INVESTIGATION OF THE CATHODIC POLARIZATION MECHANISM IN SOFCs BY MEANS OF LSM-MICROELECTRODES

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ABSTRACT

The oxygen reduction reaction at LSM cathodes was investigated by impedance and I-V measurements on thin, dense LSM microelectrodes (1000 — 8000 Å thick, 20 — 200 μm diameter). The geometry dependence of the electrode resistance yields information on the location and thus on the nature of the cathodic electrochemical reaction. We found that under cathodic bias the electrode resistance scales with the inverse of the microelectrode area. Macroscopic measurements on thin-film LSM electrodes (250 — 10000 Å, 3 x 3 mm) demonstrate the electrode resistance to be thickness-independent. This result suggests that the rate-determining step of the oxygen reduction occurs either at the surface of the thin-film LSM electrodes or at the LSM/YSZ interface. However, with increasing anodic bias the geometry dependence changes towards a linear relation between resistance and inverse microelectrode diameter indicating that the location of the rate-determining step is probably shifted to the three-phase boundary.

INTRODUCTION

The perovskite-type Sr-doped LaMnO₃ (LSM) has received tremendous attention over the last years due to its use as the air-electrode in SOFCs operating with zirconia as the electrolyte. Many efforts have been made to clarify the reaction mechanism at the cathode side (e.g. Ref. 1-21) and most researchers favor the incorporation of oxygen ions at the TPB (three phase boundary) although under certain conditions the incorporation via the bulk of the LSM is not excluded (4, 6, 11, 21). Nonetheless the nature and location of the rate-determining step is still under discussion.

As the location of the rate-determining step of the cathodic reaction is reflected in the geometry dependence of the electrode resistance, experiments are desired in which the length of the three phase boundary (3PB) and the size of the two phase boundary (2PB) can be varied in a very controlled manner. This can be achieved by using LSM microelectrodes that are patterned via photo-lithography into a thin film of LSM (20). In this contribution we report on the geometry dependence of the electrochemical properties of such microelectrodes and on the variation of this dependence with applied voltage.
EXPERIMENTAL

The measurement set-up is displayed in Fig. 1: A LSM microelectrode on a YSZ (yttria stabilized zirconia) single crystal is contacted with a tungsten-carbide tip and the impedance resp. I-V characteristics are measured between this microelectrode and an extended, backside Pt-counterelectrode. The LSM microelectrodes were lithographically prepared from LSM films deposited on YSZ single crystals (5 x 5 x 0.5 mm, (100), 9.6 % yttrium content, Crystec) by means of laser-ablation. The nominal composition of the target used for the film preparation was \((\text{La}_{0.8}\text{Sr}_{0.2})_9\text{MnO}_3\). Fig. 2 shows the edge of a broken YSZ substrate with deposited LSM-film. This figure and additional atomic force microscopy (AFM) images and secondary ion mass spectroscopy (SIMS) studies revealed that the film and hence the microelectrodes can be regarded to be dense. Details of the substrate preparation, film-growth parameters and lithography procedures can be found in Ref. (20).

Fig. 2 shows, as an example, a top-view picture of a tungsten-carbide tip contacting a 60μm LSM microelectrode. The samples were generally investigated at about roughly 750°C. For the macroscopic measurement thin films (3 x 3 mm, 250 – 10000 Å thick) were grown on both sides of a YSZ single crystal that was polished on both sides. Impedance measurements were carried out between 0.1 Hz and 1 MHz with either a Novocontrol Alpha station or a Solartron 1260 while current-voltage data were collected with a Solartron 1287 potentiostat. All measurements were performed in air. The data was analyzed with the “Zview” and “CorrView” software packages (Scribner Associates). It is important to note that the impedance of the Pt-counterelectrode was independently determined to be at least three orders of magnitude lower than the microelectrode resistances, thus eliminating the need for a reference electrode.

