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Oxygen reduction and oxidation at epitaxial model-type $Pt(O_2)/YSZ$ electrodes – On the role of PtO_x formation on activation, passivation, and charge transfer

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ABSTRACT

Epitaxial model-type platinum (Pt) film electrodes with a high three-phase boundary (tpb) density on single crystalline yttria-stabilized zirconia electrolyte, YSZ(1 1 1), are characterized electrochemically in air at a temperature of 673 K – which is comparatively low for the system $Pt(O_2)/YSZ$. By combining different electrochemical measurements including impedance spectroscopy (EIS) with and without applied potential bias, cyclic voltammetry (CV), and 'steady state' current-overpotential characteristics ($I–\eta$ curves) with different sample starting conditions, the impact of annealing time and pre-polarization on the polarization resistance and on the oxygen exchange rate are investigated in detail. A model, based on the electrochemical control of thermally grown Pt oxide, is suggested to explain the experimental results. It is assumed that Pt oxide passivates the electrode and decreases the electrocatalytic activity of Pt for the oxygen exchange reaction. Additionally, it is suggested that Pt oxide has a similar passivating effect as in aqueous electrochemistry, despite the higher temperature. Additionally, blocking impurities at the tpb and activating morphological changes are discussed. Together with the experimental results the model provides new insights in the observed electrode processes and offers routes to improve the electrode performance of $Pt(O_2)/YSZ$ at low temperature. This might be of significant interest e.g. for μ-solid oxide fuel cells (micro-SOFCs).

1. Introduction

Recently, there has been a revival of interest in the solid-state electrode system platinum (Pt)/yttria-stabilized zirconia (YSZ) driven by advances both in the field of low and intermediate temperature micro-solid oxide fuel cells (μ-SOFCs) [1–6] and in basic research [6–17]. Despite decades of research, a detailed understanding of the oxygen exchange mechanism and factors influencing the electrode kinetics and the electrocatalytic properties are still missing [18], especially at low and intermediate temperatures (the terms "low" (up to about 773 K) and "intermediate" (between about 773 K and 1073 K) are referred to their usage in the field of SOFCs, cf. [1,19,20]). This is all the more surprising, as the systematic and knowledge-based optimization of the electrode performance and an improvement of its long-term stability require a deeper understanding of the microscopic processes and their control.

Up to now, only a small number of reports are available on the oxygen reduction/oxidation (exchange) mechanism at low temperature [6,21–27], and often poorly defined Pt paste electrodes were utilized [21–23,25,26]. Rather, the dynamic behavior of Pt electrodes has been investigated typically at much higher temperatures (often between 1173 K and 1273 K) [28–32].

Driven by our previous investigation regarding the formation of Pt oxide [17] and first results about its influence on the oxygen exchange kinetics [16] we report in the present paper in detail on the oxygen exchange and electrode dynamics at 673 K in air – being a typical temperature in μ-SOFC studies. By utilizing a model-type film electrode and thereby reducing the complexity of the system, influencing factors on the oxygen exchange (time, polarization pre-conditioning with and without morphological changes) can be isolated.

Other reports suggest that the dissociative adsorption of oxygen on the electrode is the rate determining step (rds) at low temperature and ambient oxygen partial pressure conditions [21,33]. As a complication, the formation of Pt oxide on the electrode surface takes place [34–37], especially at steps on the Pt surface [38,39]. A high step density can be expected at the edges of a microstructured or porous Pt film, which form the three-phase boundaries (tpb), i.e. the sites where the oxygen exchange occurs [40,41]. Thus, Pt oxide at the tpb might have a strong (deactivating) influence on the electrode kinetics [33,42]. In fact, the formation of Pt oxide is known

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to have a passivating effect in aqueous electrolytes [43–45], being an observation which is typically disregarded in solid state electrochemistry. In addition, morphological changes of Pt electrodes on solid electrolytes can occur under strong anodic polarization and may lead to a decrease of the electrode resistance [46,47], which also has to be taken into account in discussing results of electrodes with large gas-tight areas.

The methodical approach applied in this study is explained in the following: in order to minimize the number of (potentially interfering) influencing factors, a Pt network forming a regular pattern of exclusively (1 1 1)-oriented Pt on a polished YSZ(1 1 1) single crystal (formed by partial dewetting at higher temperatures) has been used as electrode. This type of electrode provides a high density of tpb, and the well-defined structure allows the quantification of the tpb length per electrode area. First, the polarization resistance (R_{pol}) of these electrodes is determined at open circuit potential (*OCP*, $E = 0$ mV) as a function of time using electrochemical impedance spectroscopy (EIS). Due to the small excitation amplitudes typically used for this technique, the measurement does not change the electrode properties. Second, the influence of non-destructive polarization is studied by EIS, cyclic voltammetry (CV) and current-overpotential (I–η)-characteristics in the potential range of $-500\,\text{mV} < E < 100\,\text{mV}$, where no pronounced bias-induced irreversible changes of the samples are expected such as morphological changes of the Pt network or reduction of the YSZ. Third, the samples are exposed to a large anodic potential (up to $E = 500$ mV), which can cause morphological changes of the Pt network, and subsequently the properties of the electrode system are again investigated electrochemically. In summary, this approach allows to obtain information on the influence of time and different (pre-)polarization conditions. This helps to understand the influence of kinetic load on the performance of Pt(O_2)/YSZ electrodes.

