ABSTRACT

Optimisation of processing \((L_{a_{1-x}S_{x}})_{y}MnO_{3+\delta}\) composite cathodes has led to high-performance solid oxide fuel cells (SOFCs). Symmetric cells were prepared with \((L_{a_{1-x}S_{x}})_{y}MnO_{3+\delta}\) composite cathode on yttria-stabilised zirconia tapes. A homogeneous microstructure with submicron pores was obtained that has resulted in a low area-specific polarisation resistance of 0.09 \(\Omega\) cm\(^2\) at 850°C and 0.31 \(\Omega\) cm\(^2\) at 750°C, while area-specific series resistances are 0.29 \(\Omega\) cm\(^2\) and 0.61 \(\Omega\) cm\(^2\), respectively, in a symmetric cell with a yttria-stabilised zirconia tape 185 \(\mu\)m thick. The low area-specific polarisation and series resistances are attributed to a long triple-phase boundary and very good adhesion between cathode and electrolyte. By impedance measurements the activation energy of the cathode was determined to be 1.26 eV. Anode-supported cells with an active area of 4x4 cm\(^2\) show high power density of 1.44 W/cm\(^2\) at 850°C and 0.8 W/cm\(^2\) at 750°C at a cell voltage of 0.7 V.

INTRODUCTION

Reducing operating temperature from 1000°C to 850°C in SOFC systems will enable a significant cost reduction and improve long-term stability (1). This makes it possible to use cheap ferritic steels (2) instead of ceramics or chromium alloys for interconnects. The reliability and lifetime of a cell will be significantly improved by fewer problems associated with high temperature, such as fast electrode aging, interfacial diffusion between electrolyte and electrode (3), and interconnect corrosion. Moreover, the auxiliary components of a system can be produced less expensively and will be more reliable in a lower operating temperature environment. A reduction in operating temperature may be realised if electrolyte materials are found that possess higher oxide ion conductivity (4,5,6) than yttria-stabilised zirconia (YSZ). However, current SOFC systems in prototype demonstrations and precommercial projects are based on YSZ electrolyte (7-10) due to its adequate oxide ion conductivity and excellent mechanical stability (11). Accordingly, \((L_{a_{1-x}S_{x}})_{y}MnO_{3+\delta}\) (LSM) or LSM/YSZ composite are used as cathode material. In general, anode-supported cells (1,7,10) have much higher power densities than electrolyte- (9) and cathode-supported cells in a tubular design (8). A typical anode-supported cell consists of Ni+YSZ cerments as anode, YSZ as electrolyte, and LSM as cathode. Detailed analyses of the performance in a single anode-supported cell showed...
that cathode loss dominated total cell loss at 600–850°C (12). So enhancement of cell performance at 850°C and further reduction of the operating temperature to 600–800°C can be achieved primarily by improving cathode performance.

A maximum power density of close to 2 W/cm² at 800°C in the cells based on thick pellet anode was reported in a cell configuration of Ni+YSZ/YSZ/LSM+YSZ as anode/electrolyte/cathode (13,14). Such performances were obtained in the cells with relatively small area resulting in an uncertainty on the values of the power density due to edge effects. Many studies have demonstrated that a composite cathode with desirable microstructure is the key to obtaining good electric and chemical performance of the cathode (15–17). Area-specific polarisation resistances ($R_p$) as low as 0.07 $\Omega$cm² at 850°C have been achieved using functionally graded cathodes (18,19). Further studies of the impedance measurements on the graded cathodes illustrated that not only $R_p$, but also the area-specific series resistance ($R_s$) have to be considered in great detail (20). In this work, symmetric cells with LSM+YSZ composite cathode were investigated and optimised, and this has led to high-performance anode-supported cells. The relationship between the microstructure and properties was analysed in detail.