Fig. 1: Microcontact impedance analysis set-up.
RESULTS AND DISCUSSIONS

With the microelectrode set-up of Fig. 1, LSM microelectrodes of diameters down to 20 μm could be reliably contacted at elevated temperatures. Fig. 3 shows a Nyquist representation of typical impedance data taken on a 20 μm LSM microelectrode. In general, the impedance data were fitted to the equivalent circuit shown in the inset in Fig. 3. This equivalent circuit describes the electrode impedance with two depressed semi-circle arcs. The serial resistor element can be attributed to the ohmic drop, i.e. mainly to the bulk resistance of the zirconia electrolyte whereas R1, R2, Q1, and Q2 which represent the electrode reaction, are not bearing an immediate physical or chemical meaning. In this contribution we therefore limit the discussion of the results to the DC electrode resistance and the correlation with the geometry of the LSM microelectrodes. In the following text the term electrode resistance of a LSM microelectrode means the sum of R1+R2 obtained from the equivalent circuit fit.

Microelectrode Resistance vs. Diameter

In Fig. 4 the relationship of the electrode resistance versus the microelectrode diameter is displayed. Here, the results from five different samples of different thicknesses are plotted. From the result we can conclude that the microelectrode resistance $R_{\text{electrode}}$ approximately scales with the inverse of the square of the microelectrode diameter $d$. Fig. 4 also shows lines of slope $m=-2$ and $m=-1$ as a guide to the eye. The scatter can be attributed to a variety of experimental difficulties and uncertainties (e.g. different/varying sample temperatures due to different/varying thermal contacts of the Pt-paste counterelectrode with the YSZ substrate, uncertainties about the exact microelectrode diameter due to over-etching during the photo-lithographic process, non-zero and slightly time-dependent open-circuit voltages between the microelectrodes.
and the counterelectrode possibly due to a thermal gradient). In particular, the non-zero open circuit voltage of about ±15 mV does – owing to the bias-dependence of the spectra – influence the slope m of the Log (R)- Log (d)-relation.

Fig. 3: Nyquist plot of typical impedance data obtained on a 20 μm LSM microelectrode. The inset shows the equivalent circuit model that was used to fit the data.

This dependence of the microelectrode resistance on the inverse microelectrode area (∼d^2) mechanistically means that a region the size of which is proportional to the electrode area is involved in the rate-limiting step of the oxygen reduction reaction. It is worth noting that the 3PB does not seem to be involved in this rate-limiting step on our samples. Two reaction paths are usually discussed: i) dissociative adsorption of oxygen on the electrode surface with subsequent surface diffusion of the (probably charged) oxygen species to the 3PB where the oxygen is incorporated into the YSZ as an oxide ion and ii) dissociative adsorption of oxygen on the electrode surface followed by incorporation into the electrode, subsequent transport of oxide ions through the electrode bulk and transfer of the oxide ions into the YSZ across the LSM/YSZ interface. Considering these paths, four possibilities for the rate-limiting step are reasonable: a) either dissociative adsorption at the electrode surface or b) incorporation of the oxygen into the LSM or c) transport of oxide ions through the electrode bulk or d) transfer of oxide ions from the electrode bulk into the YSZ appear to be rate-determining. Despite some variations of the resistances measured in the thickness range from 1000 Å to 8000 Å an obvious trend with respect to the thickness dependence could not be observed. The involved errors, particularly due to difficulties with respect to an exact temperature measurement, might overshadow the true thickness dependence (or independence). In order to further distinguish between the different steps, reliable, thickness-dependent measurements need to be performed.
Thickness Dependence

