ELECTROCHEMICAL BEHAVIOR OF PEROVSKITE CATHODES MADE BY WET POWDER SPRAYING

K. Wippermann*, U. Stimming*,
H. Jansen**, D. Stöver**

*Inst. of Energy Process Engineering (IEV)
**Inst. of Applied Material Research (IAW)
Research Centre Jülich, D-5170 Jülich, Germany

ABSTRACT

The electrochemical behavior of La(Sr)MnO₃ cathodes made by wet powder spraying (WPS) was investigated in dependence on sintering temperature, working temperature and oxygen partial pressure. Under practical conditions of a high temperature fuel cell, the electrocatalytic activity of the cathode is good, with exchange current densities of about 500 mA/cm². The pre-exponential factors of oxygen reduction and oxygen evolution increase with overpotential, while the activation energy is potential independent for oxygen reduction and increase with overpotential for oxygen evolution.

1. INTRODUCTION

In investigating the electrochemical behavior of the high temperature fuel cell cathode it is important to vary temperature and oxygen partial pressure. This allows one to obtain fundamental information concerning the reaction mechanism of oxygen reduction and oxygen evolution. In addition, due to temperature and pressure gradients in the fuel cell stack the dependence of the current density on these parameters has to be known.

Besides the parameters of temperature and oxygen partial pressure, the geometry and chemical composition of the reaction zone, i.e. the so called 'triple contact zone', has a dominating influence on the rate constant of the oxygen exchange reaction. Hence, the fabrication parameters like sintering temperature, which determine the morphology and chemical composition of the cathode, are of great importance, as will be shown in this paper.
2. EXPERIMENTAL

The cathodes were prepared by Wet Powder Spraying (WPS), which is a new technique for the production of porous ceramic or metallic layers (1). By using a mask technique, cathode discs with a diameter of 10mm were sprayed onto the electrolyte. The latter was composed of 8mol% stabilized ZrO₂ (made of Tosoh TZ-8Y powder, fabrication by tape casting) and had a thickness and a diameter of 130μm and 19.5mm, respectively. The La₁₋ₓSrₓMnO₃ cathodes investigated in this paper had a strontium content of x=0.16, a thickness of about 50μm and a porosity of about 30%.

As can be seen from Fig.1, the counter electrode, which was painted on the electrolyte using platinum paste (Demetron 308A) had a diameter of only 8mm. This geometry provides a minimization of the ohmic drop in the electrolyte, because the potential difference of the equipotential lines at the reference electrode, which was made by a ring of platinum paste, and the equipotential lines at the working electrode is very small, in the case of the above geometry less than 1mV. This result was obtained from a mathematical study of the current and potential distribution in the electrolyte varying the ratio of the diameter of the working electrode and the counter electrode and is especially important for thin electrolytes. For further details, see (2).

The variation of the oxygen partial pressure was achieved by applying appropriate mixtures of either air and argon or oxygen and argon. Most of the measurements were carried out under symmetrical conditions, that means under the same oxygen partial pressure on both sides of the electrolyte. Only in the case of low oxygen partial pressures at the cathode, i.e. the working electrode, air atmosphere was applied at the counter electrode. In this case, a gold sealing was necessary in order to separate the working electrode and the counter electrode chambers.

With the three-electrode cell described above, steady state and potentiodynamic current/potential measurements as well as impedance measurements were performed using a Solartron 1286 electrochemical interface and a Solartron 1255 frequency response analyzer. The ac excitation voltage was always 10mV. The impedance measurements were analyzed with the computer program 'Equivalent Circuit' (3). A correction of the current/potential curves due to ohmic resistances was not necessary because the ohmic loss in the electrolyte was eliminated by the cell geometry described above and other ohmic resistances like contact resistances were negligible.
3. RESULTS

From the temperature dependence of the current density of oxygen reduction and oxygen evolution, which was investigated in a range of $T=800-1000^\circ\text{C}$ (Fig.1), Arrhenius plots were obtained from which the activation energies and the pre-exponential factors were calculated for different overpotentials. For both reactions, the pre-exponential factors increase with overpotential while the activation energy is potential independent for oxygen reduction and increase with overpotential for oxygen evolution. This result appears to be in contradiction to the 'classical' theory of charge transfer, where the electrode potential is considered to modify the activation barrier in such a way, that the activation energy of oxygen reduction is decreased with increasing cathodic overpotential, while the activation barrier of oxygen evolution is decreased with increasing anodic overpotential. Moreover, the pre-exponential factor should not be influenced by the overpotential.

The influence of oxygen partial pressure was investigated in a range of $p_{\text{O}_2} = 0.01$-1bar. Fig.2 shows Tafel plots of oxygen reduction and oxygen evolution in dependence on the oxygen partial pressure. From a double logarithmic plot of $i$ vs. $p_{\text{O}_2}$, a reaction order of 0.63 for oxygen reduction and 0 for oxygen evolution is obtained. Furthermore, a plot of the logarithm of the exchange current density, $\log i_0$ vs. $\log p_{\text{O}_2}$ shows a slope of $m=0.39$. According to Winnubst et. al. (4), with a cathodic transfer coefficient $\alpha_c = 0.5$ and an anodic transfer coefficient of $\alpha_a = 1.5$, $m_{\text{th}}$ should be 0.375, if atomic oxygen is involved in the rate determining step but $m_{\text{th}} = 0.75$, if electrons are transferred to molecular oxygen in the rate determining step.

