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Porous model type electrodes by induced dewetting of thin Pt films on YSZ substrates

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ABSTRACT

Thin Platinum films, prepared by Pulsed Laser Deposition (PLD) on single-crystalline yttria-stabilized zirconia (YSZ), show microstructurally uncontrolled dewetting upon heating to elevated temperatures. We tested several methods to induce the dewetting process, yielding a regular pattern — including structuring by masking of the surface with a Pt net and pre-coating of the YSZ surface with different substances. Electrochemical measurements prove that these electrodes show a higher exchange current density compared to untreated, fully covering Pt|YSZ systems and are morphologically stable upon electrochemical polarization and heating. Thin films structured by induced dewetting at high temperature may become useful tools as model type electrodes for surface analytical studies of electrode reactions at lower temperatures than their dewetting treatment.

1. Introduction

The Pt|YSZ electrode is the most widely employed and investigated system in solid state ionics [1]. During the use as a cathode, oxygen is reduced to O^{2-} and incorporated into the YSZ lattice (ORR: oxygen reduction reaction), as illustrated in Fig. 1. As platinum is impermeable for oxygen and as YSZ has a negligible electronic conductivity, the electrode reaction can only take place at the three phase boundary (tpb) Pt|YSZ|$O_{2(g)}$. This obvious restriction makes the Pt|YSZ electrode a typical limiting case being highly attractive for fundamental studies. Pt has the additional benefit of high-temperature stability and relatively low vapor pressure; it is chemically inert and catalyzes the ORR. It has to be noted that from the practical point of view, the kinetic restriction by the tpb and the costs for platinum are main reasons why the platinum electrode has been replaced by mixed conducting oxide electrodes, e.g. in solid oxide fuel cells (SOFC).

Defining an optimized model type electrode, a number of conditions have to be fulfilled in order to achieve the minimal chemical and microstructural complexity and – vice versa – the maximal reproducibility of the system: (a) The system should chemically be as simple as possible. A nominally "clean" Pt|YSZ electrode is already a quaternary system, and it is well known that it undergoes reactive changes at high temperatures and low oxygen activities, e.g. Pt–Zr alloy formation, blackening of YSZ [2,3]. Real Pt|YSZ electrodes contain a number of impurities, of which most originate from YSZ, i.e. Si, Al, Ca and some other metals. Even if the electrode interface is virtually clean after preparation, Si and other impurities tend to segregate to the interface during operation at high temperature [4–6]. Thus, it will be important to note the interface composition for the sake of reproducibility. Ideally, the amount of impurities should be as low as possible [7,8]. (b) The three phase boundary, the Pt|YSZ interface and the adjacent YSZ and Pt surfaces should be geometrically and microstructurally well defined, in order to allow a straightforward analysis of microscopic and spectroscopic experiments. Additionally, being able to produce different microstructural geometries would be another advantage. (c) It appears that Pt electrodes suffer from morphological changes upon severe polarization. In order to avoid morphological instabilities [9–13], patterned electrodes with a suitable ratio of tpb length to electrode interface are required. Uncontrolled imperfections like cracks, holes, interdiffusion and solid state reactions at the interface are to be avoided to the largest extent possible, as they influence the electrochemical properties of the electrode system. In this context we have studied the formation of bubbles during polarization, in which gaseous oxygen is formed underneath the Pt layer and cannot emerge through the dense surface [13]. These bubbles are preferentially formed at defects in the Pt, like buried holes within the Pt film or scratches in the electrode, which do not extend to the YSZ substrate. A regular pattern of holes with open access to the gas phase in the dense surface is assumed to be efficient in releasing the generated oxygen, at least to a certain extent. Since chemical diffusion of oxygen is fast underneath the Pt layer, the exact amount of released gas depends on the size, the number and distribution of the holes. Morphological stability goes along with this trend.

