Catalytic Properties of the Perovskite Oxide $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ in Relation to Its Potential as a Solid Oxide Fuel Cell Anode Material

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Natural gas is an extremely attractive fuel for use in fuel cells. Steam-reforming and oxidation of methane are particularly important for the direct methane fuel cell. A perovskite-related material, $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ (LSCrF), has been synthesized, and its catalytic properties as a potential anode material for solid oxide fuel cells (SOFCs) have been examined. The material exhibits an overall orthorhombic structure with $a = 5.4926(5)$ Å, $b = 5.5339(4)$ Å, $c = 7.7646(8)$ Å, and $V = 236.01(5)$ Å^3 according to the X-ray data. It is at its limit of stability under reducing SOFC anode conditions. An 11% conversion for methane steam-reforming was observed at 900 °C when the steam-to-methane ratio was 1/1. A conversion of 68% for methane oxidation with a CO_2 selectivity of 99% was achieved at 900 °C when an equimolar mixture of CH_4 and O_2 was introduced into the reactor. The partial or complete oxidation depends on both temperature and the pO_2/pCH_4 ratio. Therefore, LSCrF is a good catalyst for methane-reforming and oxidation. LSCrF is a methane complete oxidation catalyst when close to oxygen stoichiometric and a methane partial oxidation catalyst when the oxygen vacancy content increases. The anode polarization resistances in wet 5% H_2/Ar and wet H_2 are about 1.79 and 1.15 Ω cm^2, respectively, at 850 °C. This was improved to 0.98 Ω cm^2 in wet H_2 when the operation temperature was increased to 900 °C, but this is still too high for a viable SOFC electrode system.

1. Introduction

The solid oxide fuel cell (SOFC) is highly promising as a power generation system and is an all-ceramic device operating at high temperatures. Present development of SOFCs is mainly based on the yttria-stabilized zirconia (YSZ) electrolyte due to its good thermal and chemical stability, high oxide ion conductivity, and mechanical strength at high temperature.[1] The most commonly used anode materials for zirconia-based SOFCs are Ni/YSZ cermets, which display excellent catalytic properties for fuel oxidation and good current collection; however, disadvantages such as low tolerance to sulfur[2] and carbon deposition[3] when using hydrocarbon fuels and poor redox cycling, causing volume instability, are also observed. The nickel metal in the cermet tends to agglomerate after prolonged operation, leading to a reduced three-phase-boundary length and increasing resistance. Therefore, new anode materials are in demand for fuel cells using methane as the fuel. The cracking of CH_4 is problematic due to the formation of carbon, which may block the catalytic sites and the pores for gas diffusion and result in the degradation of fuel cell performance:

$$CH_4 \rightleftarrows C + 2H_2 \quad (1)$$

One of the methods to suppress carbon deposition is in situ internal reforming of methane by steam or CO_2 yielded at the SOFC anode side:[4]

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \quad (2)$$

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 \quad (3)$$

Carbon deposition may be basically avoided if methane can be directly oxidized by the oxygen transporting from the cathode side under load.[5] The partial oxidation of methane may yield CO and H_2 by reaction 4, which could be used as the fuel. Complete oxidation of methane under the SOFC conditions to produce CO_2 and H_2O (reaction 5) would be ideal although it is usually difficult to realize.

$$2CH_4 + O_2 \rightleftarrows 2CO + 4H_2 \quad (4)$$

$$CH_4 + 2O_2 \rightleftarrows CO_2 + 2H_2O \quad (5)$$

The requirements for the new SOFC anode materials are good chemical and mechanical stability under SOFC operating conditions, high ionic (O^{2-}/H^+) and electronic conductivity over a wide range of pO_2 values, good chemical and thermal compatibility with electrolyte and

