Addition of zirconia to the porous perovskite structure of a SOFC cathode reduces the cathode polarization by 60%. A conventional cell membrane equipped with this kind of cathode was fed with a fuel mixture of 50% hydrogen and 50% water vapor. With air on the cathode side it could be loaded at 850°C with 0.4 A/cm² at 0.7 V. The cell was characterized by taking current-voltage characteristics in the range of 750 to 950°C and at oxygen partial pressures of 0.01 to 1.0 bar. To separate the contribution of the cathode, impedance spectra were taken at rest potential and under increasing load within the same range of ambient conditions. The field of current-voltage characteristics of the cathode was constructed. The porous electrode model fitted to the impedance data showed that the electrode thickness is well adapted to the structure. With an electrolyte material of higher ionic conductivity it should be possible to improve the cathode further.

INTRODUCTION

At Siemens an analysis of the costs for investment and operation of power plants based on Solid Oxide Fuel Cells (SOFC) led to the conclusion that the cells have to run on natural gas and air at a voltage of 0.7 V and a current density of at least 0.3 A/cm². To reduce the power consumption of the blower which maintains the air flow on the cathode side, the oxygen utilization should be as high as 50%. On the other hand, today, Siemens SOFC stacks operate at 950°C, a temperature 100°C too high to allow the use of cheap, commercially available metals for the bipolar plates and the heat exchangers. As the overall cell resistance of a Siemens SOFC membrane is dominated by the cathode, it is this component which has to be improved first. The resistance of a „new“ cathode should not surpass 0.3 Ωcm² under the worst operating conditions, that is at a temperature of 800°C and in a mixture of 10% oxygen in nitrogen.

The Siemens SOFC /1/ is based on an electrolyte of 8 mole% yttria stabilized zirconia (8YSZ), with a thickness of about 150 μm and an area of 5x5 cm² or 10x10 cm². The electrolyte is coated by screen printing with 30 to 60 μm thick porous ceramic electrodes (size 4x4 cm² resp. 9x9 cm²). The anode consists of a Ni-8YSZ-cermet with equal volume parts of Ni and YSZ in the solid. Such an assembly of cathode, electrolyte and anode is called a MEA (Membrane Electrolyte Assembly).
Until recently, the cathode was made from a layer of the A-site deficient perovskite La$_{0.75}$Sr$_{0.2}$MnO$_3$ (LSM) yielding a polarization of 0.7 Ω cm$^2$ at 850°C in air. Investigations into SOFC cathodes carried out at Siemens and based on oxygen exchange measurements /2/ showed, that this perovskite is a poor ionic conductor. Accordingly, the penetration depth of the electrochemical oxygen reduction reaction was calculated to be less than 1 μm. The remaining thickness (30 μm) of this kind of cathode worked as an electronic current collector. To improve this, a cathode with enhanced oxygen ion conductivity was prepared by addition of 8YSZ-electrolyte to the LSM /3/. This new type of cathode was applied to electrolyte sheets and characterized by optical microscopy of cross sections and by electrochemical methods as described below.

EXPERIMENTAL

The electrochemical measurements were performed using cells of a reduced electrode area by screen printing electrodes of 1.0x1.0 cm$^2$ into the middle of a 5x5 cm$^2$ - or a 2x2 cm$^2$-electrolyte sheet. Two types of cell structures were investigated: the already described „complete“ MEA-type (anode/5 x 5 cm$^2$ -electrolyte/cathode) and the type of the „symmetric“ cathode cell structure (cathode/2x2 cm$^2$ electrolyte/cathode).

The MEAs were mounted into a housing made from alumina with a gold seal around the circumference of the electrolyte sheet to keep anode and cathode gas flow separated from one another. On the cathode side the electrical contact was established by a gold grid fixed to gold current and voltage leads and on the anode side by a comparable arrangement made from nickel. The grids were pressed to the electrodes by a load of 420 g placed on top of the alumina housing. The gas supply of both electrodes was by channels, which were machined into those parts of the housing that were pressing against the contact grids. The channels were connected to the anode and cathode gas supply, resp..

The symmetric cathode cells were prepared and electrically connected in analogy to the MEAs. Only the gas supply was different: simply two cubes of alumina, each with a channel structure in one surface, were pressed against the contact grids of gold on both sides of the cell. The arrangement was placed into a gas tight muffle of alumina heated by a furnace. Both electrodes were in contact with the gas atmosphere inside the muffle. The muffle was flushed with the reaction gas, and here the oxygen activity was controlled by a zirconia probe. The gas within the channels adjacent to the electrodes remained unstirred.

