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The course of O₂ partial pressure and electric potential across an oxide electrolyte cell

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INTRODUCTION

The basic theory for the description of solid oxide cells is in principle well developed; see e.g. the book of J. Maier [1]. In spite of this, well-respected authors are regularly publishing papers, which give erroneous conclusions, e.g. build-up of extremely high pressures of oxygen pressures inside an electrolyte if a cell is bad [2]. The reason for the errors is not always clear, and thus, it seems useful to do a detailed presentation of the course of the relevant potentials across the cell, such as the electrical potential, the electrochemical potential of electrons, and the oxygen partial pressure in pores (if present) in the electrolyte.

ARGUMENTS AND RESULTS

As in cells with liquid electrolytes there is an electrical double layer at both electrode/electrolyte interfaces. The electrical potential has in general a large jump at such an interface. In case of an unloaded cell all of the potential difference of about 1 V is taking place at the two interfaces. This is a consequence of the fact that there is no change in the oxygen stoichiometry across the electrolyte of a solid oxide cells (SOFC) using good oxide ion conducting electrolytes such as yttria stabilized zirconia (YSZ). This is in turn known from the fact that YSZ is thermodynamic stable over a potential difference of about 2 V. Thus, the course of the potential across an SOFC at open circuit voltage (OCV) looks in principle like in Figure 1 with no electrical potential gradient inside the electrolyte.
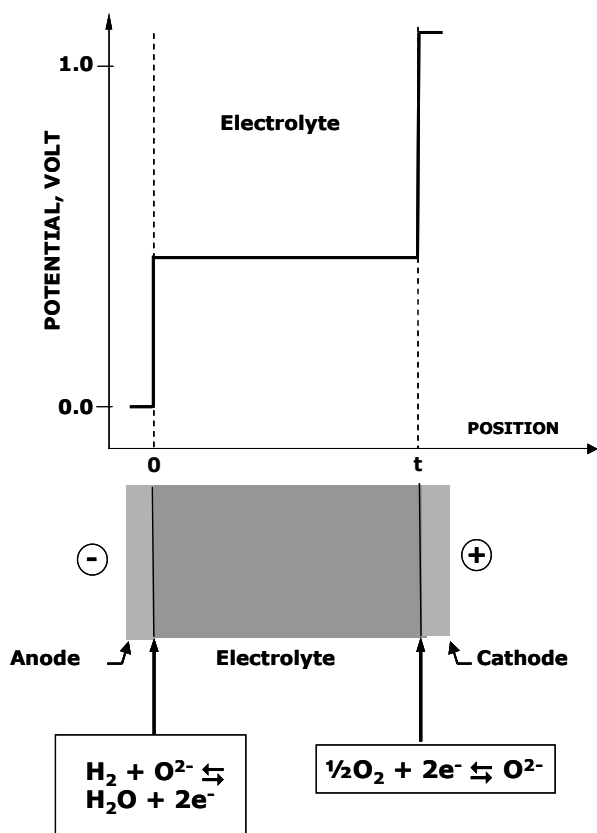

Figure 1. The course in principle of the electrical potential across an SOFC at OCV. t is the electrolyte thickness.

When SOFC is loaded the situation looks as in Fig. 2. The supply of electrons through the external current decreases the potential at the cathode and the O₂-reduction "pushes" extra O²⁻-ions into the electrolyte, which locally becomes more negative. The equivalent oxidation process makes the electrolyte more positive next to the anode. Thus, the potential difference, which drives the O²⁻-ions through the electrolyte, is created.
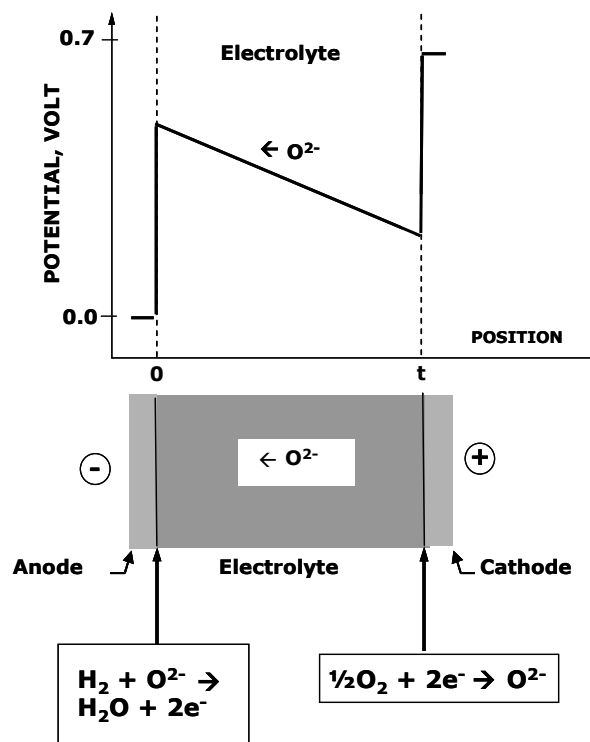

Figure 2. The course in principle of the electrical potential across a solid oxide fuel cell under an electrical load with a significant current density. The slope of the line inside the electrolyte is determined by the current density and the ionic conductivity of the electrolyte only. t is the electrolyte thickness.

It is noted that all solid electrolytes will have a small electron conductivity. The local oxygen partial pressure (in small pores) through the electrolyte is determined by the electrochemical potential of the electrons. This is the potential that goes into the Nernst equation in order to calculate the oxygen pressure; not the electrical potential. In the full paper more detailed examples of the quantitative potential courses will be given for zirconia based SOFCs.

REFERENCES

[1] J. Maier, Physical chemistry of ionic materials, Ions and electrons in solids, John Wiley and Sons, Chichester, GB (2004).
[2] A.V. Virkar, *J. Power Sources*, **172**, 713–724 (2007).

ACKNOWLEDGEMENTS