In order to eliminate some error sources accompanying the microelectrode measurements we performed thickness-dependent impedance measurements on macroscopic film electrodes. The films were grown on both sides of the YSZ substrate. In Fig. 5 the total electrode resistance (contribution from both LSM-electrodes, T=800 °C) is plotted against the LSM film thickness. Obviously, the electrode resistance does not systematically depend on the film thickness. However, there is an evident trend that the electrode resistance increases after thermal cycling between 650 and 950 °C. The area-specific resistances at 800 °C fall in the range between 20 – 80 Ωcm². Taking into account the temperature difference of about 50 °C the specific resistances obtained on the microelectrodes (160-580 Ωcm²) are comparable with those obtained on the films. Experiments to decide whether or not the resistances measured on microelectrode are also thickness-independent are running and it cannot be excluded that the preparation procedure of the microelectrodes changes e.g. the surface reaction kinetics and hence the thickness-dependence of the polarisation resistance. However, the assumption that the microelectrode polarization resistances are thickness-independent as well, leaves in our case as rate-limiting steps i) the dissociative adsorption of oxygen on the electrode surface either followed by fast incorporation into YSZ at the 3PB or into the LSM electrode or ii) incorporation into the LSM electrode (with subsequent fast diffusion of.
oxide ions through the electrode bulk to the LSM/YSZ interface) or iii) the transfer of oxide ions from the LSM electrode bulk over the LSM/YSZ interface into the YSZ. In all three cases irreversible changes caused by the thermal cycling (cf. Fig. 4) e.g. owing to reactions at the LSM/YSZ interface or to morphological / chemical changes at the LSM surface are not surprising. On the other hand, owing to the reservations mentioned above, an influence of the ion transport through the LSM on the polarization resistance of the microelectrodes cannot be excluded yet.

![Graph showing electrode resistance vs. film thickness](image)

Fig. 5: Electrode resistance of macroscopic film electrodes (3 x 3 mm) vs. the film thickness. While $R_{\text{electrode}}$ appears to be independent of the thickness there is an evident trend that the electrode resistance increases after thermal cycling. Sample temperature $T=800$ °C.

Results from I-V Measurements

Besides the impedance measurements, I-V characteristics were recorded on the LSM microelectrodes. Fig. 6 shows an I-V curve that was taken on a 30 µm LSM microelectrode. The range between −250 mV (cathodic regime) and 250 mV (anodic regime) turned out to be reversible. Under larger cathodic potential the I-V curves display a hysteresis whereas there are irreversible changes in the film morphology occurring at anodic bias above ca. 300 mV. These processes are currently under detailed investigation. The data shown in Fig. 6 was corrected for the open-circuit voltage offset (see above), the IR-drop (bulk resistance values from the fit of Fig. 3) and smoothened (CorrView software) to filter out glitches. I-V data were taken on three samples with film thicknesses of 1000 Å, 3000 Å and 8000 Å on 30 µm, 40 µm, 60 µm and 80 µm LSM microelectrodes at a nominal sample temperature of roughly 750 °C. For bias values from −200 mV to 150 mV (in steps of 50 mV) the electrode resistance under bias was calculated as the slope in a linear (V vs. I) plot ($R(V)=\Delta V/\Delta I$, with $\Delta V=30$ mV). The
resistances were then graphed for each bias value in a Log R(V) vs. Log (d) plot. Fig. 7 shows the various slopes m from linear regressions through the Log-Log plot for the different bias values. Going from cathodic to the anodic regime, the slopes change from about -2 to roughly -1. In other words the resistance changes from a proportionality to the inverse area to a proportionality to the circumference. We consider this as a strong evidence for the fact that the rate-determining step in the cathodic regime is "area-related" (m=-2, as discussed above), whereas in the anodic regime this step mainly occurs close to the 3PB. However, the uncertainties in the data on the anodic side in Fig. 7 are quite large, and hence further measurements to confirm this interesting feature are required. First impedance measurements under bias support the discussed change of the location of the rate-determining step from cathodic to anodic bias.

It can be expected that this transition of the electrochemically active region from the 3PB to the surface/2PB strongly depends on the electrode geometry. In our case, the 3PB length per area (~ 670 cm/cm² for a 60 μm LSM microelectrode) is much smaller than in porous SOFC cathodes. Therefore porous SOFC cathodes favor the process occurring at the 3PB, and even in the cathodic regime R \propto 1/(3PB length) is realistic. Hence, there is no contradiction between our results and the reported proportionality to the inverse 3PB length (1) or SIMS-studies on the electrochemically active sites of LSM electrodes (19). A numerical extrapolation of our results to porous cathodes is planned for the near future.