Additional information about the oxygen exchange reaction is obtained from impedance spectroscopy. Fig.3 shows Nyquist plots of the electrode impedance in a frequency range of $10^{-1}$-$10^4$Hz at equilibrium potential ($\eta=0$), and cathodic overpotential ($\eta = -0.2V$). In dependence on the overpotential, three ($\eta = -0.2V$) or four ($\eta = 0V$) depressed semi-arcs can be distinguished, which are mostly capacitive loops, but also inductive at low frequencies. According to the results of van Hassel et.al. (5), the best computer fit data are obtained assuming an equivalent circuit as shown in Fig.4: Here, a double layer capacitance ($C_{\text{dl}}$) is in parallel with a charge transfer resistance ($R_{\text{ct}}$) and a series of parallel combinations of three Resistances (R2-R4) and Constant Phase Elements (CPE2-CPE4). While the CPE1 at high frequency is interpreted as the double layer capacitance of 2-50 $\mu\text{F/cm}^2$, the other constant phase elements at lower frequencies are assumed to result from a concentration impedance of adsorbed oxygen species like $\text{O}_{\text{ad}}$ or $\text{O'}_{\text{ad}}$. As pointed out by van Hassel et.al. (5), inductive loops can be related to the stepwise transfer of electrons to adsorbed intermediates. Because the value of the charge transfer resistance ($R_{\alpha} = 0.24\Omega$...
at \( \eta = -0.2V \) to 0.42\( \eta \) at \( \eta = 0V \) is in the same range as the sum of the concentration resistances \( R2-R4 \), the rate of the oxygen exchange reaction is determined not only by charge transfer but also by another process, which may be adsorption or surface diffusion of intermediates.

As can be seen from Fig.5, where Tafel plots of oxygen reduction for three different sintering temperatures are shown, the influence of sintering temperature \( T_s \) is remarkable: By decreasing the sintering temperature from 1500°C to 1200°C, the current density increases by five orders of magnitude! A tentative explanation of this result can be obtained considering scanning electron micrographs of cross sections of the interface electrode/electrolyte (Fig.6): Due to the sintering process, the average diameter of the contact points between the electrode and the electrolyte increases from about 0.1\( \mu \)m at \( T_s = 1200°C \) to 5\( \mu \)m at \( T_s = 1500°C \). Parallel, the length of the reaction zone per unit area decreases from \( 2 \times 10^5 \) cm\(^{-1} \) to \( 2 \times 10^3 \) cm\(^{-1} \). If the current is normalized to the length of the reaction zone, the current densities for sintering temperatures of 1200°C and 1300°C differ only by a factor of three, whereas the current density at a sintering temperature of 1500°C remains 2-3 orders of magnitude lower. The latter can not be explained by a simple geometric effect; it is rather due to a diminished catalytic activity of the electrode material, resulting from the formation of insulating phases like \( La_2Zr_2O_7 \).

4. DISCUSSION

As shown above, perovskite cathodes made by Wet Powder Spraying show a good electrocatalytic performance under practical conditions of a high temperature fuel cell. In order to further improve these cathodes, more fundamental information about the reaction mechanism of the oxygen exchange reaction is necessary. The results of the potential and temperature dependence of the reaction together with results of the dependence on the oxygen partial pressure suggests a reaction mechanism, that proceeds via oxygen adsorption, oxygen dissociation, subsequent surface diffusion of atomic oxygen species and charge transfer (6). Together with the results from impedance measurements, it can be concluded, that the overall reaction rate is determined not only by charge transfer, but by competition of charge transfer with additional reaction steps like adsorption of oxygen on the electrode surface or surface diffusion of adsorbed oxygen species.
ACKNOWLEDGEMENTS

The authors thank T. Lennartz for carrying out the electrochemical experiments.

REFERENCES

1. A. Ruder, H.-P. Buchkremer, H. Jansen and D. Stöver, Surface & Coatings Technology, 53, 71 (1992).
2. H.G. Baunach, Diplomarbeit, RWTH Aachen (1992).
3. B.A. Boukamp, 'Equivalent Circuit', Internal Report CT89/214/128, University of Twente (1989).
4. A.J.A. Winnubst, A.H.A Scharenborg and A.J. Burggraaf, Solid State Ionics, 14, 319 (1984).
5. B.A. van Hassel, B.A. Boukamp and A.J. Burggraaf, Solid State Ionics, 48, 155 (1991).
6. E.J.L. Schouler and M. Kleitz, J. Electrochem. Soc., 134, 1045 (1987).
Fig. 1: Tafel plots for oxygen reduction and oxygen evolution, 
T = 800, 900 and 1000°C
La$_{84.16}$Sr$_{1.16}$MnO$_3$ / $T=1000^\circ$C

$E (E_{Air}) / V$

$lg [i ii (A/cm^2)]$

$p_{O_2} = 1$ bar

0.1 bar

0.01 bar

Fig. 2: Tafel plots for oxygen reduction and oxygen evolution, $p_{O_2} = 0.01$, 0.1 and 1 bar
Fig. 3: Nyquist plots of impedance measurements (Δ) and fit data (-), η = -0.2 and 0V, frequencies indicated in Hz

Fig. 4: Equivalent Circuit corresponding to the impedance measurements of Fig. 3
Fig. 5: Tafel plots for oxygen reduction, $T_s = 1200, 1300$ and $1500^\circ$C.
Fig. 6: Scanning electron micrographs of cross sections of the electrode/electrolyte interface, $T_s = 1200$ and $1500 ^\circ C$