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Electrode activation and degradation: Morphology changes of platinum electrodes on YSZ during electrochemical polarisation

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ABSTRACT

During polarisation of dense PLD Pt film electrodes on YSZ changes in the morphology of the anode appeared involving a pronounced electrode activation. These morphology changes or more precisely the formation of bubbles and their cracking were explained by a built up of gas pressure underneath the Pt film due to the evolving oxygen. For the first time a detailed study of this phenomenon was presented, including a characterisation by HRSEM, AFM, in situ optical microscopy, XRD and electrochemical measurements. The appearance and the shape of different kinds of bubbles were discussed and an internal pressure was estimated by using simple geometrical models. A diffusion of oxygen along the interface Pt/YSZ was evidenced. The observed electrode activation was related to an extension of the tpb length during the formation and cracking of the bubbles. A comparison of dense electrodes to differently prepared porous ones clearly showed that a morphology change due to overpressure only occurs on extended gas-tight electrode areas and thus, need not be considered when using sintered paste electrodes.

1. Introduction

Electrodes in solid state electrochemical cells often show a better performance after electrical polarisation for a certain period of time [1–5]. This activation plays an important role in solid state electrochemistry both for mechanistic studies [5–7] and applications, e.g. for solid oxide fuel cells (SOFCs) [8]. The changes in the electrode characteristics are sometimes reversible [3] but also occur as an irreversible process [2,5] and besides the directly opposed effect can be observed: a reduced performance after current load. Some systems show both activation as well as deactivation [5,8], depending on the current direction [9] or the examined time period [10]. After a long time of current load especially at high temperatures usually a degradation [11,12] of the cell components occurs involving a worse cell performance. With regard to long time stability of the electrochemical cells [13,14] degradation phenomena [10,15] corresponding to distinct morphological changes (Fig. 1a–e) like instabilities, cracks [16], pores or delamination [16,17] are undesired in commercial applications. Morphological modifications often lead to a different ratio of the contact area to the tpb (three phase boundary) (Fig. 1a–c), and thus, influence the electrochemical performance directly [5,18–20]. The partly overlapping concepts of degradation, ageing, activation and passivation are summarized in Table 1.

Electrode activation has been investigated for a number of different systems, especially for O_2/Pt/YSZ (yttria-stabilised zirconia) [2,3,6,20–23] which still represents the most important and best studied electrode model system in solid state electrochemistry [24,25]. Experimentally the activation effect is reflected in a current hysteresis during linear potential sweeps [2–4,20,21], in the appearance of inductances in impedance measurements [2,3,9,21,22] or simply an increased current density with time in potentiostatic experiments [3,4,9,10,21,23]. Various explanations have been suggested for the activation mechanism — in general assuming an increased number of active sites [2]. On the one hand a change in the tpb properties [4,9] — or even more precisely an increased tpb length [3,5,9,20] — has been proposed. On the other hand a change in the electrode/electrolyte interface properties [3,9,21] is accounted which, of course, cannot clearly be separated from a tpb rearrangement (Fig. 1a). Suggested reasons for this modification of properties are a changed interface composition and microstructure due to segregation and accumulation of components [26] or a different topography/morphology of the interface [10]. A current sensitive reaction zone geometry [3] and fluctuations at the interface [4] have also been assumed. More recently, it has been shown that surface migration of electrode material [5,20] can take place. Besides, in earlier studies also an extension of the electrochemical active sites to the YSZ/gas interface [27] or more active sites on the Pt surface [19] has been proposed. In addition, it has been demonstrated that impurities can cause

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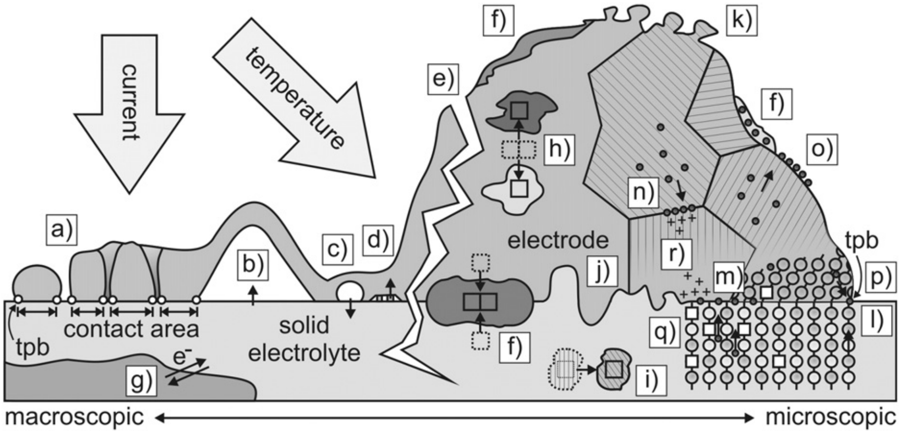