Fig. 6. Typical I-V data taken on a 30 μm LSM microelectrode. Sample temperature T~750 °C.
CONCLUSIONS

Impedance measurements on LSM microelectrodes have revealed that — at zero bias — the resistance of the microelectrodes is roughly proportional to the inverse microelectrode area. Macroscopic measurements on thin-film LSM electrodes demonstrate the electrode resistances to be thickness-independent. Extrapolating these macroscopic results into the microscopic regime implies that the rate-limiting step of the oxygen reduction reaction is in our case related to either the surface of the electrodes or to the interface between the LSM electrodes and the YSZ electrolyte. However, owing to the additional preparation step to produce the microelectrodes, a modified situation and hence an influence of the ion transport through the LSM on the polarization resistance cannot be excluded yet. I-V measurements suggest that while the rate-determining step of the electrochemical reaction in the cathodic regime is still area-related, this step is shifted towards the three phase boundary region of the LSM-electrodes when anodic voltages are applied.

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REFERENCES

1. J. Mizusaki, H. Tagawa, K. Tsuneyoshi, and A. Sawata, *J. Electrochem. Soc.* **138**, 1867 (1991).
2. J. van Herle, A. J. McEvoy, and K. Ravindranathan Thampi, *Electrochim. Acta* **41**, 1447 (1996).
3. A. Mitterdorfer and L. J. Gauckler, *Solid State Ionics* **111**, 185 (1998).
4. E. Siebert, A. Hammouche, and M. Kleitz, *Electrochim. Acta* **40**, 1741 (1995).
5. M. J. L. Ostergard and M. Mogensen, *Electrochim. Acta* **38**, 2015 (1993).
6. J. Mizusaki, T. Saito, and H. Tagawa, *J. Electrochem. Soc.* **143**, 3065 (1996).
7. H. Y. Lee, W. S. Cho, S. M. Oh, H.-D. Wiemhöfer, and W. Göpel, *J. Electrochem. Soc.* **142**, 2659 (1995).
8. H. Fukunaga, M. Ihara, K. Sakaki, and K. Yamada, *Solid State Ionics* **86-88**, 1179 (1996).
9. H. Kamata, A. Hosaka, J. Mizusaki, and H. Tagawa, *Solid State Ionics* **106**, 237 (1998).
10. A. Hammouche, E. Siebert, A. Hammou, M. Kleitz, and A. Caneiro, *J. Electrochem. Soc.* **138**, 1212 (1991).
11. A. Endo, M. Ihara, H. Komiyama, and K. Yamada, *Solid State Ionics* **86-88**, 1191 (1996).
12. M. Odgaard and E. Skou, *Solid State Ionics* **86-88**, 1217 (1996).
13. F. P. F. Berkel, F. H. van Heuveln, and J. P. P. Huijsmans, *Solid State Ionics* **72**, 240 (1994).
14. B. C. H. Steele, *Solid State Ionics* **86-88**, 1223 (1996).
15. K. Sasaki, J.-P. Wurth, R. Gschwend, M. Gödickemeier, and L.J. Gauckler, *J. Electrochem. Soc.* **143**, 530 (1996).
16. S. Wang, Y. Jiang, Y. Zhang, J. Yan, and W. Li, *J. Electrochem. Soc.* **146**, 1932 (1998).
17. F. H. van Heuveln, H. J. M. Bouwmeester, and F. P. F. van Berkel, *J. Electrochem. Soc.* **144**, 126 (1997).
18. F. H. van Heuveln and H. J. M. Bouwmeester, *J. Electrochem. Soc.* **144**, 134 (1997).
19. T. Horita, K. Yamaji, M. Ishikawa, M. Sakai, H. Yokokawa, T. Kawada, and T. Kato, *J. Electrochem. Soc.* **145**, 3196 (1998).
20. V. Brichzin, J. Fleig, H.-U. Habermeier, and J. Maier, *Electrochem. Solid St. Let.* **3** (2000) 403.
21. B. Gharbage, T. Pagnier, and A. Hammou, *J. Electrochem. Soc.* **141** (1994) 2118.