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interconnect materials, and significant catalytic effects for methane-reforming and oxidation under SOFC anode conditions. Materials with different structures, viz., perovskites, fluorites, pyrochlores, and tungsten bronzes, have been investigated as potential anode materials.[6−12] Among the potential anode materials, $LaCrO_3$-based perovskites have been examined as interconnect materials for SOFCs.[1] The latter are also potential anode materials for SOFC due to their relatively good stability in a reducing atmosphere at high temperatures[13,14] and good catalytic effect for methane-reforming at high temperatures.[4,15,16] The introduction of other transition elements onto the B-site in $La_{1-x}Sr_xCr_{1-y}M_yO_3$ (M = V, Cr, Mn, Fe, Co, Ni, Cu, etc.) has potential for improving the methane-reformation catalytic properties of such materials. Such improved catalytic effects were recently reported by Sfeir et al., using 10 mol % transition-element-doped lanthanum chromite.[15] To the best of our knowledge, reports concerning larger concentrations of transition-element dopants which might further favor the catalytic effects are scarce. Nevertheless, in a recent report, catalytic properties of $La_{0.2}Sr_{0.8}Cr_{0.2}Fe_{0.8}O_3$ and $La_{0.8}Sr_{0.2}Cr_{0.2}Fe_{0.8}O_3$ for CH_4-reforming were investigated.[17,18] Good catalytic effects for both compositions were observed although the stability of $La_{0.8}Sr_{0.2}Cr_{0.2}Fe_{0.8}O_3$ in a reducing atmosphere at high temperature is questionable. In our research, it was found that, in the $La_{0.75}Sr_{0.25}Cr_{1-x}Fe_xO_3$ series, phases with $x > 0.5$ are unstable in dry 5% H_2 at 900 °C. It is supposed that $La_{0.75}Sr_{0.25}Cr_{1-x}Fe_xO_3$ with $x \leq 0.5$ could be stable. In recent papers, good performance of the anode $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ with polarization resistance as low as 0.26 Ω cm^2 at 900 °C in wet H_2 has been reported.[19,20] Here the stability, catalytic properties, and electrochemical performance of $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_3$ (LSCrF) was investigated.

2. Experimental Section

Synthesis and Structure. Materials were prepared using both a conventional solid-state method and a combustion synthesis technique. For the solid-state method, dried La_2O_3, $SrCO_3$, Cr_2O_3, and Fe_2O_3 powders were ground under acetone and then fired at 1000−1400 °C with intermediate grindings. The combustion synthesis employed the corresponding metal nitrates and ethylene glycol as precursors. La_2O_3 and $SrCO_3$ were dissolved into dilute nitric acid to form nitrates, and then $Cr(NO_3)_3 \cdot 9H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were added to form a mixed nitrate solution of the required stoichiometry. Ethylene glycol was added and the solution refluxed at 80 °C for 2 h. After further concentration of the mixture at higher temperatures, a gel formed, combustion of which yielded a brown spongelike material. Firing this above 1100 °C resulted in the formation of the sought perovskite-related phase. The phase purity and crystal parameters were examined by XRD analysis of powders on a Stoe Stadi-P diffractometer. The surface area of the LSCrF particles was measured by the BET method on an IGA intelligent gravimetric analyzer using nitrogen as the test gas.

Chromatograph Setup. Catalytic activity experiments were carried out in a fixed-bed reactor using 135.4 mg of catalyst. The flow rates of reactive gases were controlled by mass flow meters. Water was added into the system by a very large syringe pump with 5.6 mm diameter. Heating tapes were wrapped around the pipe work system to avoid water condensation. The analysis of the reactor effluent was performed with an on-line HP chromatograph using a thermal conduction detector (TCD) and a fused silica CarboPlot P7 column (PLOT, 25 m × 0.53 mm). The data were analyzed using HP Chemstation software. The catalysts were introduced into the reactor without external pretreatment. After sealing, the temperature of the reactor was increased to 900 °C and held for 2 days with a helium flow rate of 20 mL/h since the steam-reforming of methane was improved by this mild reduction process. The degree of methane-reforming with steam or oxygen was then obtained from the gas chromatographic data.

Electrochemical Testing. To test the anode performance, a three-electrode configuration was employed, the LSCrF anode on one side, with platinum counter and reference electrodes on the other. The electrolyte used was 8 mol % YSZ (2 mm thickness and 20 mm diameter). Details of the three-electrode arrangement are described elsewhere.[12] The anode with a thickness of about 50 μm was deposited onto the YSZ electrolyte using an ethanol-based slurry and fired between 1000 and 1300 °C. Contacts for electrical measurements on the anodes were made using gold mesh fixed with a small amount of gold paste (avoiding any extra catalytic effect that Pt connections may cause).

Ac impedance spectroscopy was carried out using a Schlumberger Solartron 1255 frequency response analyzer coupled to a 1287 electrochemical interface and controlled by Z-plot electrochemical impedance software. The impedance spectra of the electrochemical cell were recorded at open circuit voltage (OCV) with a 20 mV ac signal amplitude over the frequency range 10^5 to ∼0.01 Hz.

