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Catalytic activity and performance of LSM cathode materials in single chamber SOFC

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Abstract

The catalytic activity of symmetrical LSM ($La_{0.8}Sr_{0.2}MnO_3$) cells operated under single chamber solid oxide fuel cell (SC-SOFC) conditions was investigated for methane-to-oxygen ratios R_{in} between 1 and 2. The oxidation reactions over electrodes sintered at 1100 °C (LSM_{1100}) and 1200 °C (LSM_{1200}) were studied, and the effect of any combustion was followed through electrochemical impedance spectroscopy (EIS). The activity of the LSM_{1100} electrode increases with temperature. Above 700 °C, the conversion of the oxygen species may exceed 30%. As a consequence, oxygen depletion is occurring and a low frequency semicircle in the EIS spectra becomes predominant. An increase of the sintering temperature to 1200 °C leads to a decrease in the catalytic activity. A LSM_{1100} electrode deposited on a Jülich half-cell proves to reach better performance at 600 °C than at 700 °C. On such complete cells, however, the catalytic combustion becomes much more complex than on a LSM cathode alone. We are thus proposing a comprehensive parameter, R_{out}, that is summarizing the processes inside the single chamber reactor.

Keywords: Single chamber SOFC; LSM cathode; Methane conversion; Impedance; Cell performance

1. Introduction

Single chamber solid oxide fuel cells operate under a unique mixture of hydrocarbon fuel and air [1]. High power densities have been reported, in general with the use of ceramic materials normally investigated within the scope of the more conventional dual chamber SOFC [1–6]. These good performances are explained through the catalytic properties of the electrode materials against the hydrocarbon/oxygen mixture that provide for the build-up of proper pO_2 difference over anodes and cathodes, and hence for quite satisfactory open-circuit potentials. The anode must be as much as possible selective towards the partial oxidation of hydrocarbons, in this way producing the necessary amount of H_2 and CO that will be consumed by the cell once in operation. On the contrary, the cathode must be as much as possible inert towards the oxidation of hydrocarbons and only selective to the oxygen electrocatalytic reduction.

In SC-SOFC, low pO_2 over the anode component is promoted by the use of a Ni-cermet. Indeed, in heterogeneous catalysis, it is well known that high yields and selectivity to synthesis gas are obtained with metallic nickel supported on oxide materials [7–9]. Also, some conversion to CO_2 is sometimes occurring leading to significant temperature gradients in the catalytic reactor [8]. The cathode components, on the other hand, are made of perovskite materials and their use in SC-SOFC is, however, more controversial. Indeed, these materials may also serve in environmental control, for example, as catalyst for the complete combustion of methane into CO_2 and H_2O [10–13]. Under single chamber conditions, cell performance could be decreased if such reactions are proceeding at the cathode side with fast enough kinetics. This in fact has been recently recognized and often serves as an explanation for the observed low open-circuit voltage (OCV) values [5,6,14–16]. However, as for specific surface area in heterogeneous catalysis, morphological differences induced in cathode layers by original powder size, deposition method or sintering temperature, may affect their reactivity. This may explain the relatively good performance observed with LSM cathodes exposed to a mixture of CH_4/air in SC-SOFC [1,2].

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In this work, we have investigated the catalytic activity of symmetrical LSM cells under single chamber SOFC conditions. The effect of sintering the LSM layers at 1100 and 1200 °C was examined. The experiment was conducted in a range of CH_4/O_2 ratio between 1 and 2 and operating temperature between 600 and 800 °C. Changes in mean cell temperature as well as in electrode reaction processes due to any catalytic combustion of the fuel were followed by electrochemical impedance spectroscopy. A direct effect of the catalytic activity of the cathode on cell performance was shown. Finally, we defined a parameter R_{out} that takes into account the ratio of all the outlet fuels and oxygen species as a global indicator of the catalytic reaction processes inside the single chamber.

2. Experimental

Cathode symmetrical cells were prepared by conventional screen printing technique. Thick 8YSZ (500 μm) and LSM were used as electrolyte and cathode, respectively. Cathode was consisting of two layers: (i) 50 wt.% LSM/50 wt.% YSZ as the functional layer (FL) and (ii) LSM as the contact layer (CL). LSM + YSZ powder was prepared by mixing $La_{0.8}Sr_{0.2}MnO_3$ (Praxair) with YSZ powder (Tosoh). Subsequently, inks were made from these powders with adding triton (dispersant), terpineol (solvent) and PVB (binder). FL layers were printed on each face of the electrolyte, and then dried at 150 °C before applying the CL layers. The electrodes were subsequently sintered at 1100 °C (LSM_{1100}) or 1200 °C (LSM_{1200}) for 3 h. BET measurements (Quadrasorb^{TM} *SI* Surface Area and Pore Size Analyser from Quantachrome) on the sintered LSM powders gave 1.53 and 0.87 $m^2 g^{-1}$, respectively, for LSM_{1100} and LSM_{1200}. The BET surface area given by the manufacturer for the original powder is 4.0 $m^2 g^{-1}$.

