades (0.1 Hz–100 kHz).

Figure 9. Temperature dependence of $R_1$, $R_2$, $R_3$, and $R_{p,TS}$ (= $R_1 + R_2 + R_3$) of one symmetric cell with LSTM4646/YSZ electrodes in wet $CH_4$ (squares), wet Ar/20% $H_2$ (triangles), and wet $H_2$ (circles). The electrode polarization resistances ($R_1$, $R_2$, $R_3$, and $R_{p,TS}$) were divided by 2 to give the contribution of one single electrode. In cases where arc 2 and arc 3 overlapped too extensively to be distinguished with good certainty, separate $R_1$ and $R_3$ values are not shown on the graph.

Figure 10. Calculated capacitances at the summit frequency of arc I ($C_1$), arc II ($C_2$), and arc III ($C_3$) for each impedance spectra measured. Calculations were performed according to Eq. 2 and 3 in combination with the fitting results ($R$, $Y_o$, $n$) for the impedance spectra measured at different temperatures and in wet $CH_4$ (squares), wet Ar/20% $H_2$ (triangles), and wet $H_2$ (circles).
ably enlarged arc I, while having almost the same sized arc II and III as LSTM4646/YSZ anodes. This difference helps to determine the nature of process I, as discussed below.

The fitted results of resistances and capacitances (at the summit frequency) for the impedance spectra of LSTM4646/YSZ anodes under various experimental conditions are shown in Fig. 9 and 10. As expected, $R_s$ is only a function of temperature and does not vary with the atmosphere. The activation energy for $R_s$ is calculated as $0.83 \pm 0.02$ eV, which is consistent with that of the ionic transport in YSZ in the high-temperature region (0.85 $\pm$ 0.05 eV), as reported in the literature.\(^{52}\) The dependence of the three arcs on the experimental conditions, e.g., temperature, atmosphere composition, and gas flow rate, are summarized as follows:

1. Arc I remains essentially unchanged when the atmosphere is changed from wet Ar/20% H$_2$ to wet H$_2$ or to wet CH$_4$. In contrast, both arc II and arc III vary with the hydrogen content in wet Ar/H$_2$ and show larger sizes in wet CH$_4$ than in wet Ar/20% H$_2$ (Fig. 7, 9, and 11).

2. The gas flow rate of Ar/H$_2$ has no apparent effect on the overall impedance spectra, as shown in Fig. 11.

3. Process I and II are apparently thermally activated, but process III is slightly thermally deactivated (Fig. 9). The apparent thermal activation energy for process I is roughly determined as 0.9–1.5 eV due to the large fitting uncertainty as the size of arc I is significantly reduced at higher temperatures. The activation energy for process II is 1.7 and 1.3 eV in wet CH$_4$ and wet Ar/20% H$_2$, respectively. Process III has an apparent thermal activation energy of about $-0.2$ eV in both wet CH$_4$ and wet Ar/20% H$_2$.

4. The capacitances for all three processes are essentially independent of the temperature and atmosphere composition. $C_1$, $C_2$, and $C_3$ are in the ranges of 5–20 $\mu$F cm$^{-2}$, 30–50 mF cm$^{-2}$, and 1.5–2.5 F cm$^{-2}$, respectively (Fig. 10).

The capacitance of process I is in the same order of magnitude as a typical double-layer capacitance, i.e., $\sim 10$ $\mu$F cm$^{-2}.\(^{54,55}\) In addition, process I is thermally activated and is insensitive to the atmosphere composition. Therefore, arc I can be interpreted as a charge-transfer process taking place at the LSTM4646/YSZ interface. In studies of the hydrogen oxidation reaction on a Ni/YSZ anode, a high-frequency arc was observed\(^{56}\) with similar characteristics, as can be seen here for arc I, and attributed to the transfer of charged species across the Ni/YSZ interface. In the present study, the fact that LSTM4646/YSZ anodes show a remarkably smaller arc I than LSTM4646 anodes strongly supports this interpretation. In the composite anode, the area of the LSTM4646/YSZ interface is effectively increased, leading to decreased charge-transfer resistance. This might also indicate that the ionic conductivity of the LSTM4646 phase is lower than that of YSZ.

Process II is also thermally activated and has a capacitance of 30–50 mF cm$^{-2}$. As calculated previously,\(^{52}\) adsorption of a monocharged species on a Ni/YSZ electrode surface would give a capacitance in the order of 10 mF cm$^{-2}$. By combining its sensitivity to the hydrogen concentration in wet Ar/H$_2$, this process is proposed to be linked to the dissociative adsorption of hydrogen on the electrode surface.

The capacitance of process III is larger than 1 F cm$^{-2}$. A capacitance of this magnitude is not ascribable to interfacial capacitance or chemical capacitance does not seem to be a good explanation for the large capacitance observed.

