CORRELATION BETWEEN IMPEDANCE, ACTIVATION ENERGY AND MICROSTRUCTURE OF COMPOSITE 
(La1-xSrx)3MnO3±y/Zr1.2Y2O2.05z CATHODES

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ABSTRACT

The performance of composite cathodes made from lanthanum strontium manganate (LSM) and yttria stabilised zirconia (YSZ) is strongly dependent on the composition of the two constituents, their volume fraction, the particle size distribution of the powders and the fabrication procedure. Two different types of cathodes have been tested; two-layer cathodes with an electrochemically active layer and a current collecting layer and five-layer cathodes where the electrochemically active region is graded through four layers with increasing LSM in the outermost layers. For both types of electrodes, it is generally found that lower polarisation resistances are associated with lower apparent activation energies. Correlations between the activation energy and the resistance of composite LSM/YSZ cathodes are discussed in relation to the kinetics of the oxygen reduction process.

INTRODUCTION

The polarisation drop of the cathode is one of the parameters limiting the performance of solid oxide fuel cells (SOFC). The cathodes of most SOFC systems are based on the classical material lanthanum strontium manganate (LSM). Composite cathodes, composed of LSM and yttria stabilised zirconia (YSZ) are found to have considerably better performance than cathodes produced from LSM only [1,2]. The performance of composite LSM/YSZ cathodes is strongly dependent on the composition of the constituents, the ratio between LSM and YSZ, the particle size distribution of the powders and the fabrication procedure [see for instance 1-4 and references herein].

Several results in literature indicate that the apparent activation energy of the oxygen reduction process in LSM based electrodes in contact with YSZ is close to 2 eV [5-7]. However, other literature sources show that this may be considerably lower, depending on the properties of the cathode [8-12]. Erning et al. found that the apparent activation energy of LSM cathodes decreased from approximately 2 eV to 1.4 eV upon addition of Pd as a catalyst, and to 0.9 eV by partial substitution of Mn with Co [8,9]. For the Co-doped LSM cathodes, the apparent activation energy was sensitive to the sintering temperature [10]. For lanthanum strontium ferrite cobaltite on a gadolinia doped ceria electrolyte, the activation energy for oxygen reduction was found to depend on the microstructure, as it has been determined to be approximately 1.3 eV for a porous electrode and 1.7 eV for a dense electrode structure [8].
The impedance of LSM based cathodes depends strongly on parameters such as the composition and fabrication. It is has been found that the number of processes limiting the rate of the oxygen reduction process in LSM based cathodes and the nature of the processes depends on the experimental conditions in addition to composition and processing [13]. The elementary processes may have different apparent activation energy, and therefore it is reasonable to find the above-mentioned different activation energies for different cathodes.

In summary, both the impedance and the activation energy seem to be related to the cathode microstructure. Exploring the co-variation of these parameters may improve the understanding of the kinetics of the oxygen reduction process occurring in these electrodes. In this paper, data for a number of LSM/YSZ composite cathodes fabricated with different composition and processing procedures are presented, in an attempt to correlate the impedance, activation energy and microstructure of these cathodes.

EXPERIMENTAL

Sample Preparation
Electrolyte substrates were produced from YSZ with 8 mol% Y2O3 (TZ8Y, Tosoh Corporation, Japan). Two sample geometries were tested. Three-electrode electrochemical test cells were made using pellets, as described in [13]. The area of the working electrode was about 0.4 cm². Two-electrode measurements were performed on symmetrical cells, which were produced by application of two nominally identical cathodes on each side of a YSZ foil of thickness about 180 μm [13]. The foil, of dimensions 5×5 cm², was produced by tape casting and sintering at 1350°C. The electrodes were applied and sintered, after which samples of area 0.2-0.5 cm² were cut or broken from the foil.

