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On the variability of oxygen exchange kinetics of platinum model electrodes on yttria stabilized zirconia☆

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ABSTRACT

The electrochemical polarization resistance of the oxygen exchange reaction on yttria stabilized zirconia (YSZ) was investigated by means of geometrically well-defined dense platinum microelectrodes. The polarization resistance was found to be strongly affected by two different phenomena changing the electrode kinetics. One process is only observable in oxidizing atmosphere and was almost reversible (i.e. causes degradation as well as regeneration of the electrode performance). It is attributed to the formation/decomposition of a PtO_x “phase”. The second process leads to continuous degradation and is discussed to be related to impurities accumulating at the three phase boundary (TPB). The effects of both time dependent phenomena on the electrochemical oxygen exchange at the TPB and at the Pt|YSZ interface are analyzed by means of equivalent circuits. It can be shown that the PtO_x related degradation/regeneration affects both the TPB process as well as the electrochemical process at the Pt|YSZ interface. The impurity related degradation, however, is demonstrated to only influence the TPB kinetics.

1. Introduction

The system $Pt(O_2)$|yttria stabilized zirconia (YSZ) acts as a kind of model electrode in solid state electrochemistry and is—in terms of electrode kinetics—often considered to be a relatively simple surface path system. This means that only processes on surfaces are involved in the electrochemical reaction and that the region commonly referred to as three phase boundary (TPB) plays a crucial role in the oxygen exchange mechanism [1,2]. However, in several recent studies $Pt(O_2)$|YSZ was shown to be considerably more complicated than expected from theoretical considerations and therefore attracted renewed interest in basic research [3–20]. Beside its high fundamental relevance, Pt is discussed to be a suitable electrode material for micro-solid oxide fuel cells [21–25]. Therefore, an in-depth understanding of the oxygen exchange process is also of technological interest.

A controversially discussed question deals with the rate limiting process of oxygen exchange between gas phase and oxide ion conducting electrolyte. Results published in the past have been contradictory; some studies suggested a kinetically slow charge transfer step [26,27], while others discussed either oxygen adsorption on Pt or surface diffusion or a co-limitation of both to be rate limiting [28–32]. However, these studies were mainly performed on porous Pt electrodes which can lead to highly non-trivial electrochemical responses. To avoid the consequentially challenging data interpretation, well-defined model electrodes have successfully been introduced in solid state electrochemistry [33–40]. In such model systems—in contrast to porous paste systems—the geometry and the microstructure of the electrode can be varied in a defined manner allowing a less ambiguous interpretation of measurement results.

Unfortunately, Pt thin film electrodes turned out to be prone to time dependent changes often associated with an increase of the polarization resistance (referred to as degradation). One possible origin of such effects is the segregation of impurities [8,10,19]. For example, silicon tends to concentrate at the surface of single crystalline YSZ [41–43] and such processes are suggested to cause degradation phenomena especially in case of TPB-active electrodes [44,45].

Another source of changes in the electrode kinetics of $Pt(O_2)$|YSZ is associated with the evolution or decomposition of a PtO_x “phase” [5,6,16,17,46]. From adsorption investigations such a platinum “oxide” is already known to form at elevated temperatures from adsorbed oxygen species moving to the sub-surface region [47–49]. Since PtO_x is not a stoichiometric phase, it does not show a sharp decomposition temperature and its formation range seems to be relatively broad; discussed stability ranges are 800–1100 K [46], around 900 K [47] and 400–600 K [48]. Despite these discrepancies in published values, it is concordantly reported that the amount of oxygen stored in the subsurface region depends on the temperature. Furthermore, there are studies suggesting a connection between this platinum “oxide” and the impedance of the $Pt(O_2)$|YSZ model system

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[5,6,16,17] making it a relevant factor for any thermally induced change of the electrode behavior.

In our previous studies on model type Pt thin film electrodes on YSZ (100) three different faradayic and two capacitive current pathways could be separated [11–14,50]. These different pathways were experimentally characterized by electrochemical impedance and dc methods. In a temperature range of 550-900 °C and at equilibrium conditions (i.e. without additional dc bias) an electrode surface path with a diffusion limited TPB-process was identified [11–13]. Whereas at temperatures lower than 500 °C and at equilibrium conditions a pathway through the Pt electrode (with rate limiting oxygen diffusion along grain boundaries) is dominating [13,50]. Under high cathodic polarization these two pathways are outperformed by an electrolyte surface path with oxygen reduction at the free YSZ surface. In addition, the electrochemically active sites of the two latter faradayic pathways could be visualized by ^{18}O tracer incorporation and time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis [13,14].

In all the above mentioned studies, the rate limiting step of the electrode surface path at the TPB was found to strongly depend on the thermal pre-history of the samples. Both impurity segregation and changes in a PtO_x "phase" are potential causes for these observed polarization resistance changes. In the present study, thermally induced degradation and regeneration phenomena of Pt microelectrodes on single and polycrystalline YSZ were investigated in detail by impedance spectroscopy. Based on our previous experiences this experimental method exhibits the most effective way for tracking degradation/regeneration phenomena.

