Solid State Ionics xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Oxygen reduction via grain boundary transport in thin film platinum electrodes on yttria stabilized zirconia

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ARTICLE INFO

Article history:
Received 16 June 2014
Received in revised form 5 November 2014
Accepted 6 November 2014
Available online xxxx

Keywords:
Oxygen reduction kinetics
Bulk path
Platinum microelectrodes
Polarization resistance
Grain boundaries

ABSTRACT

Model-type sputter deposited platinum microelectrodes with different grain sizes were investigated on single crystalline yttria stabilized zirconia (YSZ) by means of impedance spectroscopy. Measurements on single platinum microelectrodes could be continuously performed for >100 h and from 250 to 800 °C without losing contact. From the temperature dependence, two parallel reaction pathways for oxygen reduction could be identified. Above 450 °C, a surface path with a rate determining step located at the three phase boundary is predominant. Its polarization resistance is independent of the Pt grain size and exhibits an activation energy of ca. 1.8 eV. In the low temperature regime (<450 °C) a bulk path through Pt was verified, with an electrode polarization resistance depending on the Pt grain size. This resistance is only slightly thermally activated and the rate limiting step is most probably oxygen diffusion along Pt grain boundaries.

1. Introduction

The system platinum/yttria stabilized zirconia (YSZ) has a long history in both industrial applications and fundamental research. For example, Pt/YSZ is used in oxygen gas sensors applied for exhaust gas analysis in combustion engines [1] and in medical devices [2]. An in-depth understanding of oxygen reduction on Pt/YSZ is crucial for the development of sensors with optimized performance and high reliability [3,4]. Pt on YSZ is also an important model system for polarization studies in solid oxide fuel cells or solid oxide electrolysis cells (SOFCs or SOECs). Moreover, Pt electrodes are often employed in μ-SOFC [5–9] based on thin electrolytes and responsible for a significant part of the total polarization resistance of such cells [10].

Pt thin film electrodes are particularly attractive for studies aiming at a mechanistic understanding of the oxygen reduction reaction [11–20]. Among others, oxygen reduction on Pt thin film microelectrodes has been shown to proceed via two parallel reaction pathways [13]. In a high temperature regime (>450 °C), a "surface path" was observed, with a rate determining step depending on the three phase boundary (3PB) length. In the lower temperature regime (<450 °C), a "bulk path" was identified and oxygen transport along platinum grain boundaries (GBs) was assumed to be rate limiting. Indication of oxygen transport along GBs can also be found in Refs. [13,21–23]. An unambiguous proof of its importance in oxygen reduction on Pt/YSZ at low temperatures, however, is still missing.

The goal of this work is to analyze the rate limiting step of oxygen reduction on Pt electrodes via the bulk path, i.e. to further clarify the role of oxygen GB diffusion in platinum thin film electrodes. Therefore, electrochemical impedance spectroscopy was performed between 250 and 800 °C on sputter deposited, geometrically well-defined platinum microelectrodes with different grain sizes.

2. Experimental

2.1. Sample preperation

Platinum thin films were prepared by magnetron sputter deposition (MED 020 Coating System, BAL,TEC, Germany) of Pt (99.95% pure, ÖGUSSA, Austria) on polished YSZ (1 0 0) single crystals (9.5 mol% Y_2O_3, CrysTec GmbH, Germany), cf. Ref. [13]. Deposition took place in argon atmosphere at a pressure of 2×10^{-2} mbar without additional heating of the substrate. The film thickness of 350 nm was controlled by means of a quartz micro-balance. Micro-structuring of Pt films was performed by lift-off photolithography (ma-N 1420 negative photo resist and ma-D 533S developer for photo resist, both: micro resist technology, Germany) using a quartz photo mask (Rose, Germany) leading to circular Pt electrodes of different diameters. The size, shape and microstructure of these Pt microelectrodes were investigated by scanning electron microscopy (SEM, FEI Quanta 200 FEG, Netherlands). As counter electrode, Pt paste (Gwent Electronic Materials, UK) was applied onto the back side of the YSZ single crystals. The samples were subsequently annealed in ambient air at 750 °C for 2 h. To obtain electrodes with large grain size, samples were annealed at 800 °C for several weeks.

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http://dx.doi.org/10.1016/j.ssi.2014.11.006

Thereby Pt grains in the thin films grew from initially sub-μm sizes to several 10 μm as shown in Fig. 1. The Ø = 100 μm Pt microelectrode shown in Fig. 1b, for example, has only 3 large grains. From the absolute number of grains visible at the surface of such microelectrodes, a grain size of several 10 μm was estimated. For non-annealed Pt microelectrodes an average grain size of 100–300 nm was estimated from Fig. 1a. Thus, the GB density (total length of grain boundaries visible at the electrode surface) of the small grained Pt microelectrodes is more than 100 times larger than that of electrodes with large grains.

2.2. Measurement set-ups

Two different micro-contact set-ups were used in the experiments. The asymmetrically heated measurement set-up (Fig. 2a) allows to change the contacted electrode within seconds and thereby to gain statistical information over a large number of different microelectrodes on one and the same sample in a relatively short time. It also enables monitoring of optical changes during the measurement in real time. However, the asymmetrical heating from the bottom side and local cooling (e.g. by convection, radiation, and the contacting tip acting as a heat sink) is known to cause temperature gradients within the sample [11]. Such temperature gradients are responsible for thermo-voltages, which can lead to measurement artifacts in electrochemical experiments [24]. Moreover, in this set-up temperature cycles can hardly be performed on single microelectrodes but require subsequent contacting and de-contacting of different microelectrodes.

