CHEMICAL COMPATIBILITY OF \((\text{La}_{0.6}\text{Ca}_{0.4})_{x}\text{Fe}_{0.8}\text{M}_{0.2}\text{O}_3\) (\(x=1, 0.9; M = \text{Cr}, \text{Mn}, \text{Co}, \text{Ni}\)) WITH YSZ

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ABSTRACT

LaFeO$_3$ based perovskites are of interest as cathode material for the development of advanced SOFCs operating at temperatures significantly lower than 900 °C. The compatibility of the selected materials is a necessary demand in order to guarantee long term operation of a SOFC. Systematic investigations on the reactivity between the solid electrolyte YSZ (ZrO$_2$ + 8 mol% Y$_2$O$_3$) and the perovskites \((\text{La}_{0.6}\text{Ca}_{0.4})_{x}\text{Fe}_{0.8}\text{M}_{0.2}\text{O}_3\) (\(x=1, 0.9; M = \text{Cr}, \text{Mn}, \text{Co}, \text{Ni}\)) were carried out. The results obtained are discussed.

1. INTRODUCTION

The following three temperature regions are designated by Steele (1) for the operation of Solid Oxide Fuel Cells (SOFCs) by considering the materials properties: above 900 °C using zirconia based electrolytes with a thickness of about 150 µm, 700 to 900 °C by employing thin layers of zirconia based electrolytes supported by a thick electrode, and 500 to 700 °C by selecting ceria based electrolytes. Lower temperatures than 700 °C are possible on principle with zirconia based electrolytes depending on the extent of the practicable reduction of the layer thickness. The cathode material in these SOFCs has to meet the following requirements: high electrical conductivity, thermal and chemical compatibility, compatibility with the electrolyte, and high catalytic activity for the oxygen reduction. The perovskite oxides \(\text{La}_{1-x}\text{A}_x\text{MO}_3\) (\(A = \text{Sr}, \text{Ca}; M = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}\)) have been extensively studied for applications above 900 °C since they show good electrical conductivity (2-5). Yokokawa et al. (6,7) elucidated the chemical interactions of many of these perovskites with the zirconia based electrolyte. The compositions \(\text{La}_{1-x}\text{Sr}_x\text{MnO}_3\) are most widely used due to their good chemical and thermal compatibility with yttria stabilized zirconia (YSZ) and their high catalytic activity for the oxygen reduction (4,5,8). Syskakis et al. (9) studied the reactions between YSZ and \(\text{La}_{y-x}\text{Sr}_x\text{MnO}_3\) as well as \(\text{La}_{0.79}\text{Sr}_{0.16}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_3\).
Commercialization of SOFCs requires lowering of the operating temperatures below 900 °C. Possible materials for the development of cathodes for the use at these temperatures are Sr substituted lanthanum ferrites $\text{La}_{1-x}\text{Sr}_{x}\text{FeO}_3$ (10,11). Good electrical properties are reported at temperatures between 600 and 800 °C for $\text{La}_{1-x}\text{Sr}_{x}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$, $x=0.2-0.4$ (Ref. 11). The stability and compatibility of the selected materials under operating conditions is a necessary prerequisite in order to guarantee long term operation of an SOFC. Reactions at the interface cathode/electrolyte may lead to new phases with low electric conductivity thereby decreasing the efficiency of a SOFC for electric energy production. The results of our systematic investigations in establishing the trend of reactivities of the solid electrolyte YSZ ($\text{ZrO}_2+8$ mol% $\text{Y}_2\text{O}_3$) with the perovskites $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{M}_{0.2}\text{O}_3$ and ($\text{La}_{0.6}\text{Sr}_{0.4}$)$_{0.9}$Fe$_{0.8}$M$_{0.2}$O$_3$ ($M = \text{Cr, Mn, Co, Ni}$) are given in Refs 12,13. We here report on the continuation of these investigations by studying the reactivities of the compositions $\text{La}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.8}\text{M}_{0.2}\text{O}_3$ and ($\text{La}_{0.6}\text{Ca}_{0.4}$)$_{0.9}$Fe$_{0.8}$M$_{0.2}$O$_3$ ($M = \text{Cr, Mn, Co, Ni}$) with YSZ ($\text{ZrO}_2+8$ mol% $\text{Y}_2\text{O}_3$). These compositions are obtained by substituting Ca for Sr. The high concentration of alkaline earth metals ($x = 0.4$) is advantageous concerning the electrical properties of the perovskites.

