EPMA ON INTERFACES BETWEEN CATHODE AND ELECTROLYTE OF THE SOLID OXIDE FUEL CELL

G. Stochniol, H. Grübmeier, A. Naoumidis, and H. Nickel
Institute for Materials in Energy Systems, IWE 1, Research Centre Jülich
D-52425 Jülich, Germany

ABSTRACT

The interface of La\textsubscript{y,x}Sr\textsubscript{x}MnO\textsubscript{3}/YSZ was studied with EPMA after annealing at 1200°C to 1400°C for various times. Typical reaction products (zirconates) and a diffusion zone of Mn and La in the YSZ were determined using quantitative microanalysis. The chemical reactivity at the interface is dependent on the stoichiometry (y) and the Sr content (x) of the perovskite. An increased Sr content leads to a decreased formation of La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} but also to an increased diffusion of Mn oxide into the electrolyte material. A high Sr content (x=0.4) reveals both aspects: the formation of a La- and Mn-enriched SrZrO\textsubscript{3} layer at the reaction interface, as well as a diffusion of Mn oxide into YSZ.

INTRODUCTION

Zirconates such as La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, SrZrO\textsubscript{3} or CaZrO\textsubscript{3} might be formed at the interfaces between the cathode materials La\textsubscript{y-x}L\textsubscript{x}Mn\textsubscript{1-y}M\textsubscript{y}O\textsubscript{3} (L=Ca, Sr; M= Fe, Co, Ni) and the electrolyte YSZ (1-18), which cause an increase in the electrical resistivity and polarization of the cathode. In these investigations the diffusion of Mn from perovskites into YSZ is usually also reported depending on the perovskite composition and temperature/time treatment. Yokokawa (7) calculated the stoichiometry y for La\textsubscript{y}MnO\textsubscript{3} to be y>0.86 for La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} formation and y<0.86 for a predominant Mn diffusion at 1300 K. Although Mn diffusion in YSZ was observed in most investigations published for stoichiometric and substoichiometric perovskites, diffusion-free results were also obtained (8). Initial theoretical considerations by Yokokawa (20) try to explain this different behaviour. Especially A-deficient perovskites (3, 10, 12-14) or B-site hyperstoichiometric perovskites (18) seem to be favourable candidates for application as cathode materials in SOFC due to their decreased tendency to form bad conducting zirconate layers that lead to high overpotentials during long-time operation. On the other hand, the A-site-deficient materials probably show a higher Mn diffusivity and resulted in a contamination of the electrolyte. Primary investigations concentrate on the influence of the Mn content in YSZ (21-25) on the properties and electrochemical behaviour of this modified electrolyte composition.

In this report the influence of the Sr content on the reactivity of perovskite with YSZ is evaluated for the first time. Also, the effect of time and temperature treatments is
investigated to achieve a better understanding of the formation of zirconate layers in connection with interfacial reactivity and Mn diffusion. Critical material combinations were used and studied by EPMA in order to optimize the cathode perovskite stability.

EXPERIMENTAL

A series of experiments were carried out with double-layered pellets connecting the standard electrolyte YSZ (8% mol Y$_2$O$_3$) with differently composed cathode perovskites. For the preparation of the specimens powders of perovskite and YSZ were consequently filled in a die and consolidated under 500 MPa pressure.

The influence of time (95-400 h) and temperature (1200-1400°C) (Tab. I) on the chemical interaction was studied after heating experiments in air, especially for a comparison of non-stoichiometric Sr-free and Sr-substituted perovskites.

Cross-sections of double-layered pellets were investigated by EPMA line-scanning and step-scanning techniques. A slow-motion electron beam deflection was used for the line-scan measurements in order to achieve the best possible resolution.

In order to obtain a systematic overview of the quantitative aspects of diffusion behaviour step-scanning analyses Fig. 1(a, b) were performed on the specimens already described above. The measurements were carried out at the same positions as used for the high-resolution electronic line-scans of Fig. 2(a-d) so that a strong local relationship between the interface and the diffusion zone was guaranteed.

RESULTS

Reaction products

The chemical microanalysis of the composition of the phase formed at the interface during exposure at 1400°C was measured by quantitative EPMA using point-by-point analyses in 1 µm specimen shift. Because of the limited resolving power of the electron microprobe this method is only useful for specimens with a reaction product formation of sufficient size. Under these considerations only measurements are reliable for experiments at elevated temperatures. The following reaction products were identified after 95 h and 200 h at 1400°C.

Lanthanum Zirconate (La$_2$Zr$_2$O$_7$) was found after 95 h at the interface of YSZ to La$_{0.95}$MnO$_3$. The average composition resulting from the concentration profiles across a 3-4 µm thick reaction layer (Fig. 1a) is given in Tab. II. Mn seems to be nearly undissolved (<0.5 at.%), but there is some indication of a solid solution with Y$_2$O$_3$ suggesting a formula of (La,Y)$_2$Zr$_2$O$_7$.  

