

Short communication

## Performance of LSCF cathodes in cell tests

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### Abstract

SOFC development at Forschungszentrum Jülich is aiming at high power density and high durability to achieve cost reduction in manufacturing and installation. For higher power density, the work on materials development has been focused on improving the cathode performance using perovskites based on  $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$  (LSCF). Materials screening and preliminary investigations were carried out with  $5\text{ cm} \times 5\text{ cm}$  cells.

SOFCs with  $\text{La}_{0.58}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$  cathodes have successfully been developed giving reproducibly a power output of  $1.2\text{ W cm}^{-2}$  at  $800\text{ }^\circ\text{C}$  and  $0.7\text{ V}$  with hydrogen as fuel gas. Long-term cell tests lasting up to 3000 h revealed a degradation of the cells between 0.5 and 1.5%/1000 h of operation. This loss in performance is higher than for conventional cathodes based on  $(\text{La,Sr})\text{MnO}_3$  (LSM) and under further investigation to find the reason for the performance losses.

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### 1. Introduction

SOFCs with  $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  cathodes have successfully been developed giving reproducibly a power output of  $1.0\text{--}1.2\text{ W cm}^{-2}$  at  $800\text{ }^\circ\text{C}$  and  $0.7\text{ V}$  with hydrogen as fuel gas [1,2]. Compared with conventional cathodes based on  $(\text{La,Sr})\text{MnO}_3$  (LSM), the high power densities allow a reduction in operating temperature of about  $100\text{ }^\circ\text{C}$  by maintaining the performance at the former level with LSM cathodes. This has been demonstrated recently with a 60-cell stack test which was operated at  $660 \pm 50\text{ }^\circ\text{C}$  [3].

The performance of SOFCs with LSFC cathodes strongly depends on the processing and resulting microstructure of the cathode and the  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$  (CGO) interlayer [1,2] applied to inhibit the formation of  $\text{SrZrO}_3$  between LSFC and the YSZ electrolyte during sintering. However, also the basic physical properties of the  $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$  (LSCF) material [4,5], i.e. the oxygen exchange between the bulk and the surrounding atmosphere, the oxygen ion vacancy concentration and transport properties as well as the electrical conductivity play an important role. The adaptation of catalytic measurements on perovskite materials has shown that this method gives rapid qualitative information on the suitability of these materials as

catalysts for oxygen reduction [6,7]. On the basis of these results, a few  $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$  compositions were selected for single cell measurements. The initial electrochemical results on cell tests confirm the expectations from the catalytic measurements.

Besides the high power density also the durability of the LSCF cathodes has to be proven. For this purpose long-term cell tests have been carried out.

### 2. Experimental

The cathode material was synthesised by spray-drying [8]. For the electrochemical tests, anode-supported SOFCs were used consisting of an anode substrate (Ni/8YSZ) with an average thickness of about 1.5 mm. The substrates with a size of  $50 \times 50$  were produced by warm pressing. An electrochemically active anode functional layer (Ni/8YSZ) and an electrolyte (8YSZ) were both deposited by vacuum slip casting on de-bindered substrates and co-fired at  $1400\text{ }^\circ\text{C}$ . More details about the manufacturing process can be found elsewhere [9].

The subsequent layers of CGO and LSCF were screen-printed onto the electrolyte. The area of the cathode layers was  $40\text{ mm} \times 40\text{ mm}$ . The cells used for a comparison to the LSM cathode material ( $\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_{3-\delta}$ ) had a LSM/YSZ cathode functional layer and a LSM current collector. The CGO interlayer was sintered at  $1300\text{ }^\circ\text{C}$ . The cathode was then printed and sintered at  $1080\text{ }^\circ\text{C}$  on the interlayer resulting in a thickness of about  $45\text{ }\mu\text{m}$ .

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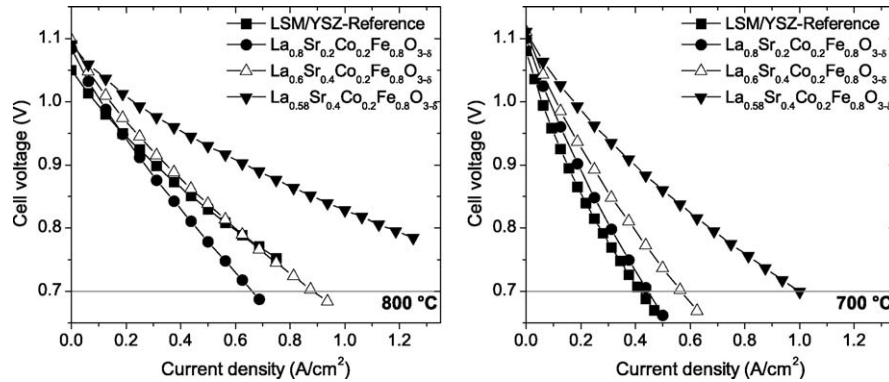


Fig. 1. Current–voltage curves at 800 and 700 °C of single cells with LSCF cathodes with different A-site compositions in comparison to cells with LSM/YSZ cathodes.

The cells with substrate dimension of 50 mm × 50 mm were used for single cell measurements as described in [10] using H<sub>2</sub>/3% H<sub>2</sub>O (1000 ml min<sup>-1</sup>) as fuel gas. The durability tests were performed at 750 °C with a constant current density of 0.5 A cm<sup>-2</sup>.

