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

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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(O₂)|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 O₂ into the gas phase, results in an activation energy of 41 kJ·mol⁻¹ and a preexponential factor of 2.0·10⁻⁶ m²·s⁻¹ for the oxygen diffusion coefficient.

Modeling NEMCA during CH₄ oxidation
The reaction-diffusion model that was validated against the PEEM experiments is used for elementary kinetic simulations of CH₄ 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 CH₄ 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