996
Strontium Zirconate (SrZrO₃) is the typical reaction product with perovskites of higher substitution degrees of Sr for La and was identified for La₀.₆Sr₀.₄MnO₃ (Fig. 1b) at a 7-8 μm interface layer. The total composition (Tab. II) includes the amount of 3 at.% (Mn+La). This composition can be explained by a solid solution of SrZrO₃ with La₂O₃ and MnOₓ in agreement with earlier EDX investigations (10).

Y₂O₃ seems to be undissolved in the perovskite material for all compositions used, whereas Zr was detected for small amounts in La₀.₉₅MnO₃. No Y could be detected in the perovskite La₀.₆Sr₀.₄MnO₃ but a small amount of Zr could be observed.

**Line-scan investigations at the interface and diffusion zone**

Different stages of the chemical reaction at the interface between perovksite and YSZ are represented by the line-scan curves in Fig. 2(a-c) where diffusion of La, Mn and Sr and zirconate formation can be observed by emitted X-ray intensities. The influence of Sr substitution for La on the suppression of interface reactions is evident, comparing the results of Sr-free perovskite (Fig. 2a+b) with those of Sr-doped perovskite (Fig. 2c). La₂Zr₂O₇ formation was only observed for Sr free La₀.₉₅MnO₃. The effect is even more significant for higher temperatures (Fig. 2a-b), where only Sr-free perovskite reacted with YSZ to form La₂Zr₂O₇. The La₀.₆Sr₀.₄MnO₃/YSZ reaction couple, Fig. 2d, showed a Sr-enriched layer of several μm thickness.

In previous XRD and SEM/EDX investigations (10, 14) on powder pellets and double-layered specimens for perovskite/YSZ compatibility tests, the diffusion of perovskite cations into the YSZ region was observed. The XRD measurements of powder mixture investigations revealed shifted 2θ reflections for zirconates and YSZ, indicating bulk diffusion of perovskite cations in the YSZ and the reaction products, which was confirmed by SEM/EDX investigations on double-layered pellets.

Quantitative measurements of the concentration profiles of Mn and La at 1400°C are presented in Fig. 3 in the same order as the line-scans in Fig. 2. The estimated values of diffusion depth, integrated mass transfer and Mn concentration at the boundary of YSZ to perovskite are given in Tab. II. Substantial effects on the quantity of concentration profiles can be seen in Fig. 3. Comparing the results of Sr-free perovskite (3a) and Sr-doped perovskite (3b), it is obvious that the substitution by Sr leads to an increased Mn release into YSZ. In every case the diffusion of Mn exceeds by far that of La, whereas Sr was not detected in the diffusion zone. The shape of the profiles (see especially Fig. 3a) is sometimes characterized by typical fluctuations between maxima and minima, which is normally attributed to the predominant grain boundary diffusion of Mn in YSZ (1, 7, 9). The fluctuation effect also seems to be true for La diffusion, but does not appear clearly due to the much lower concentration. Nevertheless bulk diffusion through YSZ grains cannot be denied with respect to former XRD results where shifted reflections were observed, and to experiments using YSZ single crystals (1).
DISCUSSION

The observation of enhanced Mn diffusion into the YSZ region leads to the conclusion that this effect is supported by the substitution of Sr for La in the perovskite. This may be related to an increased chemical activity of Mn oxide in the lanthanum manganite, neglecting kinetic effects. In contrast to these observations Kanenko et al. (5) and Taimatsu et al. (9) presented a contradictory result for stoichiometric La$_1-x$Ca$_x$MnO$_3$ perovskites with $x=0$, 0.1, 0.2. The different behaviour for Sr and Ca substitution cannot be explained at the moment.

Our observed differences in Mn concentration, as was verified by quantitative EPMA measurements on Sr-free and Sr-substituted LaMnO$_3$, lead to the assumption that the chemical activity of Mn oxide increases from La$_{0.95}$MnO$_3$ to La$_{0.85}$Sr$_{0.1}$MnO$_3$ to about the same extent at both 1200 and 1400°C (Tab. II).

However, the formed La$_2$Zr$_2$O$_7$ layer seems to be permeable for Mn diffusion, even for thicker layers, as shown in Fig. 3a, so that raising the chemical activity of Mn oxide in the perovskite leads to a higher release of Mn and resulted in a higher concentration in YSZ at the interface to La$_{2}$Zr$_2$O$_7$. An analogous diffusion profile was observed by Khandkar and coworkers (7) for La$_{0.85}$Sr$_{0.1}$MnO$_3$.