Another process that gives such large capacitance is called gas conversion.\(^{60}\) The large capacitance of this process observed by impedance spectroscopy is related to the gas composition change in the vicinity of the electrode when a current is passed onto the electrode, leading to a variation in the Nernst potential. A low-frequency arc with a capacitance of up to several F cm$^{-2}$ was observed in the impedance spectra of a Ni/YSZ electrode in wet H$_2$ at 1000°C in a three-electrode setup.\(^{54,55}\) One important feature of this process is that the associated resistance would be slightly thermally deactivated (e.g., $E_a = -0.09$ eV, as calculated and observed in Ref. 52 and 60), which is consistent with the small negative apparent thermal activation energy ($-0.2 \pm 0.1$ eV) observed in this work. However, gas conversion impedance should not be detectable in a small symmetric two-electrode cell where the electrodes are placed sufficiently close together in a common atmosphere. This is evidenced by the absence of such gas conversion impedance when the same Ni/YSZ electrode material was measured in a symmetric two-electrode cell setup (electrode area 0.25 cm$^2$, electrolyte thickness $\sim 200$ $\mu$m).\(^{54,55}\) Furthermore, gas conversion impedance can be considerably depressed with a larger gas flow rate, whereas such a behavior is not observed here. However, the small negative apparent activation energy of process III strongly supports an explanation based on the gas conversion impedance, in opposition to the chemical capacitance.

According to its origin, the appearance of gas conversion impedance depends significantly on the experimental conditions like cell/setup geometry or gas flow profile. Even in a symmetric two-electrode cell, gas conversion impedance can be avoided only when the electrodes are so close together that any gas composition variation at one electrode can be followed simultaneously at the other electrode, giving rise to a zero Nernst potential change between these two electrodes. In this work, the cell (electrode area $\sim 0.8$ cm$^2$ and electrolyte thickness $\sim 2$ mm) is much larger than that used in Ref. 60. Therefore, it is possible that the requirement for the avoidance of gas conversion impedance as stated above is not fulfilled in the current cell under the experimental conditions applied so that gas conversion impedance is still present. As the temperature is lowered, $R_s$ is slightly decreased while $R_3$ is significantly increased due to the high activation energy of process II (1.3–1.7 eV); hence, arc III...
becomes less distinct and may be fully masked by the large arc II. This trend is clearly observed, as shown in Fig. 7. Nevertheless, further work is needed to determine with certainty the real process associated with arc III.

The total polarization resistance ($R_p$) of one LSTM4646/YSZ electrode as a function of temperature and atmosphere composition is also shown in Fig. 9. In wet H$_2$, $R_p$ is 0.32 $\Omega$ cm$^2$ and 0.46 $\Omega$ cm$^2$ at 856 and 815°C, respectively. According to the apparent activation energy (1.07 ± 0.05 eV), $R_p$ is estimated by extrapolation to be 0.22 $\Omega$ cm$^2$ in wet H$_2$ at 900°C. In wet CH$_4$, it increases to 0.82 and 1.09 $\Omega$ cm$^2$ at 855 and 816°C, respectively. In comparison, the polarization resistances of LSCM/YSZ anodes (optimized by grading) at 900°C were reported to be 0.51 $\Omega$ cm$^2$ in wet Ar/5% H$_2$, 0.26 $\Omega$ cm$^2$ in wet H$_2$, and 0.87 $\Omega$ cm$^2$ in wet CH$_4$. Therefore, the electrochemical performance of LSTM4646/YSZ anode seems slightly better than that of LSCM/YSZ anode.

The performance of a fuel cell with LSTM4646/YSZ anode and LSM-based cathode is shown in Fig. 12. Wet CH$_4$ or H$_2$ is used as the fuel, and air is used as the oxidant. To separate the electrode polarization resistance from the total cell resistance, impedance spectra under open-circuit conditions corresponding to each I-V curve in Fig. 12 are measured and shown in Fig. 13. In wet H$_2$, the OCV at 900°C was 0.7 V. The peak powder density is 1.09 $\mu$g/cm$^2$ at 900°C and 0.26 $\mu$g/cm$^2$ at 900°C. According to the nearly linear I-V curve, the polarization behavior of LSTM4646/YSZ electrode in wet H$_2$ is consistent with the low-frequency intercept on the curve in Fig. 7.