3. Results and Discussion

The room-temperature XRD pattern of the LSCrF powder fired at 1400 °C for 38 h is shown in Figure 1a. The structure of $La_{0.75}Sr_{0.25}CrO_3$ at room temperature is rhombohedral with space group $R\bar{3}c$(167) by neutron diffraction.[21] It is reported that $La_{0.8}Sr_{0.2}FeO_3$ exhibits an orthorhombic structure with lattice parameters $(\sqrt{2})a_p \times (\sqrt{2})a_p \times 2a_p$ (a_p is the lattice parameter of the primitive cubic perovskite, $a_p \approx 4$ Å).[22] However, the structure of perovskite oxides is very complicated and flexible, depending on the chemical composition and ionic size involved in both A- and B-sites in the perovskite lattice.[23] The structure of $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_3$ obtained by solid-state reaction at 1400 °C is ortho-

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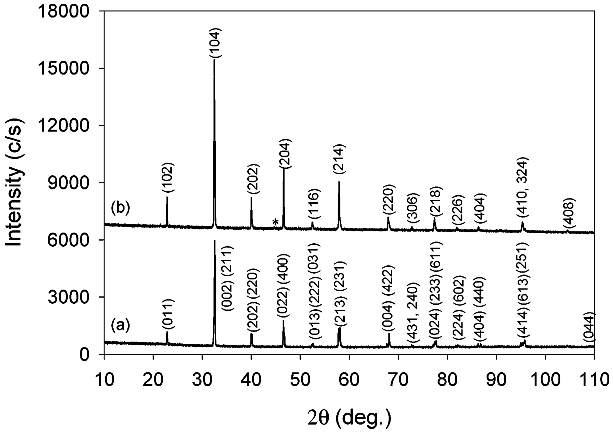

Figure 1. XRD pattern of $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_3$ obtained at 1400 °C (a) and after heating in 5% H_2 at 900 °C for 120 h (b). The asterisk indicates the (110) diffraction peak of iron (JCPDF card 6-696).

rhombic with $a = 5.4926(5)$ Å, $b = 5.5339(4)$ Å, $c = 7.7646(8)$ Å, and $V = 236.01(5)$ Å^3 according to the X-ray data (Figure 1a). To study the chemical stability of LSCrF at high temperatures in a reducing atmosphere, LSCrF powder obtained by solid-state reaction at 1400 °C was heated in 5% H_2/Ar at 900 °C for 120 h. The XRD pattern of the reduced sample is shown in Figure 1b. XRD analysis indicates that the main phase of the reduced $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ has a rhombohedral structure. A very weak peak at $2\theta \approx 44.66°$ with relative intensity 0.7% cannot be indexed, which could be the strongest (110) diffraction peak of iron (JCPDF card 6-696). The appearance of a trace amount of iron in the reduced sample indicates that LSCrF is at its stability limit under SOFC anode conditions. The reduction process might be kinetically controlled; thus, the long-term stability would be questionable. The structure of the reduced LSCrF changed to a higher symmetry, but the perovskite structure was retained. The reduced LSCrF is most probably rhombohedral ($R\bar{3}c$(167)) and may be described as a hexagonal unit cell with $a = 5.5149(10)$ Å, $c = 13.483(4)$ Å, and $V = 355.13(15)$Å^3. The thermogravimetric analysis (TGA) of $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ performed in dry 5% H_2 indicates 1.12 wt % total weight loss between 500 and 950 °C, which corresponds to 0.16 atomic oxygen. The weight loss would be 0.25 atomic oxygen if all iron were reduced from Fe^{3+} to Fe^{2+}, assuming iron exhibits +3 valence when prepared in air at 1400 °C. It is most likely that the iron oxidation state is mixed at +2.75 in 5% H_2 and that very little if any Fe metal is produced on the TGA time scale.

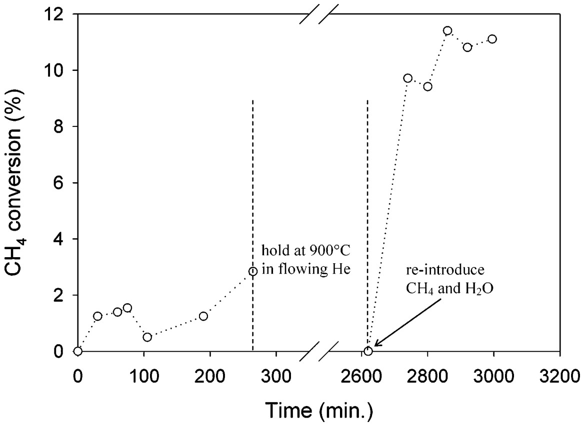

Figure 2. Methane conversion as a function of time at 900 °C with a CH_4/H_2O ratio of 1/1. The flow rates of CH_4, H_2O, and He were 12, 12, and 36 mL/h, respectively. Only 20 mL/h of He was passed during aging at 900 °C.