2. EXPERIMENTAL

Perovskite powders of the compositions ($\text{La}_{0.6}\text{Ca}_{0.4}$)$_x$Fe$_{0.8}$M$_{0.2}$O$_3$ ($x = 1, 0.9$; $M = \text{Cr, Mn, Co, Ni}$) were prepared by using drip pyrolysis at Haldor Topsoe A/S, Lyngby, Denmark. Some of the as received powders were not completely monophasic (cf. Section 3). All powders were, therefore, calcined at 900 °C for 173 ks in order to dissolve in the perovskite lattice small amounts of additional phases. The result of this treatment was checked by XRD analysis. Homogeneous mixtures were then prepared by grinding equimolar amounts of the perovskites and YSZ in an agate mortar by the use of an ethanol suspension. SEM analysis revealed the homogeneity of the mixture and a particle size of typically 1 to 3 μm. Cylindrical pellets, diameter 5 mm, height 1 mm, obtained by pressing the powder mixtures, were annealed in the furnace at different temperatures and over different periods to obtain information on possible reactions and their kinetics. Phase analysis was carried out by SEM/EDX and XRD with Co$K_{\alpha1}$ radiation.

3. RESULTS

XRD analysis revealed that most of the eight as received samples were single-phase materials. The samples $\text{La}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ and ($\text{La}_{0.6}\text{Ca}_{0.4}$)$_{0.9}$Fe$_{0.8}$Ni$_{0.2}$O$_3$ contained additionally small amounts of NiO and NiFeO$_4$. Small amounts of Fe$_2$O$_3$ were detected as second phase in the sample ($\text{La}_{0.6}\text{Ca}_{0.4}$)$_{0.9}$Fe$_{0.8}$Co$_{0.2}$O$_3$. The calcination carried out in our laboratory (cf. Section 2) improved the phase homogeneity and the crystallization. However, the additional phases were still detectable. Figure 1 shows as an example the XRD patterns for the sample ($\text{La}_{0.6}\text{Ca}_{0.4}$)$_{0.9}$Fe$_{0.8}$Ni$_{0.2}$O$_3$ before and after the additional calcination.
The pellets of the powder mixtures (Section 2) were annealed in air at a temperature of 1000 °C. Short-term (170 - 250 ks) and long-term (4680 ks) annealing experiments were carried out. XRD analysis showed that new phases are formed in the pellets by the annealing caused by chemical reactions between the perovskite powders and the YSZ. CaZrO₃ was the main reaction product for the stoichiometric and substoichiometric samples with M = Co, Ni. A main reaction product was also formed by the corresponding samples with M = Cr, Mn. The clear assignment of the XRD peaks of this product to a known phase is difficult. A comparison of the XRD pattern of the unknown phase with those in the literature indicates the formation of a hydroxide phase (see Section 4). Figures 2 and 3 show as an example the XRD patterns for three perovskite/YSZ powder mixtures containing the peaks for CaZrO₃ and the peaks which cannot be assigned. Small amounts of NiO and NiFe₂O₄ are additionally present in the (La₀.₆Ca₀.₄)₀.₈Fe₀.₈Ni₀.₂O₃/YSZ mixtures (cf. Figure 2). These phases were also detected in La₀.₆Ca₀.₄Fe₀.₈Ni₀.₂O₃/YSZ mixtures. The XRD patterns of the (La₀.₆Ca₀.₄)₀.₈Co₀.₂O₃/YSZ mixtures (x = 1, 0.9) showed small amounts of CoFe₂O₄ in addition to CaZrO₃. The peaks of the perovskite (La₀.₆Ca₀.₄)₀.₈Fe₀.₈Ni₀.₂O₃ are shifted to lower angles with increasing annealing time. The lines of the perovskite merge with those of CaZrO₃ for an annealing time of 4680 ks. Similar shifting of the perovskite lines was observed for the La₀.₆Ca₀.₄Fe₀.₈Ni₀.₂O₃/YSZ and (La₀.₆Ca₀.₄)₀.₈Co₀.₂O₃/YSZ mixtures (x = 1, 0.9). The samples (La₀.₆Ca₀.₄)₀.₈Fe₀.₈M₀.₂O₃ (x = 1, 0.9; M = Cr, Mn) were additionally annealed at 1000 °C over 900 ks in order to check whether the unknown peaks mentioned above (cf. Fig. 4) are formed by the reaction with YSZ. No decomposition of the sample material was observed as exemplified by the XRD pattern of La₀.₆Ca₀.₄Fe₀.₈Ni₀.₂O₃ obtained after the annealing.