The electrochemical measurements were performed using an electrochemical interface 1286 and a frequency response analyzer 1255 both from Solartron or the electrochemical measurement device IM6 from Zahner elektrik. In case of the MEA type cells, current-voltage characteristics were taken as well as impedance measurements at rest potential and at a number of points along the current-voltage
characteristic. Symmetric cathode cells were only investigated by impedance spectroscopy at rest potential, to guarantee the symmetry of the system. All impedance measurements were performed with an amplitude of 10 mV to keep the system within the linear region.

Different ambient conditions were applied to the cell: the temperature was varied in the range of 750 to 950°C and the oxygen partial pressure on the cathode side was varied from 0.01 to 1 bar by mixing oxygen with nitrogen or helium. (When nitrogen is exchanged with helium the diffusion coefficient within the gas changes by a factor of 3.6; by this way gas diffusion effects can be identified).

With MEAs the cathode gas flow was fixed to 1000 sccm/min to keep the oxygen utilization under load below 5% even at high dilution of oxygen. In this case the anode side was always flushed with the same gas mixture of 50% hydrogen and 50% water vapor, prepared by passing hydrogen through a membrane humidifier. The flow rate was 500 sccm/min. There are two reasons for using this kind of fuel gas: firstly, for thermodynamic and kinetic reasons, this mixture is much more comparable to a technical fuel gas than „dry“ hydrogen and secondly, the anode polarization which in dry hydrogen may dominate the overall cell resistance is at minimum with this mixture /4/.

RESULTS AND DISCUSSION

The cross-section of a LSM-YSZ-cathode layer is shown in fig. 1. The porous structure has a thickness of about 30 μm. It is impossible to distinguish between the LSM and YSZ particles. In fig. 2 the perovskite within this layer has been removed by etching in hydrochloric acid, so that the zirconia structure is left. Its resistance against scratching shows, that the zirconia particles are firmly sintered to one another and to the electrolyte sheet. This is an important prerequisite for good ionic conduction within the cathode structure. A severe disadvantage of such a mixed cathode layer is its high electronic sheet resistance of about 50 Ω. To avoid an inhomogeneous current distribution across the cell this value must be lowered to a few Ω. This is achieved by an additional porous LSM layer working as a current collector. A cross-section of this bilayer electrode is shown in fig. 3. Here the thickness of the working layer is 20 μm, that of the current collecting layer is about 35 μm. The porosity is varying from 30 to 40%. The kinetic properties of this kind of bilayer cathode were been investigated by means of MEAs and symmetrical cells.

Fig. 4 shows the voltage-current-curves of a MEA taken at 850°C and at various oxygen partial pressures on the cathode side. In all cases the open circuit voltages are equal to the thermodynamic values. Operated with air, the cell can be loaded with a current density of 0.4 A/cm² at 0.7 V. To reach the same load conditions, former cathodes made from pure LSM had to be operated at 950°C.
A typical impedance spectrum of a MEA is plotted as a Nyquist diagram in Fig. 5. Two relaxations are clearly separated. The low frequency arc (20 Hz) is mainly due to the cathode. A contribution from a gas diffusion effect of the anode side in the 10 Hz range has only a negligible amplitude under the prevailing operating conditions /4/. The high frequency arc is caused by the anode. This statement is supported by comparing the spectrum of the MEA at open circuit potential with the spectrum of a symmetrical cathode cell (fig. 5). The operating conditions for the symmetrical cell were the same as those for the cathode in the MEA. To account for the fact that the spectrum of the symmetrical cell includes the contributions of two cathodes in series, their relaxation amplitudes have been divided by two. It is obvious that the cathode yields only a small signal in the high frequency range (10 kHz).

For further analysis all spectra have been fitted by the following model:

\[
Z_{\text{POR}} = \sqrt{R_p \cdot Z_{\text{CT}}} \cdot \coth \sqrt{\frac{R_p}{Z_{\text{CT}}}}
\]

\[
Z_{\text{POR}}: \text{impedance of the porous electrode (DC value: } R_{\text{POR}})\]
\[
R_p: \text{integral resistance of the electrolyte within the electrode}\]
\[
Z_{\text{CT}}: \text{integral charge transfer impedance (DC value: } R_{\text{CT}})\]  

As an example Fig. 6 shows, how the model fits the measured data. It must be emphasized that this linear model of the porous electrode can only describe the electrode in a load range where the charge transfer kinetic is linear. This is the case at open circuit and low currents. Nevertheless, the model was applied also to the spectra recorded under load, but only with the objective to determine the DC amplitudes of the anode and the cathode relaxation, resp. This is justified as the relaxations stay well separated from one another even under load.