**EXPERIMENTAL**

Symmetric cells were produced by spraying two identical LSM+YSZ cathodes on each side of an approximately 190-μm-thick YSZ foil and followed by sintering (17). The cathodes were characterised by impedance spectroscopy using a Solartron 1260 impedance analyser in a frequency range of 0.1 Hz–2.5 MHz (17,20). The $R_p$ and $R_s$ were extracted from the spectra using EQUIVCRT (21). The microstructures of the symmetric and full cells were investigated using a low-vacuum scanning electron microscope (Jeol LV5310). Anode-supported cells were produced by tape casting the anode support and spraying the NiO-YSZ active anode and YSZ electrolyte layer, followed by co-sintering. Then the cathode was sprayed and sintered (1,22). The cells with an active electrode area of 4×4 cm² were tested in a setup designed at Risø (12). The cells were tested using humidified hydrogen with 5% water as fuel and air as oxidant. Current loads up to 40 A were recorded to obtain power densities. The cell tests were performed in the temperature range from 850°C to 650°C.

**RESULTS AND DISCUSSION**

Figure 1 shows typical impedance spectra measured at 650°C to 950°C for a symmetric cathode cell. A series of $R_p$ and $R_s$ was extracted from the curves according to the indication shown in the spectrum C obtained at 650°C. When samples were measured at high temperature, a typical high-frequency inductance was observed, as shown in Figure 1A, 1B, and 1D. The induction tails were more pronounced at the higher temperature and can be corrected with an inductance of around 5×10⁻⁸H, ascribed to the instrumentation and leads. The $R_s$ can be simply defined as the following:

$$R_s = R_e + 2\Delta R$$

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Figure 1. Impedance spectra of a symmetric cell with LSM composite cathode obtained in air and OCV condition for different temperatures. Area of the cell is approximately 0.38x0.38 cm².

Here, $R_e$ is the ideal area specific electrolyte resistance and the $\Delta R$ is the resistive contribution from the cathode/electrolyte interface. $R_e$ changes according to the temperature and is dependent on the composition of the electrolyte and other factors such as aging (23). In general $R_e$ should be independent of processing. In contrast, $\Delta R$ is determined by the effective contact area at the electrode/electrolyte interface. It is strongly dependent on microstructure. This definition is similar to the calculation using effective area $A_{eff}$ as used by others (24,25). In symmetric cells, it is easier to separate the ideal electrolyte resistance and the interfacial resistance due to the two interfaces involved. We can calculate $R_e$ following the formula:

$$R_e = \frac{L}{\sigma} \tag{2}$$

Here, $L$ is the thickness of YSZ tapes and $\sigma$ is the conductivity of YSZ electrolyte. In our experiment, we used $\sigma = 8\times10^{-2}$ S/cm at 850°C and 3.4$\times10^{-2}$ S/cm at 750°C for YSZ (23). (The conductivity is given as $\sigma T = 1.51\times10^6 \exp(-0.94 \text{ eV/kT}) \text{ S cm}^{-1}\text{K}$, where $k = 8.6112\times10^{-5}$ eV/K). There are much lower conductivities ($\sigma = 2.5\times10^{-2}$ S/cm at 800 °C) reported in the reference (26) compared with the data used here. In our laboratory we used the $\sigma$ data extracted from the YSZ pellets (23), where same type of YSZ powder was used for producing both the YSZ pellets (23) and the YSZ tapes used in this work. The cathode performance is summarised in Table 1. An $R_p$ as low as 0.06 $\Omega\text{cm}^2$ at 850°C and 0.24 $\Omega\text{cm}^2$ at 750°C has been obtained for sample S1, shown in Table 1. The
corresponding $R_s$ values are 0.33 $\Omega \text{cm}^2$ at 850°C and 0.7 $\Omega \text{cm}^2$ at 750°C. The $\Delta R$ from the cathode/electrolyte interface calculated, according to formulas [1] and [2], were 0.045 and 0.075 $\Omega \text{cm}^2$ at 850°C and 750°C, respectively. The $\Delta R$ in percentage of $R_s$, $\Delta R(\%)$ is 16% at 850°C and 12% at 750°C for sample S1. This indicates that the loss in terms of $R_s$ is dominated by the electrolyte loss itself. The thickness was measured here for each small square of the symmetric cells.