The amount of the CaZrO₃ phase formed in the annealed pellets was estimated from the XRD patterns of different YSZ/CaZrO₃ powder mixtures. The CaZrO₃ in these mixtures was supplied by CERAC Inc., Milwaukee, USA. The area of the main peak in the XRD pattern of the YSZ as well as the area of the three peaks at the position \( d \sim 2.86 \, \text{Å} \) of the CaZrO₃ were determined and the ratio of these areas used for the evaluation. Figure 5 shows the calibration curve for the determination of the CaZrO₃ phase. The peak at the position \( d \sim 2.86 \, \text{Å} \) for M = Cr and Mn was also selected for the estimation of the relative amount of the unknown phase formed by the reaction with YSZ.

Small pieces of each pellet were taken out of the furnace after different time periods in order to analyze the progress of the reactions by XRD during the short-term experiment. Figures 6 and 7 show the time dependent formation of the CaZrO₃ phase and the unknown phase. The amount of these phases is given as a function of \( t^{0.5} \) in order to indicate a diffusion controlled reaction kinetics. Samples A in Figure 6 and all samples in Figure 7 were prepared as described in Section 2. Samples B (Figure 6) resulted by crushing and mixing of samples A in an agate mortar after 180 ks of annealing at 1000°C. The mixing was carried out to speed up the equilibration process.

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The Co and Ni containing samples of the long-term experiments were additionally investigated by SEM/EDX. Ca depleted regions with perovskite composition as well as areas with high Ca and Zr content (CaZrO₃ phase) were detected. The regions with perovskite compositions contained up to 14 at% Zr. Moreover, grains of YSZ composition were detected. The Ca content in this phase amounted to about 10 at%.

4. DISCUSSION

Figures 6 and 7 show the progress of the reactions for the formation of the CaZrO₃ phase and the unknown phase. The figures indicate a high chemical reactivity between the perovskites considered in this work and the YSZ. The reactivity for (La₀.₆Ca₀.₄)₄Fe₀.₈M₀.₂O₃ (y = 1, 0.9; M = Co, Ni) is the highest as it can be derived from the steep rise of the corresponding curves. The first XRD peaks indicating the detection of the CaZrO₃ phase were already detectable after 300 s of annealing. In contrast to this no CaZrO₃ phase was found in the (La₀.₆Ca₀.₄)₄Fe₀.₈M₀.₂O₃/YSZ mixtures with x = 1, 0.9 and M = Cr, Mn. Figures 6 and 7 show a retarded formation of the unknown reaction phase in these mixtures. First XRD lines were observed after 40 ks (Figure 6) and 600 ks (Figure 7). The unknown phase might be a metal hydroxide according to Section 3. The determination of a metal hydroxide can be explained by the formation of a hygroscopic metal oxide as primary reaction product. The hydroxide determined is formed by the reaction of the primary oxide with the moisture in the air and in the vaseline used in the preparation of the sample powder for the XRD analysis.

The S-shape behaviour of the curves in Figures 6 and 7 can be explained by the formation of the nuclei for the new phases and the fast growing of these nuclei at their initial stage. After short time the inflection point is reached and the growth curve approaches to a straight line indicating the diffusion controlled linear region in these solid state reactions.

The different reactivities and reaction products mentioned above (cf. Figures 6, 7) can be explained on the basis of the stability of the tetravalent state of the B site metals in the perovskite phases and by the introduction of the following notation for the perovskites with stoichiometry and substoichiometry on A site:

\[
(La_{a+6}Ca_{a-6})(Fe,M)^{IV}_{a+26} (Fe,M)^{III}_{a-26} O_{3-\delta}V_{\delta} \quad \text{and} \quad [1]
\]

\[
(La_{a+6}Ca_{a-6})_{1-\delta} (Fe,M)^{III}_{a+26-2.5\delta+26} (Fe,M)^{IV}_{a-26+2.5\delta-26} O_{3-3-\delta} \left( \delta + \varepsilon \right) V_{\delta} \quad \text{[2]}.
\]

This notation shows that the partial substitution of the divalent Ca for the trivalent La leads to the formation of tetravalent atoms on B sites and to some extent, \( \delta \), to the formation of oxygen vacancies. The substoichiometry, \( \delta' \), on A site increases the
formation of tetravalent atoms on B sites. In addition, the number of oxygen vacancies is raised by $\varepsilon$.