In wet CH$_4$, the fuel cell performance in wet CH$_4$, however, is much poorer than in wet H$_2$. The OCV at 856°C is only 0.86 V, and a limiting current density is observed. According to the symmetric cell measurement, the polarization behavior of LSTM4646/YSZ anodes in wet CH$_4$ looks very similar to that in wet Ar/H$_2$. In combination with the low OCV and limiting current observed with a fuel cell, it is thought that the LSTMBased466/YSZ electrode does not have significant electrocatalytic activity for the direct oxidation of CH$_4$. Instead, the power output of the fuel cell in wet CH$_4$ can be primarily attributed to the oxidation of a small fraction of H$_2$ at the anode, which might be produced by steam reforming. After operation in wet CH$_4$, the fuel cell performance recovers immediately and returns completely to its initial level when the gas is switched back to wet H$_2$, indicating that no significant carbon deposition occurred on the electrode during operation in wet CH$_4$. In fact, this is in accordance with the observed low OCV in wet CH$_4$, because a good cracking catalyst would lead to a high H$_2$ concentration and hence a high OCV, at least temporarily.

While this material shows good electrochemical performance for the oxidation of H$_2$, its long-term stability under typical anode conditions remains another major concern. To examine this, a symmetric cell was exposed to wet Ar/20% H$_2$ at 795°C. Ar/20% H$_2$ was humidified at room temperature (20–28°C). The electrode polarization resistances ($R_1$, $R_2$, $R_3$, and $R_4$) were divided by 2 to give the contribution of one single electrode.

Figure 12. Electrochemical performance of a single fuel cell operated with wet H$_2$ or wet CH$_4$ as fuel gas and air as oxidant at different temperatures. The cell is electrolyte (213-μm-thick YSZ) supported, with LSTM4646/YSZ anode and LSM-based cathode.

Figure 13. Impedance spectra under open-circuit conditions of the fuel cell corresponding to Fig. 11. Both anode and cathode contribute to the impedance spectra.

Figure 14. Time dependence of $R_1$, $R_2$, $R_3$, and $R_4$ of one symmetric cell with LSTM4646/YSZ electrodes in wet Ar/20% H$_2$ at 795°C. Ar/20% H$_2$ was humidified at room temperature (20–28°C). The electrode polarization resistances ($R_1$, $R_2$, $R_3$, and $R_4$) were divided by 2 to give the contribution of one single electrode.
LSTM and YSZ might thus be affected, also leading to an increased charge-transfer resistance. After this stage, $R_T$ and $R_C$ remain nearly stable with time. Neglecting the periodic fluctuations, $R_T$, $R_C$, and $R_A$ can be regarded as stable during the measurement time. Careful examination discloses that the periodic fluctuations have a period of 24 h. Therefore, this is likely caused by the day and night room temperature fluctuations (20–28°C), giving rise to a water content fluctuation in Ar/20% H₂ because the gas is simply humidified at ambient temperature. Compared to $R_T$, the relative fluctuation of $R_A$ seems larger (note its small absolute values). Therefore process III is more sensitive to the water content than process II. It is found that higher water content corresponds to smaller $R_A$. This would lead to better anode performance when a real fuel cell is operated at high fuel utilization, generating a high concentration of water in the anode chamber.

Conclusions
Perovskite oxides, La$_{0.4}$Sr$_{0.6}$Ti$_1$-$x$Mn$_x$O$_3$ ($x = 0, 0.2, 0.4, 0.6$), were synthesized and evaluated in detail as new anode materials for SOFCs. The charge compensation mechanism as a function of oxygen partial pressure and Mn content is considered to play a key role in determining the crystal structure as well as the electrical property. Among the compositions studied, La$_{0.4}$Sr$_{0.6}$Ti$_{0.8}$Mn$_{0.2}$O$_3$ (LSTM4646) shows an electrical conductivity of 1.5 S/cm at 810°C and $\rho$(O$_2$) of $\sim$10$^{-10}$ bar. In addition, it is thermally and chemically compatible with YSZ electrolytes.

Three processes govern the electrochemical performance of LSTM4646 or LSTM4646/YSZ electrodes in wet Ar/H₂ or wet CH$_4$. The two high-frequency processes are proposed to be charge transfer at the LSTM4646/YSZ interface and dissociative adsorption of hydrogen on the electrode surface. The third process corresponds to a very large capacitance (1.5–2.5 F cm$^{-2}$) and is slightly thermally deactivated. It is thus tentatively ascribed to gas conversion impedance.

LSTM4646/YSZ composite anodes show better electrochemical performance than LSTM4646 anodes. The polarization resistance is as low as 0.32 Ω cm$^2$ in wet H₂ at 856°C; therefore, an electrolyte-supported H$_2$/air fuel cell with an LSM/YSZ cathode yields a power density of 365 mW cm$^{-2}$ at a terminal voltage of 0.7 V. In addition, it is stable in a moderately humidified hydrogen atmosphere. However, this anode shows insignificant electrocatalytic activity for the direct oxidation of methane. The chemical expansion of dense LSTM4646 material between air and wet Ar/4% H₂ is as much as 0.6% at 817°C and is not reversible. This property would restrict the application of this material for electrolyte-supported cells and/or small-sized SOFCs like the integrated planar-type SOFC.

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D83