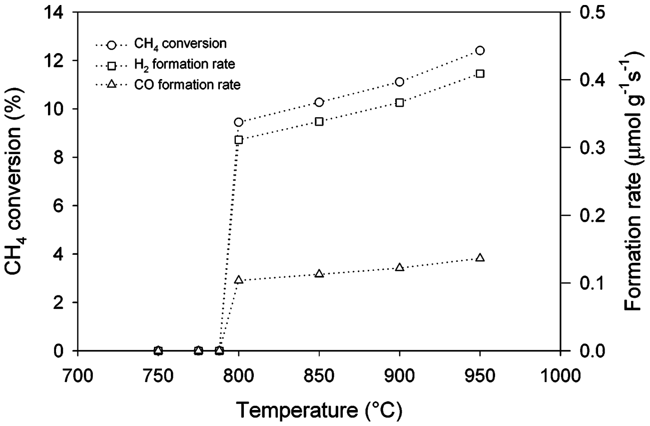

Figure 3. Methane conversion as a function of temperature. The flow rates of CH_4, H_2O, and He were 12, 12, and 36 mL/h, respectively.

The LSCrF for catalytic tests was prepared by a combustion method and fired at 1100 °C for 4 h. The specific surface area of the sample is 4.59 ± 0.14m^2/g measured by the BET method. The catalyst was fired at this high temperature because this temperature would be necessary to get a good contact between the LSCrF anode and the YSZ electrolyte in fabricating the SOFC although the specific surface area is quite small, which may affect the efficiency of the catalyst. A temperature of 1100 °C is also the minimum required to get a single perovskite LSCrF phase. The catalytic effectiveness of LSCrF for steam-reforming of methane was tested at different temperatures. The initial test indicates that less than 2% of the methane was converted at a temperature as high as 900 °C when the molar ratio of CH_4/H_2O was 1/1. As shown in Figure 2, after holding at 900 °C for 4 h, the methane conversion was only 2.84%. It seems that there is an activation process for the catalytic process. The LSCrF powders were left in the reactor at 900 °C flowing with only 20 mL/h of helium for 39 h. After the test was restarted with the same gas composition, the methane conversion was stable over 5 h, with a conversion of about 11%. The increased activity of the LSCrF catalyst may be related to surface modification during the aging process; possibly this is related to a slight oxygen loss. The increased catalytic activity is unlikely to be due to carbon deposition since the steam/methane ratio is 1/1, which is quite high. The oxygen partial pressure of helium is above 10^{-5} atm; thus, it is clear that metallic iron is not formed during the helium anneal. Indeed, it should be noted that although LSCrF shows a very slight tendency to evolve iron under dry 5% H_2, the oxygen partial pressure used in these reforming tests was several orders of magnitude higher. Therefore, iron exsolution should not be expected.

Figure 3 shows the methane conversion as a function of temperature when the CH_4/H_2O ratio was fixed at 1/1. It is found that, below 800 °C, the reaction for steam-reforming of methane does not happen but be-

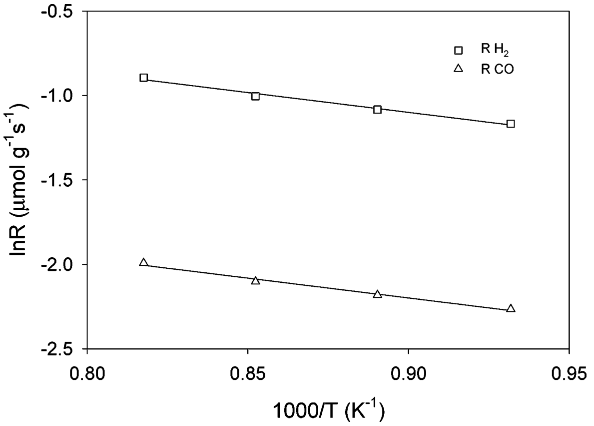

Figure 4. Arrhenius plots of ln R_{H2} (□) and ln R_{CO} (Δ) vs 1000/*T* for steam-reforming of methane with equimolar methane and steam.