### 3. Results and discussion

#### 3.1. Performance of LSCF in comparison to LSM

The electrochemical performance of different LSCF-based cathodes in comparison to the state-of-the-art LSM cathodes can be seen in Fig. 1.

Comparing the two materials without A-site deficiency (La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> and La<sub>0.8</sub>Sr<sub>0.2</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub>) the performance was better with higher Sr content. A higher amount of Sr<sup>2+</sup> ions instead of the trivalent lanthanum on the A-site is known to increase the ionic and electronic conductivity and the surface exchange of oxygen, which can be explained by the larger number of oxygen vacancies and electronic holes [11,12]. However, the thermal expansion coefficient also increases with higher Sr content [11], which can cause mechanical problems.

The influence of a slight A-site deficiency on the electrochemical properties is seen in the *I*-*V*-curves of the cells with La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> and La<sub>0.58</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> cathodes. The performance is significantly higher for the substoichiometric than for the stoichiometric material. The main reason for this might be that the oxygen defect concentration is higher for the substoichiometric than for the stoichiometric powder [13]. It is also known, that the A-site deficiency influences the sintering activity and the stability with regard to Sr depletion. While the sintering temperature was adopted to the different sintering activity to give a similar microstructure as described in [2], the cell performance with La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> also decreased due to a partial spallation of the cathode during the measurement, which is thought to result from higher mechanical stresses due to the higher sintering temperature of 1200 °C. Of the compositions investigated, the cells with a La<sub>0.58</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> cathode achieved the highest current densities of 1.76 A cm<sup>-2</sup>, at 800 °C and 0.7 V.

In comparison to the performance of a state-of-the-art LSM/YSZ composite cathode, which is used as the standard material for stack tests at Forschungszentrum Jülich, the current densities at 800 °C of the cells with the La<sub>0.58</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> cathode are nearly two times higher than for the LSM/YSZ cathode. Comparing the two diagrams in Fig. 1 and focussing on the temperature dependence, the higher electro-catalytic activity of the LSCF compositions becomes evident in comparison to LSM. The difference in performance between the various LSCF compositions is nearly the same for 800 and 700 °C, while the performance of the LSM/YSZ cells has a stronger temperature dependence, resulting in a stronger increase of overpotential with decreasing temperature. Thus, the electrochemical benefits of the La<sub>0.58</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> cathode are even more pronounced at temperatures of 700 °C and below.

#### 3.2. Endurance tests

Endurance tests regarding the long-term electrochemical behaviour of two SOFCs with LSCF cathodes were carried out for a period of 5200 and 2000 h, respectively (Fig. 2). Both single cells were tested at 750 °C under a constant load of 0.5 A cm<sup>-2</sup>.

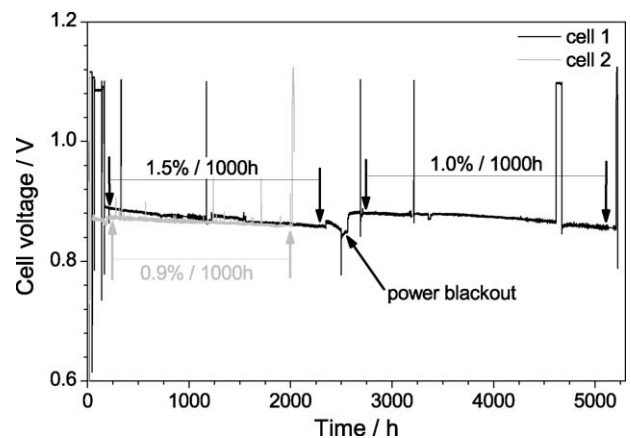


Fig. 2. Long-term behaviour of two LSFC-based cells (at 750 °C and a load of 0.5 A cm<sup>-2</sup>). The LSCF powder of cell 1 was delivered by ECN (The Netherlands) the LSCF powder of cell 2 was spray-dried as FZJ.

For the first cell, an average degradation rate of about 1.5% per 1000 h was measured in the first 2200 h, which decreased to 1.0% for the last 2600 h. For the second cell, the degradation was about 0.9% per 1000 h. These values are rather high degradation rates for single cell measurements. However, these measurements show that operation times targeted for mobile applications (about 5000 h) are already feasible with these cathode materials. Possible reasons for the degradation include further SrZrO<sub>3</sub> formation at the interface of YSZ and CGO, coarsening of the cathodes' microstructure due to sintering effects and a degradation of the 8YSZ electrolyte. Further work is in progress to determine the reasons for the loss in performance.

#### 4. Conclusions

The applicability of mixed ionic-electronic conductive (La,Sr)(Co,Fe)O<sub>3</sub> perovskites as SOFC cathodes was compared with state-of-the-art LSM/YSZ cathodes. Although there are problems with regard to chemical stability and thermal expansion, some of the materials proved to be superior in electrochemical performance.

The performance especially for cathodes made of La<sub>0.58</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> was significantly higher than that of conventional LSM/YSZ cathodes. It was shown that the A-site deficiency plays an important role for the performance of the material. SOFCs with La<sub>0.58</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> cathodes showed high power densities, in particular at low temperatures (at 0.7 V: 1.23 W cm<sup>-2</sup> at 800 °C, 1.0 W cm<sup>-2</sup> at 750 °C and 0.7 W cm<sup>-2</sup> at 700 °C). This is about twice the power density of the reference LSM/YSZ cells.

The loss in performance during operation is approximately 1% per 1000 h. Further investigations are in progress to find the reasons for the performance losses of these single cells.

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