The second measurement set-up includes a novel, symmetrically heated sample holder, designed to reduce the influence of temperature gradients; it is sketched in Fig. 2b. It provides a precisely adjustable and measureable sample temperature with minimal temperature gradients in the region of the sample, and it enables long-time measurements on one and the same microelectrode from room temperature up to 1000 °C without losing contact. Since all contacting parts of the symmetrically heated set-up are inside a tube furnace during the measurement, the contacting procedure has to be done prior to the measurement i.e. outside the hot zone. Establishing an electrical contact between tip and microelectrode is performed by a micromanipulator and is monitored by a USB-microscope (Fig. 2b, small photographs). After electrode contacting, the sample is transferred into the hot zone of the tube furnace and fast changes of the contacted electrode are therefore not possible. Detailed information on the two micro-contact set-ups and a discussion on the role of temperature gradients are published elsewhere [24].

2.3. Impedance spectroscopy

Electrochemical characterization of the platinum microelectrodes was done by means of two-point impedance measurements using an Alpha-A High Resolution Dielectric Analyzer (Novocontrol, Germany). In both set-ups, electrochemically etched Pt/Ir tips were used to electrically contact the platinum microelectrodes. In the symmetrically heated set-up, the porous platinum counter electrode on the back side of the YSZ substrate was contacted via a Pt sheet beneath the sample (Fig. 2b). In the asymmetrically heated set-up, the counter electrode contact was established on the top side by a second Pt/Ir tip (Fig. 2a). Impedance spectra were recorded at temperatures between 250 and 800 °C in the frequency range of 10^6 Hz to 10^{-3} Hz (10^{-2} Hz in the asymmetrically heated set-up) with a resolution of 5 points per frequency decade.

3. Results and discussion

Impedance measurements on annealed electrodes with large grains were performed in the symmetrically heated set-up on several Ø = 200 μm microelectrodes, each contacted once and measured from 250 °C to 800 °C and back to 250 °C with total measurement times much larger than 100 h. The results were then compared with measurements on small grained Pt electrodes, which were conducted in the asymmetrically heated set-up (Fig. 2a) and already reported in an earlier study [13]. Additional cross-check experiments were also performed on large grained electrodes in the asymmetrically heated set-up to exclude systematic errors caused by the use of different set-ups.

Impedance spectra for electrodes with small and large grains are shown in Fig. 3 and both consist of a large semicircle in the low frequency range, a small shoulder in the medium frequency range (Fig. 3c) and a high frequency intercept. For low temperatures, the high frequency intercept, which reflects the spreading resistance of ion conduction in YSZ [11,25], develops into a more or less complete arc. Its capacitance and thus also its relaxation time is determined by the stray capacitance of the set-up, which exceeds the true bulk capacitance of the microelectrode.

Parameterization of the spectra was carried out by the complex nonlinear least square (CNLS) fit software Z-View2 (Scribner, USA) using the equivalent circuit shown in Fig. 3d. Therein R_{ysz} represents the spreading resistance of ion conduction in YSZ and the two serial R-CPE elements are used to fit the electrode impedance. To account for non-ideal capacitive behavior, constant phase elements (CPE_A and CPE_B) instead of ideal capacitors were employed. The partly or fully developed high frequency (YSZ bulk) arc was not taken into account in the data analysis and the corresponding capacitance is therefore not included in the equivalent circuit. In all cases, R_B is several orders of magnitude smaller than the total electrode polarization resistance (R_{tot}) and thus negligible compared to the main electrode resistance R_{rds}. R_B and CPE_B were only added to obtain high fit quality and thus being able to extrapolate the spectrum to low frequencies. Hence, the equivalent circuit does not imply a simple mechanistic interpretation of the impedance

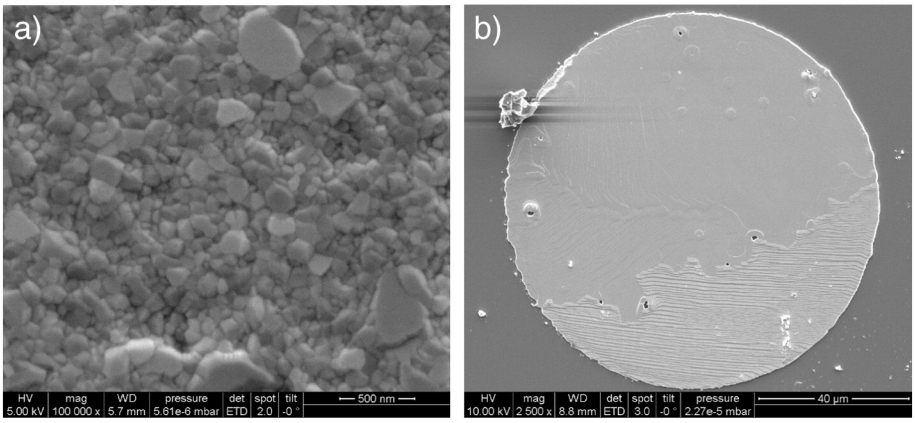

Fig. 1. SEM images of platinum microelectrodes a) non-annealed with small grains and b) annealed with large grains.