2. Experimental

2.1. Sample preparation and characterization

Partly dewetted Pt electrodes were grown by pulsed laser deposition (PLD) on one-sided polished YSZ(1 1 1) single crystals (Crystec, Germany; 9.5 mol% Y_2O_3) using a Pt target (Ögussa, Austria; purity: 99.95%) and the following PLD parameters: wave length (λ) of 248 nm, pulse energy (E) of ~250 mJ, argon background pressure (p_{Ar}) of $\sim 10^{-2}$ mbar, and a distance between target and substrate (d) of ~4.5 cm. Dewetting of the Pt film was caused by a high substrate temperature of $T \sim 800$ K during deposition and the low laser pulse rate of $r = 2$ Hz (cf. [48,49] for the preparation and crystallographic properties of connatural fully covering and adhering electrodes). A Pt-coated alumina mask was pressed onto the substrate during ablation to obtain circular shaped Pt working electrodes (WE) with a macroscopic area (A) of $\sim 16\,\text{mm}^2$.

For characterization of the morphology, crystallographic structure, and film thickness of the electrodes, scanning electron microscopy (SEM, Merlin, Zeiss, Germany), X-ray diffraction (XRD, θ–2θ-scans, Cu $K_{\alpha1,2}$, Siemens Daco-MP D500/501, Germany), and profilometry (Alpha-Step IQ, KLA Tencor, USA) were used. The tpb length was estimated by image analysis using the software Adobe Photoshop (version CS4 extended).

Silver paste (Hans Wolbring GmbH, Germany) was applied as counter electrode (CE) on the unpolished side of the YSZ crystal opposite to the Pt electrode and sintered shortly at 773 K (heating rate: $100\,\text{K}\,\text{h}^{-1}$, cooling down after reaching the temperature).

2.2. Electrochemical measurements

The electrochemical measurements were carried out in a tube furnace at 673 K (temperature checked with a second thermocouple) using a potentiostat/galvanostat (Zahner IM 6, Germany). Platinum wires were used as electrical contacts and pressed on the electrodes for ensuring good contact. The electrode potentials E given in this study are referred to the counter electrode. The two-point measurement setup was chosen to avoid artifacts during impedance measurements [50,51]. The silver paste electrodes were tested and exhibited a linear current–voltage (I–E) response in good approximation at the current densities used in this study. At low current densities in the order of about $10\,\mu\text{A}\,\text{cm}^{-2}$ the *IR*-drop of the counter electrode and electrolyte are actually negligible. For the Tafel plots an *IR* correction was carried out using resistance values (R) determined by EIS.

The EIS measurements were carried out with an ac amplitude (ΔE) of 10 mV at *OCP* or small potentials ($E = \pm 100$ mV). At higher potentials an amplitude ΔE of 20 mV was used to achieve a better signal-to-noise ratio. The polarization resistance R of the Pt electrode was determined by fitting (software ZSimpWin, EChem Software) equivalent circuits to the measured impedance spectra given below.

"Steady state" I–η curve measurements ("η" is used here instead of "E" after *IR* correction) were collected using a very small sweep rate of $100\,\mu\text{V}\,\text{s}^{-1}$ and details for the CV measurements can be found in the text.

3. Results and discussion

3.1. Sample characterization

Fig. 1a shows representative SEM images of the dewetted electrode structure. The tpb length of these samples was determined to be in the range of 300–$600\,\text{m}\,\text{cm}^{-2}$ which is in the same order of magnitude as the values reported for nanopore patterned [1] or partly dewetted Pt samples [6] optimized for high performance; the thickness of the Pt films was between 70 nm and 100 nm (note that the tpb length for Pt paste electrodes was determined to be between $5\,\text{m}\,\text{cm}^{-2}$ and $20\,\text{m}\,\text{cm}^{-2}$ [52]). The platinum network formed by dewetting can be considered to be "kinetically frozen" on the YSZ ceramics [6,53–55]: high temperatures above about 823 K lead to further dewetting and finally to the formation of isolated Pt particles [6,27,53]. At 673 K the electrodes turned out to be entirely morphological stable with respect to temperature-induced changes within the time of our experiments.

XRD (Fig. 1b) indicates an epitaxial growth of the Pt(1 1 1) network on YSZ(1 1 1); all small reflexes in the logarithmic intensity plot are a result of other wavelengths such as Cu K_β and W L_α.

3.2. Electrochemical measurements without morphological changes ($E \leq 100$ mV)

3.2.1. The influence of time and polarization precondition on the polarization resistance

The influence of the time (t) at a temperature of 673 K on the area specific electrode polarization resistance ($R_{\text{pol}}A$) of a pristine sample is depicted in Fig. 2a. R_{pol} increased with time and a linear relationship between R_{pol} and the square root of time ($t^{1/2}$) was found (equivalent circuit used here for fitting impedance spectra: R_{YSZ}–$(RQ)_{\text{CE}}$–$(RQ)_{\text{WE}}$ with Q = constant phase element). Note that there is a small uncertainty regarding the absolute value of time due to the previous sintering of the counter electrode and the temperature equilibration (~0.5 h) before starting the measurement after reaching the testing temperature. After completing the series of EIS measurements depicted in Fig. 2a, a CV measurement was carried out which is shown in the inset of Fig. 2a. Within the first negative sweep (black arrow) the current density (IA^{-1}) did not increase significantly until a minimum negative potential