The assumption of increasing chemical activity of Mn oxide due to the partial substitution of Sr for La is confirmed by considering some aspects of the phase diagram of the La-Sr-Mn oxide system. In previous investigations (26), it was found that only the Sr-free perovskite exists in a relatively large range of substoichiometry (cation ratio 0.8<A/B<1) while with increasing Sr substitution only a small A-cation deficiency was observed. Larger A-cation deficiency leads to precipitation of Mn$_3$O$_4$ as a second phase. At the phase boundaries between the single- and two-phase regions the chemical activity of manganese oxide becomes unity according to thermochemical considerations. The larger the distance from these phase boundaries in the single-phase region the lower is the chemical activity of manganese oxide.

The enhanced release of Mn$_3$O$_4$ from A-site-deficient and Sr-containing perovskites without YSZ (26) and the diffusion of Mn into YSZ might also be discussed with respect to the inadequate oxygen coordination number of the Mn$^{4+}$ ions in the perovskite system. The small radius of Mn$^{4+}$, 53 pm (27), does not fit very well into the octahedral oxygen surrounding given in the perovskite structure. Furthermore, a high amount of A-site substoichiometry, the Sr$^{2+}$ substitution or any zirconate formation enhancing the A-site substoichiometry, decreases the Mn$^{3+}$/Mn$^{4+}$ for electroneutrality reasons, beneath the possibility of oxygen release. Mn$_3$O$_4$ precipitation (26) or, as seen here in connection with YSZ, Mn diffusion will be the result of a stabilizing reaction. The diffusion investigations of Lau and Singhal (1) with non-doped stoichiometric
LaMnO$_3$ and YSZ are not a contrary result as LaMnO$_3$ is well known to have Mn$^{4+}$ ions and is better described by LaMnO$_{3+\delta}$.

The solubility of La$_2$O$_3$ in the SrZrO$_3$ layer was also detected by other EPMA investigations (11). This zirconate was formed by the reaction of YSZ and perovskites containing Co on the B-site. The high tolerance for host cations in perovskite structures is well known, whereas the pyrochlore composition La$_2$Zr$_2$O$_7$ seems to be replaceable only for small amounts on La lattice site places with very similar cations in size and valence (La$^{3+}$: 116 pm, Y$^{3+}$: 101.9 pm (27) for coordination number 8) but not for large cations with a lower valence than for Sr$^{2+}$ (126 pm).

REFERENCES

1. S. K. Lau and S. C. Singhal, Proc. Corrosion 85, Boston, March 1985, p. 345/1.
2. O. Yamamoto, Y. Takeda, R. Kanno and T. Kojuma, Proc. of the 1st Int. Symp. on SOFC, Florida 1989, p. 242.
3. G. Shen, O. Yamamoto, Y. Takeda and N. Imanishi in "Recent Advances in Fast Ion Conducting materials", B. V. R. Chowdari, Q. Liu and L. Chen, Editors, Singapore 1990, p. 395.
4. A. Mackor, T. P. M. Koster, J. G. Kraaijkamp, J. Gerretsen and J. P. G. M. van Eijk, Proc. of the 2nd Int. Symp. on SOFC, Athens 1991, p. 463.
5. H. Kaneko, H. Taimatsu, K. Wada and E. Iwamato, ibid, p. 673.
6. J. A. Labrincha, J. R. Frade and F. M. B. Marques, ibid, p. 684.
7. Khandkar, S. Elangovan, M. Liu: Solid State Ionics, 52, 57-68 (1992).
8. J. A. M. Roosmalen and E. H. P. Cordfunke, Solid State Ionics, 52, 303, (1992).
9. H. Taimatsu, K. Wada, H. Kaneko and H. Yamamura, J. Am. Ceram. Soc., 75, [2], 401, (1992).
10. G. Stochnioli, E. Syskakis and A. Naoumidis, Proc. on SOFC: "Materials, Process, Engineering and Electrochemistry", 5th IEA Workshop on SOFC, Jülich 1993, p. 25.
11. E. Ivers-Tiffeeé, M. Schießl, H. J. Oel and W. Wersing, Proc. of the 3rd Int. Symp. on SOFC, Hawaii 1993, p. 613.
12. G. Stochnioli, E, Syskakis, A. Naoumidis, K. Wippermann, W. Schaffrath and H. Nickel, Proc. of the 6th IEA Workshop, Rome 1994, p. 211.
13. G. Stochnioli, E. Syskakis, A. Naoumidis and H. Nickel, Proc. of the 2nd Int. Conf. on "Ceramics In Energy System", London 1994, p. 91.
14. G. Stochnioli, E. Syskakis, A. Naoumidis and H. Nickel, submitted to J. Am. Ceram. Soc.
15. B. C. H. Steele, Proc. of the 1st European Solid Oxide Fuel Cell Forum, Lucerne 1994, p. 375.
16. Y. Takeda, Y. Sakaki, T. Ichiwara, N. Imanishi, O. Yamamoto, M. Mori, N. Mori and T. Abe, Solid State Ionics, 72, 257 (1994).
17. L. Kindermann, D. Das, H. Nickel and K. Hilpert, these proceedings.
18. C. Clausen, C. Bagger, J. B. Bilde-Sørensen and A. Hornwell, 14th Risø Int. Symp. on Material Science 1993, p. 237.
19. H. Yokokawa, N. Sakai, T. Kawada and M. Dokya, J. Electrochem. Soc., 138, 2719 (1991).
20. H. Yokokawa, T. Horita, N. Sakai, T. Kawada and M. Dokya, Proc. of the 1st European SOFC Forum, Lucerne 1994, p. 425.
21. T. Kawada, N. Sakai, H. Yokokawa and M. Dokya, Solid State Ionics, 50, 189 (1992).
22. T. Kawada, N. Sakai, H. Yokokawa and M. Dokya, Solid State Ionics, 53-56, 418 (1992).
23. P. Bohac, A. Orliukas and L. J. Gauckler, Proc. of the 1st European SOFC Forum, Lucerne 1994, p. 651.
24. S. Widmer, K. R. Thampi, C. Revilliod and A. J. McEvoy, ibid, p. 681.
25. I. Voigt and A. Feltz, Solid State Ionics, 63-65, 31 (1993).
26. E. Syskakis, B. Robens and A. Naoumidis, J. de Physique IV, Colloque C7, Suppl. J. de Physique III, Vol. 3, 1429 (1993).
27. R. D. Shannon, Acta Cryst, A 32, 751 (1976).

