ELECTROCHEMICALLY INDUCED SPILLOVER AND DIFFUSION ON PT(111): PEEM IMAGING, KINETIC MODELING AND THE NEMCA EFFECT

C. Hellwig[1], E. Mutoro[2], B. Luerßen[2], J. Janek[2], W. G. Bessler[1]
[1]German Aerospace Center (DLR), Institute of Technical Thermodynamics, Stuttgart, Germany
[2]Justus-Liebig-Universität, Institute of Physical Chemistry, Giessen, Germany

wolfgang.bessler@dlr.de

Keywords: EPOC, NEMCA, spillover, diffusion, PEEM, modeling

Introduction

Electrochemically induced oxygen diffusion on electrode surfaces plays an important role in solid state electrochemistry, especially in the context of electrochemical promotion of catalysis (EPOC), also referred to as non-faradaic electrochemical modification of catalytic activity (NEMCA) [1]. The $Pt(O_2)|YSZ$ system is a model system in solid state electrochemistry as well as for EPOC studies. Here, the so-called "spillover oxygen" is generated at the three-phase boundary of solid electrolyte (YSZ, yttria-stabilized zirconia), electrode (Pt) and gas phase during anodic polarization and diffuses onto the electrode surface. While spillover itself is a well-known phenomenon, the detailed mechanism of the NEMCA effect is still subject of discussion. In order to gain more insight into these processes we have performed a combined experimental and theoretical study.

Oxygen spillover experiments and modeling

The spreading of spillover oxygen was imaged by photoelectron emission microscopy (PEEM) on dense and epitaxial Pt film electrodes, prepared by pulsed laser deposition [2]. Experiments were carried out under ultra high vacuum (10^{-9} mbar) at temperatures between 700 K and 860 K. Two different models, an analytical solution of Fick's 2nd law of diffusion [3] and a numerical reaction-diffusion model [4], are used to obtain diffusion coefficients and activation energies from the experimental data. Results are shown in Fig. 1.

The analysis by Fick's 2nd law of diffusion is used as a first approximation as the boundary conditions are very simplified. The numerical reaction-diffusion simulation, which includes recombinative desorption of O_2 into the gas phase, results in an activation energy of 41 $kJ\cdot mol^{-1}$ and a preexponential factor of $2.0\cdot 10^{-6}$ $m^2\cdot s^{-1}$ for the oxygen diffusion coefficient.

Modeling NEMCA during CH_4 oxidation

The reaction-diffusion model that was validated against the PEEM experiments is used for elementary kinetic simulations of CH_4 partial oxidation over Pt. A surface kinetic mechanism by Deutschmann et al. was used [5]. Conditions were chosen to represent the NEMCA experiments by Tsiakaras and Vayenas [6]. The experimentally observed NEMCA effect during cathodic polarization could be qualitatively reproduced by the model.

Conclusions

A combined experimental and modeling study of oxygen spillover and surface diffusion was carried out. The diffusion coefficient of atomic oxygen on Pt(111) could be determined. The parameters were used to simulate the NEMCA effect in the case of CH_4 partial oxidation over Pt.

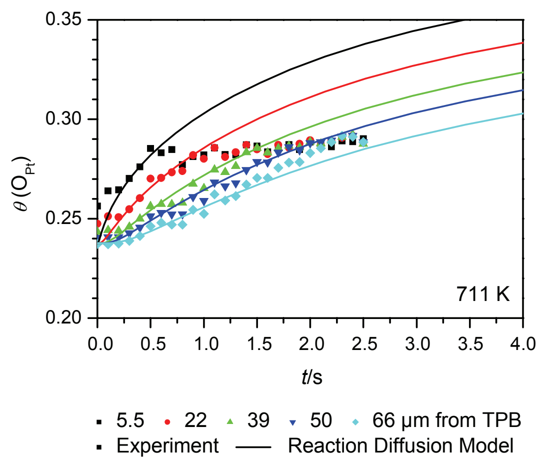

Fig. 1: Experimental and simulated surface coverages of atomic oxygen versus time after the application of voltage for different distances from the three-phase boundary (TPB).

References

[1] C. G. Vayenas et al., Electrochemical Activation of Catalysis, Springer 2002.
[2] G. Beck, H. Fischer, E. Mutoro, V. Srot, K. Petrikowski, E. Tchemychova, M. Wuttig, M. Rühle, B. Luerßen and J. Janek, Solid State Ionics 178 (2007) 327-337.
[3] B. Luerßen, E. Mutoro, H. Fischer, S. Günther, R. Imbihl and J. Janek, Angew. Chem. Int. Ed. 45 (2006) 1473-1476.
[4] W.G. Bessler, S. Gewies and M. Vogler, Electrochim. Acta 53 (2007) 1782-1800.
[5] O. Deutschmann, R. Schmidt, F. Behrendt and J. Warnatz, Proc. Combust. Inst. 26 (1996) 1747-1754.
[6] P. Tsiakaras and C.G. Vayenas, J. Catal. 140 (1993) 53-70.