The cathode surface area was 14 mm × 23 mm and the electrolyte dimension 16 mm × 25 mm according to the schematic shown in Fig. 1(a). Although slight modifications have been brought, the experimental set up for cell testing is very similar to the one described earlier [1]. The changes to the cell support led to a total volume of about 0.34 cm^3 above each electrode. The set up is schematically shown in Fig. 1(b). Before the NiO-YSZ reduction, the cell was heated to a nominal temperature of 700 °C. Reduction was performed under atmospheric pressure in an argon/methane mixture flowing over the cell. The exhausted gas was analyzed in real-time with a mass spectrometer (MS) from Pfeiffer-Balzers (Quadripole model Prisma ©). Synthetic air was used by mixing oxygen with an appropriate amount of Ar-5%He gas. Nitrogen (N_2) is replaced by Ar to avoid the overlapping in the mass unit $m/z = 28$ which is observed for the cracking patterns of N_2, CO and CO_2. The intensity of the electrical signal corresponding to the partial pressure of each component is normalized against the He one and calibrated in flow rate. The MS was operated in a multi-channel mode to analyze simultaneously CH_4, H_2, CO, CO_2, O_2 and H_2O from the outlet stream. Data collecting and processing were performed through computer. A thermocouple was placed in front of the cell at its inlet for measuring the local temperature during operation. Identical LSM_{1100} cathodes were deposited on Jülich half-cells to examine the effect of any catalytic activity on cell performance. Briefly, a Jülich half-cell is composed of a thick (∼1.5 mm) and porous anode (Ni-8YSZ cermet) manufactured by warm pressing. It is sintered between 1200 and 1250 °C. Over this substrate, a thin anode functional layer (8 μm thick Ni-8YSZ) of finer microstructure and an electrolyte layer (8 μm thick 8YSZ) are further applied by vacuum slip casting. The whole half-cell is next sintered at 1400 °C. Cell polarization and impedance measurements were investigated using a Solartron 1286 Potentiostat and a Solartron SI 1260 Impedance/Gain Phase Analyzer in a two-electrode configuration.

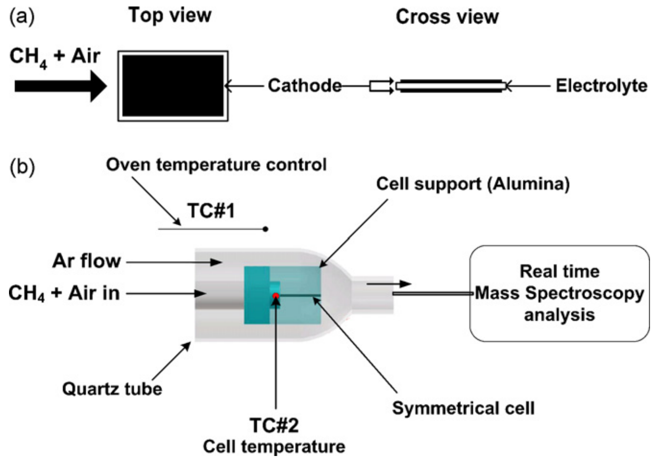

Fig. 1. Schematic drawing of: (a) the LSM symmetrical cell; (b) the experimental set up.

3. Results and discussion

3.1. Conversion of methane over LSM symmetrical cells

As mentioned before, particle size and cathode morphology are significantly affecting the catalytic activity of LSM layers. The sintering temperatures of LSM_{1100} and LSM_{1200} were chosen to further examine this effect. Fig. 2 presents the salient details obtained on each layer. One can first observe that the coalescence of the LSM particles sintered at 1200 °C leads to a noticeable growth in particle size. Furthermore, on a more macroscopic scale as shown in the inserts, an important densification of the layers occurs with only a 100 °C increase in the sintering temperature. The cathode thickness decreases from ∼75 μm at 1100 °C to ∼30 μm at 1200 °C. The above observations are consistent with the measured surface areas of the sintered powders (see Section 2) and confirm the higher specific and catalytic surface areas obtained on LSM_{1100}. As will be shown just below, LSM_{1100} will be much more active than LSM_{1200} towards CH_4 conversion.

The catalytic activity of the LSM electrodes was studied as a function of both the operating temperature between 600 and 800 °C, and the ratio (R_{in}) of methane-to-oxygen. The reason for studying this last parameter resides on our earlier studies on