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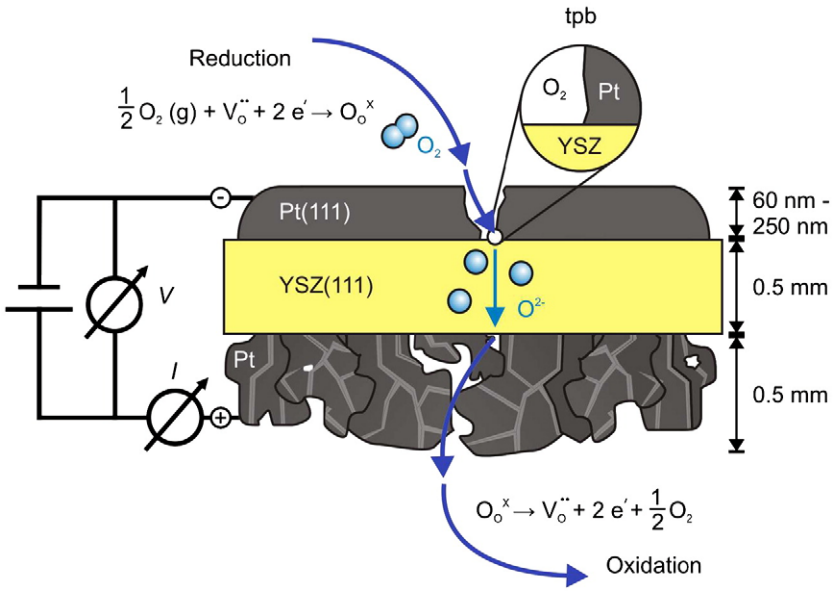

Fig. 1. Schematic cell arrangement with a thin film working electrode (here under cathodic polarization).

In general, four cases of electrode microstructures are conceivable, as displayed in Fig. 2. The ideal preparation route should offer access to all four types, being easily adjustable to the required situation. This means by changing certain preparation parameters, all microstructures/morphologies can be prepared. With our presented techniques, once the way of preparation has been chosen and the system is deposited, it is only possible to change the obtained geometry from fully covering to porous – e.g. with an annealing treatment – however, switching back to fully covering layers or between nearly single-crystalline and polycrystalline microstructures is not possible. This adaptability makes it possible to produce different microstructures of the same Pt|YSZ electrode system and consequently employ them in different investigations and applications.

In this paper we present techniques suited to accomplish all four cases of the Pt|YSZ electrode system. Nearly single-crystalline, fully covering films [14,15] (Fig. 2D) can be prepared easily with PLD on

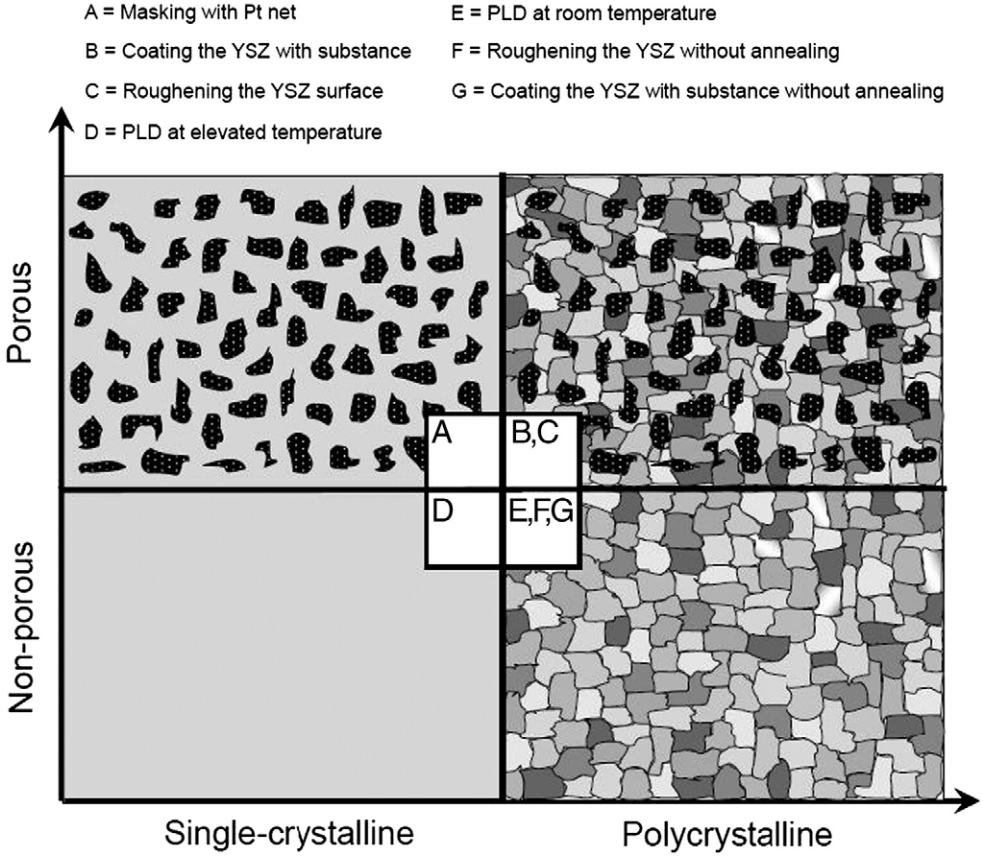

Fig. 2. Accessible electrode microstructures as well as reported and new fabrication techniques.