### Table 1. Summary of the Properties of Symmetric Cathode Cells.

| Sample No. | $T(\degree \text{C})$ | $L(\mu \text{m})$ | $R_p(\Omega \text{cm}^2)$ | $R_s(\Omega \text{cm}^2)$ | $\Delta R(\Omega \text{cm}^2)$ | $\Delta R(\%)$ |
|------------|-------------------|-----------------|------------------|------------------|------------------|------------|
| S1         | 750               | 190             | 0.24             | 0.70             | 0.075            | 12         |
| S1         | 850               | 190             | 0.06             | 0.33             | 0.045            | 16         |
| S2         | 750               | 185             | 0.31             | 0.61             | 0.035            | 6          |
| S2         | 850               | 185             | 0.09             | 0.29             | 0.030            | 12         |

Deconvolution of the impedance spectra using EQUIVCRT (21) has revealed that $R_p$ for the improved cathodes is decreased mainly by the decrease in the resistance of the combined dissociative oxygen adsorption and incorporation process (27). Further details of the evaluation of the impedance spectra will be published later.

Further improvement of the adhesion between cathode and electrolyte allows optimised $R_s$ and $R_p$ with 0.29 $\Omega \text{cm}^2$ and 0.09 $\Omega \text{cm}^2$ at 850°C and 0.61 $\Omega \text{cm}^2$ and 0.31 $\Omega \text{cm}^2$ at 750°C in sample S2, as shown in Table 1. $\Delta R(\%)$ decreased from 12 and 16% for sample S1 to 6 and 12% for the improved sample S2 at 750°C and 850°C, respectively.

One has to consider that the resistance contribution from the interface is in a much larger portion when the electrolyte thickness is much thinner. In fact, this is the case for the anode-supported cells, where the electrolyte is about 10 $\mu \text{m}$ (22). Assuming unchanged $\Delta R$ and conductivity for different thickness, one can estimate $\Delta R_{10\mu\text{m}}(\%) = \frac{\Delta R}{(R_e/10\mu\text{m}+\Delta R)}$ for a 10-$\mu\text{m}$-thick electrolyte. (Here, $R_e/10\mu\text{m}$ is the electrolyte resistance of 10-$\mu\text{m}$ thick YSZ.) This would result in $\Delta R_{10\mu\text{m}}(\%) = 78\%$ at 850°C and $\Delta R_{10\mu\text{m}}(\%) = 72\%$ at 750°C, based on the results from S1; and $\Delta R_{10\mu\text{m}}(\%) = 71\%$ at 850°C and $\Delta R_{10\mu\text{m}}(\%) = 55\%$ at 750°C based on the results from S2. This illustrates the improvement in performance. If we assume that the YSZ electrolyte thickness is 10 $\mu \text{m}$ in the anode-supported cell, the $R_e$ will be 0.0125 $\Omega \text{cm}^2$ at 850°C and 0.029 $\Omega \text{cm}^2$ at 750°C in our experimental conditions. Then the total $R_s + R_p$ will be approximately 0.13 $\Omega \text{cm}^2$ at 850°C and 0.37 $\Omega \text{cm}^2$ at 750°C for the estimation of an anode-supported cell with 10-$\mu\text{m}$-thick electrolyte.

Figure 2 shows the microstructure of the symmetric cell S2. From the low magnification picture in Figure 2A, a homogeneous microstructure with even distribution of the LSM and YSZ was observed for the composite cathode across the whole thickness, illustrated by an even contrast in the backscatter SEM picture. The high-magnification picture (Figure 2B) shows good adhesion at cathode/electrolyte interface and homogeneously distributed submicron pores. Good electric and chemical performance is believed to be related to such microstructure.
Figure 2. SEM pictures of the cross section for the symmetric cell S2.

Figure 3 shows the Arrhenius plot of the $R_p$ obtained from impedance measurements in air and open circuit voltage (OCV) condition. The activation energy of the LSM/YSZ cathode polarisation was found to be about 121 kJ/mol (1.26 eV). This is lower than what was reported previously (19,28), which is in the range of 1.3 to 2 eV. The activation energy for $R_s$ (YSZ) in a symmetric cell with LSM/YSZ composite cathodes was also calculated from the impedance measurements in the temperature range from 300° to 950°C, which is shown in Figure 4. The activation energy 98 kJ/mol was obtained for this sample. This is consistent with 99 kJ/mol obtained by Bonanos et al. (20).