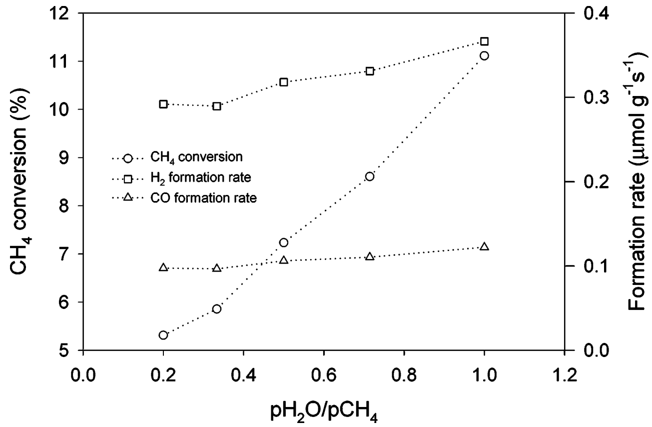

Figure 5. Methane conversion as a function of the pH$_2$O/pCH$_4$ ratio at 900 °C. The total flow rates of CH$_4$ and H$_2$O were fixed at 24 mL/h. The flow rate of He was 36 mL/h.

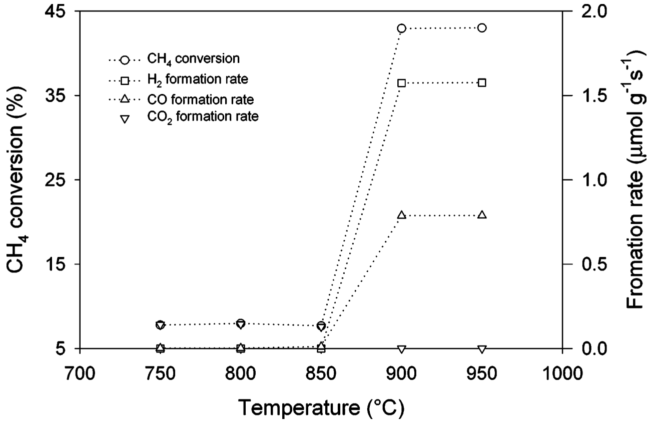

Figure 6. Methane conversion as a function of temperature. The flow rates of CH$_4$, O$_2$, and He were 20, 4, and 36 mL/h, respectively.

comes significant when the temperature approaches 800 °C. This process is reversible when the temperature is adjusted between 788 and 800 °C. Above 800 °C, the methane conversion increased with the enhancement of temperature and reached 12.4% at 950 °C. The formation rates of H$_2$ and CO reach 0.41 and 0.14 μmol g^{-1} s^{-1}, respectively, at 950 °C. The relatively low formation rate may be due to the low surface area of the catalyst which was prefired at 1100 °C. Figure 4 shows the Arrhenius plots of the H$_2$ and CO formation rate against 1000/*T*. A linear relationship was observed which gives an apparent activation energy of 19.53 kJ/mol. To investigate the methane conversion as a function of the steam-to-methane ratio, the methane conversion with different pH$_2$O/pCH$_4$ ratios at 900 °C was investigated (Figure 5). The flow rate of the carrier helium was 36 mL/h, and the total flow rate of steam and methane was fixed at 24 mL/h. The methane conversion linearly increased with the pH$_2$O/pCH$_4$ ratio. Clearly the more steam, the easier the reforming according to reaction 2. The reaction equilibrium may move to the right when more steam is put into the system. At 900 °C, the methane conversion at a pH$_2$O/pCH$_4$ ratio of 1/5 is only half that for an equimolar steam and methane mixture. However, the formation rates of H$_2$ and CO are less sensitive to the pH$_2$O/pCH$_4$ ratio than methane conversion as shown in Figure 5. No CO$_2$ was detected during the steam-reforming experiments, indicating that LSCrF is not a good catalyst for the gas shift reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (6)$$

However, the formed carbon monoxide is a fuel for SOFCs and may be further oxidized by the oxygen transported from the cathode.

In a real anode environment of a solid oxide fuel cell, oxygen may be transported from the cathode into the anode under polarization. The reactions between methane and oxygen are very important. To study the methane conversion with temperature, the pCH$_4$/pO$_2$ ratio was fixed at 5/1. Figure 6 shows the methane conversion as a function of temperature at 900 °C when the pCH$_4$/pO$_2$ ratio is fixed at 5/1. It was found that, below 850 °C, the methane conversion is about 7.8%; however, it jumps to ~43% when the temperature reaches 900 °C, indicating LSCrF is not a good methane oxidation catalyst at a temperature below 900 °C. Similar to the steam-reforming process, this process is reversible. The theoretical equilibrium conversion of methane at a pCH$_4$/pO$_2$ ratio of 5/1 is only 40%. The extra conversion above 900 °C may come from the cracking of methane according to reaction 1, which may result in carbon deposition unless the coexisting steam in a real SOFC anode environment can remove the carbon by the following reaction:

$$C + H_2O \rightleftarrows CO + H_2 \qquad (7)$$

The yielded CO may further react with steam to form CO$_2$ and H$_2$ according to reaction 6.