Fig. 1. Electrochemical driven changes and temperature effects of the electrode/solid electrolyte system a) formation of holes, dewetting, evaporation or surface migration of electrode material [5]; b) delamination, formation of bubbles or pores; c) dissolution, formation of pores [34]; d) material deposition; e) strain, crack formation; f) solid state reactions [34,35]; g) material oxidation/reduction [36]; h) material decomposition, phase separation; i) phase transition/formation; morphology changes or instabilities at the j) interface [4,61] or k) surface (e.g. due to annealing); segregation of l) components or m–p) impurities and their accumulation at m) interfaces [15,26,31,32], n) grain boundaries [15,32], o) surfaces or the p) tpb [26], thereby influencing, e.g. q) the defect chemistry [26], r) the space charges [37] or i) causing phase transitions [9].

activation as well as passivation [15,28–33]. However, beyond these basic explanations only a few activation or degradation mechanisms have been proposed and described in detail so far [5,26], because of the large number of different processes, which have to be considered. Fig. 1 illustrates electrochemical driven and temperature induced changes of solid state electrochemical cells on macroscopic and microscopic scale. For purposes of clarity interactions between these different processes are not drawn in, which of course can occur.

In the present context we try to distinguish temperature effects from the ones caused by current flow and will not include those in the discussion. Furthermore, we reduce the complexity by investigating a simple model system (Pt/YSZ). Pt was chosen as electrode material due to its high melting point (effects in Fig. 1a, k reduced) and due to the availability of structurally well characterised electrodes with a minimised amount of impurities [38] (little impact on processes m–p in Fig. 1. Since it is a one component metal (less influence of process depicted in Fig. 1e) electrode, we can exclude changes in the electrode composition (Fig. 1h), assuming that no interface reaction (Fig. 1f) between Pt and YSZ takes place [39]. In addition, oxygen has a low solubility and diffusivity in Pt [40] leading to oxygen excorporation from the solid electrolyte during anodic polarisation confined to the tpb or an electrode functional zone in the vicinity of the tpb [24,25]. Using an electrochemical cell consisting of an oxygen-tight electrode with virtually no tpb and an oxygen ion conductor (YSZ), the oxygen transported towards the electrode cannot easily escape into the gas atmosphere. Thus, the formation of gaseous oxygen underneath the electrode can be expected which should cause an overpressure leading to mechanical deformation or structural modification of the electrode (Fig. 1b). This mechanical phenomenon necessarily leads to a time dependent electrochemical performance, corresponding to an electrode activation or passivation.

To our knowledge the overpressure effect underneath gas-tight electrodes has not been described in literature in detail. Gür et al. [23] investigated non-porous sputtered platinum electrodes on scandia-stabilized zirconia at 1173 K and found a porous structure after 11 months of continuous use. They suspected the formation of small “gas pockets” at the anode/electrolyte interface. Bay et al. explained their experimental results with the presence of a gas reservoir at the Pt/YSZ interface [21]. In previous studies we evidenced the appearance of such gas bubbles occurring during electrochemical polarisation by SPEM (Scanning Photo Emission Microscopy) [41] and more recently by SEM images [42]. Hendriks et al. intentionally avoided the blistering of the working electrode due to release of oxygen by only applying small potentials [43]. Brichzin et al. [44] observed a similar morphological change in the microstructure of dense LSM electrodes by optical microscopy. We also assume that changes due to overpressure frequently appear when using dense electrodes, e.g. sputtered ones [6] or electrodes prepared by electrostatic spray deposition [45].

In this study, we investigate the bubble formation on gas gas-tight Pt electrodes deposited on YSZ by PLD (pulsed laser deposition) during anodic polarisation. We explain why different types of bubbles appear and why each class of bubbles shows a narrow size distribution. We discuss the shape of these bubbles using geometrical descriptions and estimate the oxygen pressure inside them on the basis of simple models. We further clarify whether this mechanical effect can be considered as a reason for electrode activation in general and finally compare differently prepared Pt electrodes with respect to their use as model systems for kinetic studies.

2. Experimental

2.1. Sample preparation

We used (111)-oriented YSZ single crystals (one side polished) for the preparation of all samples (Crys Tec GmbH (Germany), thickness 1.5 mm, surface roughness of the polished side <0.5 nm). In a first step the counter (CE) and the reference electrodes (RE) were prepared on the unpolished side of the YSZ substrates by sintering Pt paste (Ferro GmbH Electronic

Table 1
Attempt of a classification of the concepts of degradation, ageing, activation and passivation/deactivation in solid state electrochemistry and catalysis

concept	“degradation”/[“ageing”]	“passivation”/”deactivation”		“activation”	
definition	macroscopic change in morphology or composition associated with a reduced cell performance [in the course of time]	reduced performance		improved performance	
effect	worse cell performance, reduced long time stability	electrode passivation	catalytic passivation	electrode activation	catalytic activation
		reduced cell performance (after current load/ thermal treatment)	reduced performance of a catalytic reaction (“inhibition”)	improved cell performance (after current load/thermal treatment)	improved performance of a catalytic reaction (“promotion”), e.g. NEMCA [46]