The cathodes consisted of two to five layers, deposited by airborne spraying. The electrochemically active zone was an LSM/YSZ composite, denoted as the c-layer, composed either of one layer, or four sub-layers. Cathodes with a c-layer of uniform composition had an LSM content of 50-60 weight%. In the others, the composition and microstructure were graded, with the highest LSM content furthest from the electrolyte. The c-layer was sintered at temperatures between 1100°C and 1300°C. Its total thickness was 5–35 μm.

A pure LSM layer, denoted as the ccc-layer, was applied for current collection. This layer was made by application of two nominally identical LSM sprayings with intermediate drying and sintering at the same temperature as the c-layer. After sintering, the ccc-layer thickness was about 40 μm.

The LSM used in the examples below was (LaₐₓSrₜ₋ₓ)ₓMnO₃₋ₘ with x = 0.15 or 0.25 and y = 0.9 or 0.95. The YSZ fraction of the c-layer was TZ8Y or TZ3Y (YSZ with 3 mol% Y₂O₃, Tosoh Corporation, Japan).

Electrochemical Measurements
The composite electrodes are tested electrochemically using a three-electrode, four-wire set-up (polarised and open circuit measurements) or by a simple two-electrode, four-wire
measurement using symmetrical cells (open circuit measurements). In the three-electrode test an as yet unsintered LSM tape cast foil and a channelled LSM pellet may be attached to the working electrode to improve current collection. In this test the counter electrode consisted of Pt paste, while the reference electrode was a Pt bead. The distance between the working electrode and the reference electrode was about 2 mm. For the two-electrode test, Pt paste was painted on the composite electrodes and a Pt mesh was pressed into contact with each side of the test cell to ensure proper current collection. For both types of test cells, four electrochemical cells were placed in a furnace and measurements were performed on one cell at a time. The test atmosphere was air.

Impedance measurements were performed at open circuit voltage (OCV) or at several applied cathodic potentials (three electrode measurements only) at temperatures between 700°C and 1000°C. The measurements were carried out using different Solartron instruments (S1250 + S1286 or S1280). The maximum frequency used in the impedance measurements was 20 and 65 kHz depending on the frequency response analyser used. The lowest measuring frequency was 1-100 mHz. The amplitude applied between the working and the reference electrode was 14 mV rms and 6-12 points per decade of frequency were measured going from high to low frequency.

For the symmetrical cells, the measured electrode response corresponds to the sum of the two nominally identical electrodes. In the figures presented below, the electrode response has been divided by two. This means that the polarisation resistance read on the plots is the average of the two electrodes investigated. This value can be compared directly to the polarisation resistances measured using three-electrode cells on a single electrode.

In order to illustrate the number of processes hidden in the impedance spectra, some of the data presented in the following are deconvoluted by equivcrt [14] using the simplest possible equivalent circuit, i.e. series connection of parallel RQ-elements, in which Q stands for a constant phase angle element [14].

RESULTS

A number of LSM/YSZ composite cathodes with different composition, microstructure and construction have been tested at Risø. In this work the general trends observed with respect to impedance, microstructure and apparent activation energy are presented.

For the apparent activation energy of the composite cathodes, one trend seems clear. The lower the polarisation resistance, the lower the activation energy, as illustrated in Fig. 1. The apparent activation energies are determined from plots of \( \log(R_p) \) versus \( 1/T \). The data in this figure are obtained for composite cathodes sintered at various temperatures between 1100°C and 1300°C, having different LSM composition, powder processing, electrode structure (two or five layers) and sample geometry. The cathodes which have shown the lowest polarisation resistances are those sintered at low temperature (about 1100°C), having c-layer consisting of either one layer or four layers graded in composition.
Some of the data have been deconvoluted using *equivcrt* [14] to obtain details about the correlation between the apparent activation energy and the polarisation resistance. In another publication it was shown that the impedance of LSM/YSZ composite cathodes may include up to five processes, which can be numbered A – E from high to low frequency [13]. These processes have the following tentative interpretations: A and B relate to transport processes through the composite, arc C is ascribed to competing elementary processes in the overall oxygen reduction process, arc D relates to gas diffusion in a stagnant layer above the electrode and, finally, arc E is an inductive process related to activation of process C [13]. In this work, arcs D and E are not considered, as these processes were not evident in the impedance spectra from which the data shown in Fig. 1 were obtained.

