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SEPARATION OF DIFFERENT OXYGEN REDUCTION PATHS ON LANTHANUM MANGANITE (LSM) THIN FILM MODEL ELECTRODES

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Introduction
Sr-doped lanthanum manganite (LSM) is the most used cathode material in solid oxide fuel cells (SOFC). Nevertheless, many aspects of the oxygen reduction at LSM are not completely understood. Despite being a poor ion conductor, LSM electrodes may reduce oxygen via two different mechanisms: one path via the three phase boundary (TPB) (surface path) and another path including oxygen bulk diffusion (bulk path). The impedance and parameters affecting their individual relevance are still under debate [1,2]. In this contribution several experimental tools are combined to separate and quantify the kinetic parameters of both reaction paths.

Experiments
Thin films of La$_{0.6}$Sr$_{0.4}$MnO$_3$ (LSM) (100-300nm) where deposited via pulsed laser deposition (PLD) on yttria-stabilized zirconia single crystals (100) (YSZ). Micro-electrodes (ME) were prepared by photolithography, chemical or ion beam etching (IBE). The relevance of the reaction pathways was modified by different electrode sizes and TPB lengths. Additional magnetron sputtered Pt layers on LSM were used to partly block the bulk path. Fig. 1 displays examples of several electrode geometries.

![Fig. 1. Electrode geometries with (b,d,e) and without (a) platinum capping layers](image)

Kinetic properties of the electrodes were analyzed by electrochemical impedance spectroscopy (EIS) and $^{18}$O tracer exchange with secondary ion mass spectroscopy (SIMS) analysis.

Results and Discussion
$^{18}$O incorporation and SIMS measurements were used to localize the oxygen reduction sites and distribution. Moreover oxygen diffusion and incorporation resistance in LSM was calculated from SIMS $^{18}$O tracer profiles and compared with EIS data.

In electrical measurement, the mechanism change between surface and bulk path is evidenced by several observations: change of the activation energy, characteristic electrode geometry dependence, effect of the Pt capping layer and varying shape of the impedance spectrum. Among others, the observed change of mechanism is strongly influenced by a variation of the TPB length from long (LSM$_1$) to short (LSM$_2$), Fig. 1 and Fig. 2. Moreover, after reproducible measurements for several days (4 cycles 600-850°C, LSM$_1$) the high temperature slope was modified by a heat treatment (940°C).

A comparison between LSM and Pt electrodes [3] gives further information on the role of the electrode material in TPB-related kinetics.

![Fig. 2. Arrhenius-plot of two thin film LSM electrodes with platinum capping layer. The TPB length of LSM$_2$ and LSM$_1$ differs by the factor of 50.](image)

Conclusions
Mechanism changes of oxygen reduction on LSM thin films and ME were reproducibly measured. The activation energy varies with temperature from around 1.2eV at low (300°C) to around 2.8eV at high (900°C) temperatures. The transition temperature can be shifted by blocking specific pathways, changing the electrode geometry and heat treatments.

References

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