Figure 3. Arrhenius plot of the cathode area specific polarisation resistance, $R_p$, obtained from the measurements in air and OCV condition.
Figure 4. $\sigma$·T versus 1/T plot for $R_s$ (YSZ) in the symmetric cell with LSM/YSZ composite cathode. The measurement temperatures range from 300 to 950°C.

Figure 5 shows the I-V curves of an anode-supported cell produced using the improved cathode processing technique. The cells with an active area of 4×4 cm² were tested using humidified hydrogen with 5% H₂O as fuel and air as oxidant. The hydrogen flow was 30 L/h and airflow was 140 or 170 L/h. Figure 6 demonstrates the high power density achieved in the relative large anode-supported cell using the optimised cathode.

Figure 5. I-V curves obtained under a hydrogen flow of 30 L/h with 5% water vapour. The cell temperature was measured right on top of the cell.

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Table 2 summarises the performance of the anode-supported cell. Here $T_{\text{imax}}$ is the measured cell temperature at maximum current. ASR is the area specific resistance of the anode-supported cell ($\text{ASR} = (\text{OCV} - V)/i_{\text{max}}$, $V$ is the cell voltage, and $i_{\text{max}}$ is the maximum current density. Almost theoretical OCVs were obtained, indicating tight electrolyte, optimal electrical potential through the cell, and tight cell test house. Power density as high as 1.44 and 0.8 W/cm$^2$ at 850°C and 750°C, respectively, has been achieved at 0.7 V. This is twice the power density achieved in our previous results (7). This indicates that the anode-supported cell with improved LSM/YSZ composite cathode has the potential to be operated at 700°C with a power density of more than 0.5 W/cm$^2$.

Figure 7 shows the unpolished cross-section of the anode/electrolyte/cathode layers in the anode-supported cell with high performance. The 8--10-μm-thick electrolyte is dense and in good contact with the anode. Series resistance contribution from the interface between the anode (Ni+YSZ) and the electrolyte (YSZ) could be very small due to the co-sintering process at high temperature such as 1300°C--1400°C. Early discussion of the Δ$R_{10\mu m}$(%) indicates that the resistive contribution from the interface at cathode/electrolyte might be significant. In the figure the LSM/YSZ composite cathode is very homogeneous and has good contact with the YSZ electrolyte. Thus the microstructure of the cathode in the symmetric cells shown in Figure 2 is reproduced in the anode-supported cell in Figure 7.

Table 2. Performance of the Anode-Supported Cell (4×4 cm$^2$ active area).

| Temperature ($^\circ$C) | $T_{\text{imax}}$ ($^\circ$C) | OCV (V) | Current at 0.7 V (A) | Power density at 0.7 V (W/cm$^2$) | ASR ($\Omega$cm$^2$) |
|------------------------|-----------------|---------|---------------------|-----------------------------------|---------------------|
| 850                    | 864             | 1.070   | 32.9                | 1.44                              | 0.175               |
| 800                    | 816             | 1.082   | 26.7                | 1.17                              | 0.209               |
| 750                    | 758             | 1.092   | 18.3                | 0.8                               | 0.305               |
| 700                    | 708             | 1.101   | 11.7                | 0.51                              | 0.47                |
| 650                    | 655             | 1.111   | 6.6                 | 0.29                              | 0.845               |
CONCLUSIONS

1. Low area specific polarisation resistance of 0.06 Ωcm² at 850°C and 0.24 Ωcm² at 750°C have been achieved in symmetric cells using LSM composite cathodes.
2. Improvement of the cathode/electrolyte interface has resulted in a lower series resistance of the symmetric cathode cells.
3. Processing optimisation has led to a homogeneous microstructure with submicron pores through the entire cathode and a good adhesion between cathode and electrolyte.
4. Power density of 0.8 W/cm² at 750°C and 0.5 W/cm² at 700°C has been achieved at a cell voltage of 0.7 V in the anode-supported cell with an active area of 4x4 cm².

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