The DC amplitude of the cathode relaxation of a MEA is equal to the slope of the current-voltage characteristic of the cathode at the same current. Taking the DC amplitudes of the cathode relaxation as a function of the load, it is possible to construct
the current-voltage characteristic of the cathode. This procedure was applied to the complete set of impedance data which were recorded for every measured value of the current within the field of current-voltage characteristics of a MEA taken at 750 to 950°C and under oxygen partial pressures (on the cathode side) ranging from 0.01 to 1.0 bar. The results are given by the figs. 7, 8 and 9. Fig. 9 shows, that even at 750°C and in 10% oxygen the bilayer cathode yields a current density of 125 mA/cm² at a polarization of 127 mV, corresponding to an average resistance of 1.0 Ωcm². In 10% oxygen at 850°C the resistance dropped to 0.26 Ωcm².

The influence of gas diffusion polarization can be identified clearly at an oxygen pressure of 0.05 bar and lower: in Fig. 7 and 8 the corresponding voltage-current characteristics are shown twice: in one case they are based on data measured with nitrogen as inert gas, in the other case they are based on data measured with helium. The diffusion coefficient calculated from literature data /5/ increases by a factor of 3.6 when a nitrogen/oxygen mixture is changed to a helium/oxygen mixture. In the experiment a voltage drop of 15% (or 6 mV at 0.25 mA/cm²) at 950°C and of 10% (or 9 mV at 0.25A/cm²) at 850°C is observed. At 750°C (Fig. 9 ) no effect is established. This is explained by the weak temperature dependence of a gas diffusion polarization in contrast to the resistance of the activated processes within the cathode. The location of the gas diffusion polarization on the cathode side is still subject to further investigations. But under technical operating conditions (oxygen partial pressure ≥ 0.1 bar) the influence of gas diffusion on the cathode side can be neglected.

The porous electrode model was applied to fit the impedance data of a MEA taken at open circuit at various temperatures and oxygen partial pressures. Thus the dependence of the parameters R_P and R_CT on temperature and oxygen partial pressure is determined.

The activation energy for ionic conduction within the porous YSZ matrix of the working layer of the cathode is derived from the Arrhenius plot of fig. 10. The activation energy is changing from 0.77 eV to 1.1 eV depending on temperature and oxygen partial pressure. But in pure oxygen the activation energy (0.77 eV) is found to be temperature independent and close to the value of that of the electrolyte sheet (0.77 eV).

The activation energy of the charge transfer resistance is about 1.4 eV in oxygen and air (fig. 11). This is significantly less than the value of 2 eV observed with symmetric cells and with MEAs which have not been „activated“ by a DC current (a value as high as 2 eV for the activation energy of the charge transfer resistance was also reported by /2/ and /7/). It has to be mentioned here, that a MEA which operates the first time under load, shows the phenomenon that the cathode polarization slowly decreases until this improvement finally subsides. With the bilayer cathode, the effect is of minor importance at 950°C but at lower temperatures the cathode activation may last several days or even more, so that it is hard to establish the steady state. As such an activation procedure may not be applied to a symmetrical cell, the cathodes of such a cell remain
comparable to the cathode of a not activated MEA. Only at 950°C a symmetrical cell and a MEA which was loaded prior to the impedance measurement at rest potential yield comparable impedance spectra.

Fig. 12 and 13 show the dependence of the resistance of the porous electrolyte and of the charge transfer resistance on the oxygen partial pressure. The first parameter hardly depends on partial pressure at 850 and 950°C. At 750°C the dependence could be like $p^{1/2}$. The oxygen pressure dependence of the charge transfer reaction is approximately $p^{1/2}$ at 750°C but at higher temperatures, the results do not fit to a simple power law. Considering these results one has to keep in mind, that the kinetic parameters derived from fitting the porous electrode model to the impedance data become uncertain at a high temperature (950°C) and low oxygen partial pressure. In this case, gas diffusion is of increasing importance, but the applied model cannot account for this effect.