Figure 6 shows that most of the Ca in the perovskites $\text{La}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.8}\text{M}_{0.2}\text{O}_{3}$, $\text{M} = \text{Co, Ni}$, reacted forming the CaZrO$_3$ phase. The high reactivity can be explained on the basis of the above notation by the low stability of the tetravalent state of Co, Ni, and Fe leading to a destabilization of the perovskite on substituting Ca for La. This supports the reaction with the ZrO$_2$ of YSZ forming CaZrO$_3$, by which Ca leaves the perovskite lattice. Substoichiometry on A site decreases the thermodynamic activity of Ca in the perovskite thereby diminishing the driving force for the CaZrO$_3$ formation (Figure 7) compared to $\text{La}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.8}\text{M}_{0.2}\text{O}_{3}$, $\text{M} = \text{Co, Ni}$, (Figure 6). Substoichiometry, on the other hand, increases this driving force since more B site atoms have to become tetravalent in comparison to stoichiometric perovskites. The observed decrease of the reactivity by the introduction of A site substoichiometry might be explained by the preponderance of the first effect.

The reactions of the perovskites with $\text{M} = \text{Cr, Mn}$ are completely different from those with $\text{M} = \text{Co, Ni}$ explained above. Cr and Mn form stable tetravalent states as compared to Co and Ni. This favours the retention of Ca in the perovskite lattice. In addition, part of the Ca dissolves in the YSZ as shown by the SEM/EDX results (Section 3). These two aspects can explain the non-observation of the CaZrO$_3$ phase in $(\text{La}_{0.6}\text{Ca}_{0.4})_x\text{Fe}_{0.8}\text{M}_{0.2}\text{O}_{3}/\text{YSZ}$ mixtures with $x = 1, 0.9$ and $\text{M} = \text{Cr, Mn}$.

The shift of the peaks in the XRD pattern for the perovskites $(\text{La}_{0.6}\text{Ca}_{0.4})_x\text{Fe}_{0.8}\text{M}_{0.2}\text{O}_{3}$ ($x = 1, 0.9; \text{M} = \text{Co, Ni}$) to small angles (Section 3) can indicate the enhancement of the volume of the unit cell caused by the dissolution of the CaZrO$_3$ phase. This is supported by the Zr content in the perovskite phase determined after the annealing at 1000 °C by SEM/EDX. The solubility of CaZrO$_3$ in $\text{La}_{1-x}\text{Ca}_x\text{Fe}_3\text{O}_9$ is reported in Ref. 14.

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Fig. 1: XRD patterns of La_{0.6}Ca_{0.4}Fe_{0.8}Ni_{0.2}O_3 as received (a) and after calcination over 173 ks at 900°C (b)
Fig. 2: XRD patterns of La$_{0.6}$Ca$_{0.4}$Fe$_{0.8}$Ni$_{0.2}$O$_3$/YSZ mixtures after annealing at 1000°C over 300 s (a), 3.6 ks (b), 28.8 ks (c) and 4680 ks (d)
Fig. 3: XRD patterns of (La$_{0.6}$Ca$_{0.4}$)$_3$Fe$_{0.8}$Mn$_{0.2}$O$_3$/YSZ mixtures with $x = 1$ (a) and $x = 0.9$ (b) after annealing at 1000°C over 4680 ks

Fig. 4: XRD pattern of La$_{0.6}$Ca$_{0.4}$Fe$_{0.8}$Ni$_{0.2}$O$_3$/YSZ after calcination at 1000°C over 900 ks
Fig. 5: Ratio of areas of the main XRD peaks of CaZrO$_3$ and YSZ, $A(\text{CaZrO}_3)/A(\text{YSZ})$, for different compositions of the CaZrO$_3$/YSZ powder mixtures.

Fig. 6: Amount of the CaZrO$_3$ and not identified phases in La$_{0.6}$Ca$_{0.4}$Fe$_{1.2}$M$_{0.8}$O$_3$/YSZ mixtures, $M = \text{Cr, Mn, Co, Ni}$, after different annealing times at 1000°C (mol% denotes molar fraction of CaZrO$_3$ with reference to 1 mol of YSZ at $t = 0$).
Fig. 7: Amount of the CaZrO₃ and not identified phases in \((\text{La}_{0.6}\text{Ca}_{0.4})_0.9\text{Fe}_{0.8}\text{M}_{0.2}\text{O}_3/\text{YSZ}\) mixtures, \(\text{M} = \text{Cr, Mn, Co, Ni}\), after different annealing times at 1000°C (mol% denotes molar fraction of CaZrO₃ with reference to 1 mol of YSZ at \(t = 0\)).