![Graph](image)

Fig. 1. Apparent activation energy versus the polarisation resistance measured at 850°C (air and open circuit voltage) for LSM/YSZ composite cathodes with various composition and processing parameters.

The data were fitted using the equivalent circuit shown in Fig. 2. This circuit contains an inductance, L, ascribed to the measurement leads. The series resistance, $R_s$, is mainly due to the ohmic drop in the electrolyte. The processes A–C are represented by three RQ elements, where $R$ is a resistance and $Q$ is a constant phase element. This model may not give the best possible description of the impedance of composite LSM/YSZ cathodes, but is sufficient for determining the polarisation resistance and apparent activation energy of the various processes.

The only process that seems to be present in all impedance measurements for LSM/YSZ composite cathodes, is arc C [13]. This arc often gives the dominant contribution to the overall impedance. The results presented in the following are focussed on process C, as this process is assumed to represent the actual oxygen reduction/oxidation process.

![Diagram](image)

Fig. 2. Equivalent circuit used for fitting the data. L is an inductance, $R_s$ is the electrolyte series resistance, $R$ is a resistance and $Q$ is a constant phase element. $R_p = R_A + R_B + R_C$. 
Fig. 3 shows the apparent activation energy of process C, $E_{a,\text{process } C}$, and the summit frequency of process C (when plotted in the complex plane), $f_{\text{max,process } C}$, versus the polarisation resistance. $E_{a,\text{process } C}$ increases with increasing polarisation resistance, as also observed for the total apparent activation energy (Fig. 1). The same trend is observed by plotting $E_{a,\text{process } C}$ against the polarisation resistance of process C. $f_{\text{max,process } C}$ is found to decrease with increasing polarisation resistance (Fig. 3). The decrease in $f_{\text{max,process } C}$ is higher than what can be accounted for by the increase in the polarisation resistance of process C.

![Fig. 3. Examples of the apparent activation energy (closed symbols) and the summit frequency (open symbols) of arc C plotted versus the polarisation resistance measured at 850°C (air open circuit voltage) for LSM/YSZ composite cathodes with various composition and processing parameters.](image)

The parameter which has so far been found most strongly to affect the polarisation resistance and its activation energy is the sintering temperature [13]. The summit frequency of arc C tends to decrease with increasing sintering temperature [7,15-19]. The microstructure is also affected by the sintering temperature. An example of this is given in Fig. 4 for two cathodes sintered at 1300°C and 1150°C, respectively. Larger grains and a less uniform pore size distribution are observed for the cathode sintered at 1300°C. The most important parameter affected by the microstructure is believed to be the triple phase boundary (TPB) between electrode, electrolyte and gas phase. This parameter decreases with increasing particle size. In the graded composite structures, which show low apparent activation energies, the triple phase boundary is thought to be particularly long.

**DISCUSSION**

The data presented here show that the apparent activation energy of LSM/YSZ composite cathodes is correlated to the polarisation resistance. The lower the polarisation resistance, the lower the activation energy. This trend seems to hold independently of parameters like composition, sample structure, sample processing and test geometry. For Ni/YSZ cermet the apparent activation energy has also been found to increase with increasing sintering temperature [20].

The activation energy of Process C, which is ascribed to the actual oxygen reduction process, seems to have similar dependence on the polarisation resistance as the total
apparent activation energy. This indicates that the overall performance of composite LSM/YSZ cathodes is strongly influenced by the features of process C.

Fig. 4. LSM/YSZ cathodes produced from the same slurry, sintered at 1300°C (left) and 1150°C (right). The micrographs were obtained with backscattered electrons, thus the LSM phase looks brighter than the YSZ phase. The scale bar corresponds to 10 μm.