Of course, both CO and H$_2$ may be used as the fuel in a fuel cell by direct reaction with O$_2$ from the anode surface or the three-phase boundary (TPB) depending on the material and porosity of the anode. However, in the real conditions of a fuel cell using methane as the fuel, the partial or complete oxidation of methane is particularly important because the high steam/methane ratio is difficult to achieve on start-up although the steam concentration may increase with the continuous operation of the fuel cell. It should be noted that, below 900 °C, a large amount of CO$_2$ but no hydrogen was detected, indicating that complete oxidation happens according to reaction 5. Only trace CO was observed below 900 °C. On the contrary, no CO$_2$ but only H$_2$ and

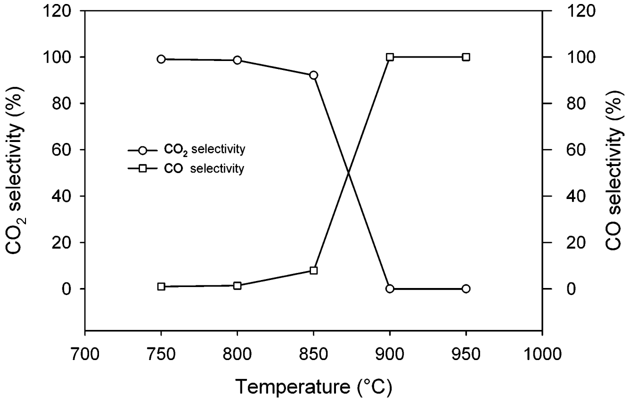

Figure 7. CO and CO_2 selectivity as a function of temperature. The flow rates of CH_4, O_2, and He were 20, 4, and 36 mL/h, respectively.

CO were detected above 900 °C, indicating partial oxidation under these conditions. The formation rate of H_2 is twice that of CO further, confirming that reaction 4 happens.

During the oxidation, besides the methane conversion efficiency, the CO and CO_2 selectivities are very important. The CO and CO_2 selectivities as a function of temperature for methane oxidation at a pCH_4/pO_2 ratio of 5/1 are shown in Figure 7. It was observed that, at a temperature below 900 °C, the main oxidation product is CO_2. The CO selectivity increased but CO_2 selectivity decreased with increasing temperature. Above 900 °C, the CO selectivity is 100%, indicating partial oxidation. Therefore, LSCrF is a complete methane oxidation catalyst below 900 °C. The complete oxidation dominates the process when the temperature is lower than 900 °C accompanying a lower methane conversion (Figure 6).

The different catalytic behaviors of LSCrF below and above 900 °C are related to its oxygen content in the lattice, which affects its surface condition. At lower temperature, the atmosphere is not reducing enough to make LSCrF lose lattice oxygen to form oxygen vacancies. Assuming some Fe^{n+} ions are in the 4+ state in LSCrF prepared in air due to charge compensation by the introduction of Sr^{2+} at the A-sites

$$\mathrm{La}_{\mathrm{La}}^{\times} + \mathrm{Fe}_{\mathrm{Cr}}^{\times} \xrightarrow{\mathrm{SrO}} \mathrm{Sr}_{\mathrm{La}}' + \mathrm{Fe}_{\mathrm{Cr}}^{\bullet} \qquad (8)$$

Under strong reducing conditions, some Fe^{4+} ions are reduced to Fe^{3+} accompanying the loss of oxygen or the formation of oxygen vacancies:

$$2\mathrm{Fe}_{\mathrm{Cr}}^{\bullet} + \mathrm{O}_{\mathrm{O}}^{\times} \Leftrightarrow 2\mathrm{Fe}_{\mathrm{Cr}}^{\times} + \mathrm{V}_{\mathrm{O}}^{\bullet\bullet} + {}^{1}/_{2}\mathrm{O}_2(\mathrm{g}) \qquad (9)$$

The formation of oxygen vacancies changes the surface condition of LSCrF; therefore, its catalytic properties change as well. From the experimental results, the near oxygen stoichiometric LSCrF is mainly a methane complete oxidation catalyst and oxygen-deficient LSCrF is a methane partial oxidation catalyst. On the other hand, the CO_2 selectivity may change with different reactant ratios. To investigate the effect of the pO_2/pCH_4 ratio on the methane conversion and product selectivity, the catalytic properties at different pO_2/pCH_4 ratios at 900 °C were investigated.