2. Experimental

2.1. Sample preparation and characterization

Platinum thin film microelectrodes were prepared by sputter deposition (MED 020 Coating System, BAL-TEC, Germany) of platinum (99.95% pure, ÖGUSSA, Austria) onto yttria stabilized zirconia (YSZ) electrolyte. Both YSZ (100) single crystals (9.5 mol% Y_2O_3, Crystec, Germany) and polycrystalline YSZ were used for this purpose. The polycrystalline YSZ substrates were produced from YSZ powder (8 mol% Y_2O_3, Tosoh, Japan) by isostatic pressing and sintering at 1550 °C for 2 h.

For platinum deposition the substrate was heated to 700–800 °C in $2 \cdot 10^{-2}$ mbar argon. At 100 mA sputter current typical film thicknesses of about 400 nm were obtained for approximately 10 min deposition time. The Pt films were micro-structured by standard photolithography (ma-N 1420 negative photoresist, micro resist technology, Germany) followed by an etching step in hot nitro hydrochloric acid. After etching, the samples were annealed for 48 h at 850 °C in air. For more details regarding the microelectrode preparation, the reader is referred to Refs. [11,12].

Scanning electron microscopy (FEI Quanta 200 FEG) was used to characterize the platinum microelectrodes—the resulting micrographs are shown in Fig. 1: (a) and (b) display freshly prepared electrodes on single crystalline and polycrystalline YSZ substrate, respectively. The thin films are dense but Pt grain boundaries are clearly visible, indicating a polycrystalline growth of the Pt film on both substrates. In Fig. 1(e) circular shaped microelectrodes of different diameters are shown. In the present study, 191 μm (largest), 91 μm (second largest) and 44 μm (fourth largest) electrodes were used. The Pt thin films remained virtually dense during the measurements as can be seen from Fig. 1(c) and (d) for electrodes on single and polycrystalline YSZ substrate, respectively (the dark dots in Fig. 1(c) are not pores but bubbles). Therefore the microelectrodes are considered to be sufficiently stable at given temperatures.

Further thin film characterization was done by x-ray diffraction (XRD) measurements on an X'Pert PRO Diffractometer (Panalytical) with copper anode and X'Celerator detector with a Ni-K_β-filter. The diffraction patterns in Fig. 2(a) and (b) were obtained on 400 nm thick annealed Pt films on single crystalline (100) and polycrystalline YSZ, respectively. The Pt films on YSZ (100) are exclusively, those on polycrystalline YSZ predominantly (111) oriented; the latter ones also exhibit some tiny reflexes of other Pt orientations. It should be noted that after annealing both types of samples also show some small peaks which could not be identified; a possible match was found with tetragonal YSZ or an Y_2O_3 phase. Enrichment of Y-rich phases and impurities at the surface of YSZ were also found by means of low energy ion scattering (LEIS) as reported in Ref. [42]. However, from our XRD-data an unambiguous phase identification is not possible so far.

2.2. Electrochemical characterization

Impedance spectroscopy measurements were performed at temperatures between 550 and 760 °C. A detailed description of the setup for such kinds of electrochemical measurements on microelectrodes at elevated temperatures is given in Ref. [13]. The impedance measurements were conducted using an Alpha-A High Performance Frequency Analyzer with a POT/GAL 30 V 2A test interface, which was run in ac mode (hardware and control software: Novocontrol, Germany). The recorded frequency typically ranged from 500 kHz to 50 mHz, but was adjusted if necessary; the root-mean-square value of the ac voltage was 10 mV (since this value is significantly lower than k_BT/e_0 we can safely assume a linear response). To avoid any polarization of the Pt electrodes by a possible thermovoltage, a pseudo 4-point measurement with a blocking capacitor was used; details are described in Ref [13]. In the main part of the study, impedance spectra were continuously recorded after reaching a certain temperature and the relations between the time dependence of the impedance and the measurement temperature or thermal pre-history were characterized. The measurements for a given set temperature were only conducted after a constant local temperature was reached. This temperature stability was examined from the spreading resistance caused by ion conduction in the electrolyte [11,13].

3. Results and discussion of phenomena changing the electrode kinetics

Electrochemical impedance measurements of Pt microelectrodes on single crystalline YSZ showed a distinct non-steady state behavior, and both increasing as well as decreasing polarization resistances could be observed within the measurement intervals. In the following these two changes are called degradation and regeneration, respectively. An exemplary measurement showing degradation after an initial regeneration is depicted in Fig. 3 (previous to the shown measurement at 746 °C the sample was annealed at about 650 °C). This and a number of other results (further discussion see below) suggested that in case of Pt on YSZ (100) two different processes are involved in the time dependent changes: A reversible one which leads to either degradation or regeneration and an irreversible one which causes a continuous degradation. In contrast to single crystalline samples, Pt electrodes on polycrystalline YSZ exhibited only the reversible process. It will be shown in the following that experiments using Pt thin film electrodes grown on both single crystalline YSZ (100) and polycrystalline YSZ enabled us to separate the corresponding processes and characterize them individually.

3.1. Pt electrodes on polycrystalline YSZ

Empirically it was found that long thermal pre-treatments of samples with polycrystalline electrolyte resulted in a stable polarization resistance without any indication of degradation or regeneration of the electrode impedance. After changing the temperature to values above and below the preceding annealing temperature, the electrodes exhibited regeneration and degradation, respectively. In Fig. 4 such a