1000
### Tab. I  Perovskite compositions and temperature/time treatments

| Composition           | Temperature / Time          |
|-----------------------|----------------------------|
| La$_{0.95}$MnO$_3$    | 1200°C: 400 h / 1400°C: 95 h |
| La$_{0.85}$Sr$_{0.1}$MnO$_3$ | 1200°C: 400 h / 1400°C: 95 h |
| La$_{0.6}$Sr$_{0.4}$MnO$_3$ | 1400°C: 200 h             |

### Tab. II  EPMA of YSZ diffusion zone in double-layer experiments with La$_{0.95-x}$Sr$_x$MnO$_3$ perovskites

| Experimental conditions | Sr content in La$_{y-x}$Sr$_x$MnO$_3$ | Diffusion length (µm) | Mass transfer (µg/cm$^2$) | Concentration at YSZ boundary (wt%) |
|-------------------------|----------------------------------------|-----------------------|--------------------------|-----------------------------------|
|                         | x(Sr)                                  | Mn       | La         | Mn       | La       | Mn       |
| Temperature Time        |                                       |          |            |          |          |          |
| 1200°C                  | 0.0                                    | 50       | 20         | 80       | 40       | 1.0      |
| 400 h                   | 0.1                                    | 70       | 25         | 390      | 90       | 2.6      |
| 1400°C                  | 0.0                                    | 60       | 30         | 250      | 70       | 2.3      |
| 95 h                    | 0.1                                    | 90       | 40         | 960      | 400      | 4.2      |

### Tab. III  Quantitative analysis (at.%) of reaction products at YSZ/perovskite interfaces after heat-treatments at 1400°C for 95 h and 200 h

| Perovskite               | Mn | Sr | Y  | Zr  | La  | Reaction Time (h) | Reaction Products  |
|--------------------------|----|----|----|-----|-----|-------------------|-------------------|
| La$_{0.95}$MnO$_3$       | 0.45 | --- | 1.40 | 18.2 | 16.3 | 95                | La$_2$Zr$_2$O$_7$ |
| La$_{0.6}$Sr$_{0.4}$MnO$_3$ | 1.6 | 17.6 | --- | 19.0 | 1.4  | 200               | SrZrO$_3$         |
Fig. 1. Step-scanning analysis

(a) YSZ - La_{0.6}Sr_{0.4}MnO_{3} annealed at 1400 °C for 95 h

(b) YSZ - La_{0.95}MnO_{3} annealed at 1400 °C for 200 h
Fig. 2. Line-scans across the interface

(2a) YSZ - La$_{0.95}$MnO$_3$ annealed at 1200 °C for 400 h

(2b) YSZ - La$_{0.95}$MnO$_3$ annealed at 1400 °C for 95 h
Fig. 2. Line-scans across the interface

(2c) YSZ - La$_{0.85}$Sr$_{0.1}$MnO$_3$ annealed at 1400°C for 95 h

(2d) YSZ - La$_{0.6}$Sr$_{0.4}$MnO$_3$ annealed at 1400°C for 200 h
Fig. 3. Diffusion profiles into YSZ for double-layered pellets with different perovskites.