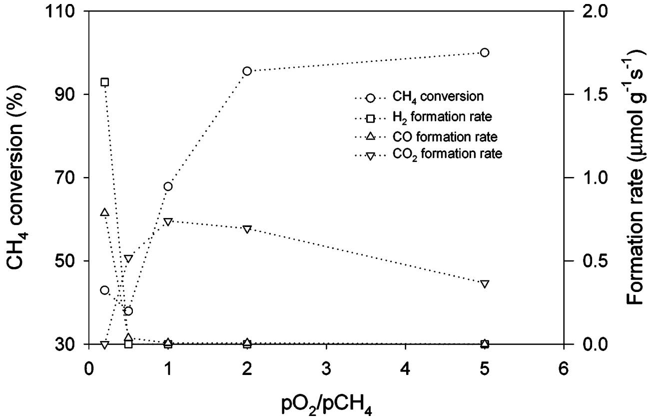

Figure 8. Methane conversion as a function of the pO_2/pCH_4 ratio at 900 °C. The total flow rates of CH_4 and O_2 were fixed at 24 mL/h. The flow rate of He was 36 mL/h.

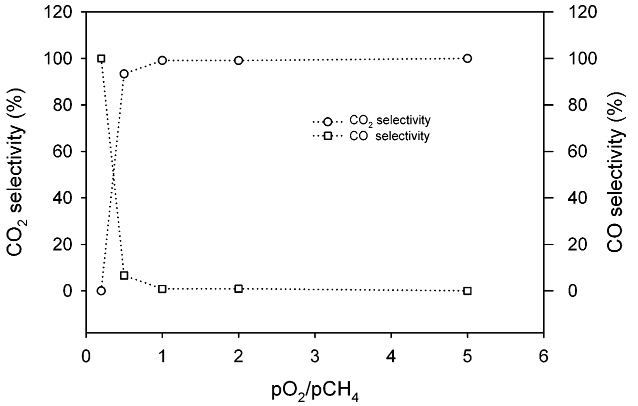

Figure 9. CO and CO_2 selectivity as a function of the pO_2/pCH_4 ratio at 900 °C. The total flow rates of CH_4 and O_2 were fixed at 24 mL/h. The flow rate of He was 36 mL/h.

As described above, the oxidation of methane may be partial or complete according to reactions 4 and 5, respectively. Partial oxidation of methane is not welcome because it may decrease the energy efficiency of methane usage and emit toxic CO. If possible, a complete oxidation of methane is ideal. The methane conversion at 900 °C as a function of the pO_2/pCH_4 ratio is shown in Figure 8. The CO and CO_2 selectivities are also shown in Figure 9. The methane conversion is increased with an enhanced pO_2/pCH_4 ratio. A methane conversion of 68% was achieved at 900 °C when equimolar CH_4 and O_2 were introduced into the reactor. The methane conversion reached 96% when the molar ratio of O_2 to CH_4 was 2/1. A CO_2 selectivity of 99% was observed when the pO_2/pCH_4 ratio was above 1, indicating complete oxidation of CH_4 under this experimental condition. To obtain complete oxidation of methane at 900 °C, the pO_2/pCH_4 ratio must be larger than 1. Therefore, the products of the oxidation process depend on both the temperature and the pO_2/pCH_4 ratio. No hydrogen and only trace amounts of CO were detected when the pO_2/pCH_4 ratio was higher than 0.5, indicating complete oxidation under the conditions. The higher the pO_2/pCH_4 ratio, the higher the pO_2 in the system. In this case, LSCrF is a methane complete oxidation catalyst, which is consistent with the catalytic behavior of LSCrF with increasing temperature at a fixed pO_2/pCH_4 ratio of 0.2 (Figure 6). These results further

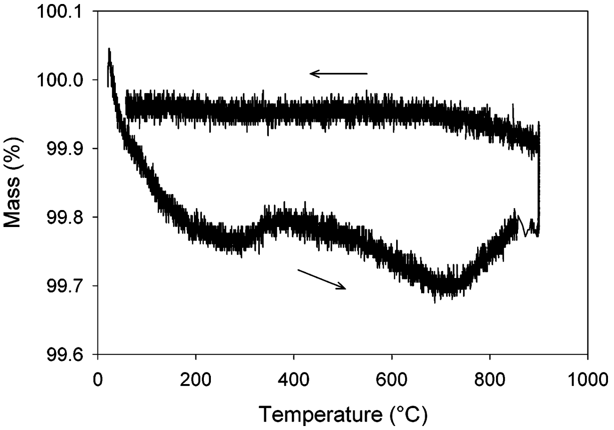

Figure 10. TGA analysis of $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ in air after the catalytic test, heating at 5 °C min^{-1} to 900 °C, holding for 2 h, and then cooling at 5 °C min^{-1}.