Considering the design of the bilayer cathode an important parameter characterizing the structure of the working layer is the optimum thickness $d_{110}$. It is defined here by the condition that for a working layer with the thickness $d_{110}$, the corresponding value of $R_{\text{POR}}$ be only 10% larger than that for an infinitely thick working layer. This yields

$$d_{110} = 1.52 \cdot d \cdot \sqrt{\frac{R_{\text{CT}}}{R_p}}$$

[2]

Here $d$ denotes the actual thickness of the working layer. For the bilayer cathode investigated here, the optimum thickness $d_{110}$ is plotted in fig. 14 as a function of the oxygen partial pressure for various temperatures. It is obvious that for the technical application (oxygen pressure $\geq$ 0.1 bar) the optimum thickness of the working layer is for all temperatures above 750°C lower than 20 μm. Therefore the actual thickness of the working layer, which is just 20 μm, is sufficient and a further increase of the thickness would not result in a decrease of its polarization.

CONCLUSIONS

The described bilayer cathode is considered as an essential step towards a SOFC cell which is able to operate in the temperature range from 750 to 900 °C and at oxygen partial pressures as low as 0.1 bar as derived from requirements of system cost and efficiency. The simple porous electrode model showed to be useful to analyze the polarization of this kind of electrode. With the so far prepared structure of the working layer the optimum thickness is already realized. It is expected, that a further improvement can be achieved by replacing the 8YSZ in the working layer by an electrolyte material with higher ionic conductivity. In this case the optimum thickness of the working layer may increase. Finally, as the cathode resistance is now comparable
or even smaller than the resistance of the electrolyte sheet, this component has to be improved as well.

ACKNOWLEDGMENTS

This work was partially funded by the German Federal Ministry for Education and Research under project number 03M27478.

REFERENCES

1. W. Wersing, E. Ivers-Tiffée, M. Schiessl, H. Greiner, International Symposium on Solid Oxide Fuel Cell, Nagoya/Japan, 1989, p.21.
2. E. Wessel, Untersuchungen zur Festkörperdiffusion und zum Oberflächenaustausch von Sauerstoff an keramischen Mischleitern für Kathoden in Hochtemperaturbrennstoffzellen, thesis, University of Dortmund, 1995.
3. We thank N. Landgraf, R. Männer and H. Schichl for the preparation of the cells.
4. J. Geyer, H. Kohlmüller, H. Landes, R. Stübner, these proceedings.
5. K. Mund, G. Richter, F. von Sturm, J. Electrochem. Soc., 124, p.1 (1977).
   H. Göhr, J. Söllner, H. Weinzierl, 34th I.S.E. Meeting Erlangen 1983, Poster 0715, (1983).
6. Landolt-Börnstein, Zahlenwerte und Funktionen, 6. Aufl., Band 2, Teil 5a, Springer Verlag, Berlin 1969.
7. M. Juhl, S. Primdahl, C. Manon, M. Mogensen, J. Power Sources, 61, p.173 (1996).
Fig. 1: Cross-section of a zirconia containing cathode layer.

Fig. 2: Cross-section of a zirconia containing cathode layer, etched in hydrochloric acid.

Fig. 3: Cross-section of a bilayer cathode.
Fig. 4: Current-voltage characteristics of a MEA with a bilayer cathode at 850°C.

Fig. 5: Impedance spectrum of a MEA in comparison with that of a symmetric cathode cell both taken at 950°C, p(O₂)=1 bar and rest potential.

Fig. 6: Impedance spectrum of a MEA and fitted model curve, 850°C, p(O₂)=0.21 bar, rest potential.
Fig. 7: Voltage-current characteristics of a bilayer cathode at 950°C and at different oxygen partial pressures adjusted by mixing with N₂ or He.

Fig. 8: Voltage-current characteristics of a bilayer cathode at 850°C and at different oxygen partial pressures adjusted by mixing with N₂ or He.

Fig. 9: Voltage-current characteristics of a bilayer cathode at 750°C and at different oxygen partial pressures adjusted by mixing with N₂ or He.

Fig. 10: Arrhenius plot of the resistance of the electrolyte within the cathode at different oxygen partial pressures.
Fig. 11: Arrhenius plot of the charge transfer resistance of the cathode at different oxygen partial pressures.

Fig. 12: Dependence of the resistance of the porous electrolyte within the cathode on oxygen partial pressure.

Fig. 13: Dependence of the charge transfer resistance within the cathode on oxygen partial pressure.

Fig. 14: Dependence of the optimum working layer thickness on the oxygen partial pressure.