The observed decrease in the polarisation resistance and apparent activation energy as a function of decreasing sintering temperature may be related to the microstructure. The same holds for the increase in summit frequency of process C. From micrographs, it is clear that the particle size increases with sintering temperature and, therefore, that the TPB decreases. It is often stated that the magnitude of the polarisation resistance is directly related to the TPB length, see for example ref. [15], as the majority of the active reaction sites are assumed to be situated at or close the TPB. However, the TPB is not the only parameter affected by sintering temperature. At high sintering temperature the migration of cations (mainly Mn) from the cathode to the electrolyte is faster, as also pointed out by Erning et al. [10]. At higher sintering temperature a redistribution of the materials is also faster, which may allow foreign phases and impurities to collect at the grain boundaries. If these phases are poorly conducting, this may limit the reaction rate and thus cause an increase in the polarisation resistance. This would also affect the activation/passivation of process C, which is tentatively related to foreign phases at the grain boundaries [13]. Further discussion of foreign phases and their influence is given in [21].

In electrodes sintered at high temperature, both the relatively low TPB length and the presence of foreign phases close to the TPB may cause the apparent activation energy to be higher than for electrodes sintered at lower temperature. However, it is not clear why the summit frequency of process C decreases more with increasing sintering temperature than can be accounted for by the increase in the polarisation resistance of process C. This may indicate a change in mechanism, i.e. that the balance between the competitive processes in the oxygen reduction mechanism such as surface diffusion and breaking of the oxygen molecule bonds [13 and references herein] depends on the sample processing. Other parameters, like sample composition and structure do not seem to affect the reaction rate as much as the sample processing (sintering procedure). Based on the present data it is not possible to make further interpretation of the nature of process C.

The observed correlation between polarisation resistance, microstructure and apparent activation energy may explain some of the discrepancies found in the literature on LSM-based cathodes (see for instance the literature survey in ref. [13]). If the electrode
performance is poor (high activation energy) the mechanism/kinetics may be different from those of a well-functioning cathode (low activation energy). Examining these correlations for devices of a wide range of performance may help in designing better ones in the future.

Another way of looking at this above correlation is by analogy to the Meyer-Neldel rule, observed in ionic conductors differing in the doping level; see for example ref. [22] and citations therein. According to this rule, the activation energies and pre-exponentials of the conductivity of such systems have a linear relationship. There are many instances where the rule has been invoked, but few where it has received a satisfactory explanation. The authors are not aware of previous cases where Meyer-Neldel-like behaviour has been noted in connection with electrode processes.

SUMMARY

Data have been analysed for a number of LSM/YSZ composite cathodes fabricated using different powder compositions, powder processing, electrode structure, sample geometry and sintering conditions. The polarisation resistances and apparent activation energies show a positive correlation. The parameter found most strongly to affect the polarisation resistance and activation energy is the sintering temperature; decreasing polarisation resistances are observed with decreasing sintering temperature.

The sintering temperature affects the microstructure, and in particular the TPB length, which decreases with increasing sintering temperature. Furthermore, the distribution of foreign phases at the TPB may be affected by the sintering temperature. These changes may also have influence on the balance between the reaction rate limiting steps and, thus, the activation energy.

Several processes may limit the performance of LSM/YSZ processes, as several overlapping arcs may be observed when plotting the data in the complex plane. One of these arcs is ascribed to competing elementary processes in the oxygen reduction mechanism. The apparent activation energy of this process increases with increasing polarisation resistance. The summit frequency of this arc decreases with increasing sintering temperature. This together with the change in activation energy with sintering temperature suggests that the rate limiting process may change depending on the sintering temperature. Further analysis of these systems is required to determine the nature of and the balance between the competitive rate limiting processes.

In summary it has been found that the performance, microstructure and apparent activation energy of composite LSM/YSZ cathodes is correlated. A better understanding of this correlation may be the key to improving the performance of such cathodes.

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