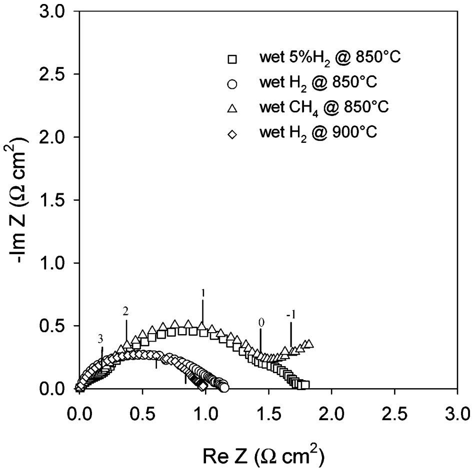

Figure 11. Anode polarization of the $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ anode in different wet atmospheres (3% H_2O). $R_p = 0.98$, 1.15, 1.79, and 1.52 (first arc) Ω cm^2 from left to right in the plot.

demonstrate that LSCrF is a methane complete oxidation catalyst at high pO_2.

The TGA analysis of the LSCrF sample in air after the catalytic test is shown in Figure 10. The initial weight loss of 0.23 wt % below 300 °C may be attributed to the desorption of the surface-adsorbed water and other gases. The slight weight gain between 300 and 370 °C is due to the reoxidation of the reduced LSCrF sample. The weight should keep increasing during the reoxidizing process until LSCrF is fully oxidized; however, instead of increasing, the weight starts decreasing above 370 °C, which may be due to the oxidation of carbon. Weight gain was observed again after carbon was removed at 710 °C. Extrapolation of the data would suggest that the contributions to the overall weight change are approximately −0.1 wt % due to carbon oxidation and +0.5 wt % due to reoxidation. This value for reoxidation is consistent with the anticipated oxygen partial pressure in the catalysis tests.

The impedance spectra of the LSCrF anode in wet 5% H_2/Ar, wet H_2, and wet CH_4 at OCV are shown in Figure 11 (three-electrode test configuration). The anode polarization resistances in wet 5% H_2/Ar and wet H_2 (~3% H_2O) are about 1.79 and 1.15 Ω cm^2, respectively, at 850 °C. It was improved to 0.98 Ω cm^2 in wet H_2 when the operation temperature increased to 900 °C. It was found that the conductivity of LSCrF is only 0.21 S/cm in 5% H_2 at 900 °C, which may cause the relatively large anode polarization resistance due to the difficulty in electron transfer at the TPB. When wet methane was used as the fuel, another arc appeared at a frequency lower than 1 Hz which may be related to methane-reforming.[4] An alternative possibility is carbon deposition, which may block the pores of the anode, and under these circumstances the impedance for methane diffusion would increase; therefore, an additional semicircle at low frequency appears.[12] A small amount of carbon was observed after the anode polarization test.

4. Conclusions

The perovskite oxide LSCrF has been synthesized and examined as an anode material for SOFCs. The catalytic properties of LSCrF for CH_4-reforming were investigated under different conditions. The perovskite-based material exhibits an overall orthorhombic structure with $a = 5.4926(5)$ Å, $b = 5.5339(4)$ Å, $c = 7.7646(8)$ Å, and $V = 236.01(5)$ Å^3 according to the X-ray data. It is at its stability limit under SOFC anode conditions. An 11% conversion for methane steam-reforming was observed at 900 °C when the steam-to-methane ratio was 1/1. A conversion of 68% for methane oxidation was achieved at 900 °C when an equimolar mixture of CH_4 and O_2 was introduced into the reactor. The methane conversion reached 96% if the molar ratio of O_2 to CH_4 was 2/1. A CO_2 selectivity of 99% was observed when the pO_2/pCH_4 ratio was above 1, indicating complete oxidation of CH_4 under the experimental conditions. LSCrF exhibits good catalytic effects in methane-reforming and oxidation. The LSCrF is a methane complete oxidation catalyst when close to oxygen stoichiometric and a methane partial oxidation catalyst when the oxygen vacancy content increases. The small degree of cracking at a temperature above 900 °C may limit its application. The anode polarization resistances in wet 5% H_2/Ar and wet H_2 are about 1.79 and 1.15 Ω cm^2, respectively, at 850 °C. It was improved to 0.98 Ω cm^2 in wet H_2 when the operation temperature was increased to 900 °C, but this is still more than the maximum 0.2 Ω cm^2 target for an electrode if the overall cell area specific resistance is to remain below 0.5 Ω cm^2. Although the reforming activity of this material seems quite good, its electrochemical performance is significantly inferior to that of the Mn analogue $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$.

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