Solid State Ionics 180 (2009) 1019–1033

Contents lists available at ScienceDirect

Solid State Ionics

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

The electrode model system $Pt(O_2)|YSZ$: Influence of impurities and electrode morphology on cyclic voltammograms

E. Mutoro [a], B. Luerßen [a], S. Günther [b], J. Janek [a,*]

[a] Institute of Physical Chemistry, Justus-Liebig University Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany
[b] Department of Chemistry, Ludwig-Maximilian-University München, Butenandtstr. 11, D-81377 München, Germany

ARTICLE INFO

Article history:
Received 20 January 2009
Received in revised form 8 April 2009
Accepted 17 April 2009

Keywords:
Cyclic voltammetry
EPOC
Impurity
Model system
Morphology
NEMCA
Pt
PLD
Silicon
Silica
Spillover
YSZ

ABSTRACT

This study is focused on the influence of impurities and electrode morphology on cyclic voltammograms (CV) of one of the most prominent solid state electrode systems, $Pt(O_2)|YSZ$, exemplifying the difficulties in unequivocal interpretation of CV in the solid state in general. By investigating differently prepared electrodes—either by Pt paste or pulsed laser deposition (PLD)—with and without an Si containing additive, the impact of both effects can be separated. For characterisation of the sample SEM, XRD, EDX, Tof-SIMS, XPS, and XPEEM have been used. We demonstrate that the presence of impurities can change the shape of CV and even cause peaks, a fact which has not been considered so far. The processes which theoretically can cause a CV peak in the electrode system $Pt(O_2)|YSZ$ are discussed. We reconsider the information unambiguously obtainable from CV studies, and we comment on the controversial questions of the formation of interface Pt oxide and the appearance of spillover oxygen in CV studies. A compact commented survey of literature on CV studies of the system $Pt(O_2)|YSZ$ is given.

1. Introduction

The high temperature oxygen electrode is perhaps the most important electrode system in solid state electrochemistry, and the $Pt(O_2)|YSZ$ (yttria stabilised zirconia) electrode can be considered as the corresponding prototype material system, comparable to the $Pt(O_2)|H_2O$ electrode in aqueous electrochemistry.

Among the electrochemical methods for the study of electrode processes, CV (cyclic voltammetry) plays an important role as one of the simplest and fastest methods without the requirement of expensive equipment. Correspondingly, one finds numerous CV studies of Pt|YSZ electrodes in the literature which, unsatisfactory, are controversial in a number of points [1–36]. Although the first CVs have been published more than 25 years ago, major questions are still not answered, as most of the experiments have been conducted on poorly defined electrodes with respect to composition, morphology, and microstructure. Up to now, two main problems were not always properly addressed:

(a) Electrode microstructure: In liquid state studies, the use of single crystal surfaces improved our understanding of electrode kinetics considerably and is a standard there, at least after the introduction of flame annealing of electrode surfaces by Clavillier [37]. On solid electrolytes, single crystal electrodes were not available until recently, when Beck et al. demonstrated that virtually single crystalline epitaxial Pt film electrodes on YSZ single crystals can be prepared by PLD (pulsed laser deposition) [38]. The electrochemical characterisation of these electrodes is part of this paper.
(b) Impurities: Reproducible electrode studies in the liquid state rely on the use of pure components with a minimum impurity level. So far, the corresponding influence of impurities on the kinetics of (high temperature) electrodes on solid electrolytes has mostly been neglected, especially in the discussion of CV results. This factor is also addressed in the present paper.

In particular, we attempt to distinguish between impurity and morphology induced effects on CV. To this end, we investigated model electrodes and varied systematically only one sample parameter, e.g. the tpb length or the impurity content. Knowing that impurities can influence the electrode kinetics, we chose to study the impact of glass, mainly containing silicon, as Si represents an ubiquitous contamination in the Pt|YSZ system [39–41], and it is already known to have an impact on electrochemical processes [40,42] and on the formation of Pt oxides

---

* Corresponding author.
E-mail address: juergen.janek@phys.chemie.uni-giessen.de (J. Janek).

0167-2738/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ssi.2009.04.012

[43]. In addition, usually glassy sintering aids are added to commercial Pt pastes.

In general, the basic question which processes in the system Pt(O_2)|YSZ can theoretically cause a CV peak at all is not answered consistently in the literature—e.g. the influence of spillover oxygen which is important for the so called EPOC (electrochemical promotion of catalysis)—and thus we will comment on that.

Another important aspect for interpreting CVs is the question whether a Pt oxide forms at the interface Pt|YSZ during anodic polarisation. Even though there is no direct, i.e. spectroscopic, evidence for such an oxide, it has frequently been used for explaining features in CVs [4–6,14,15,25,30,32–34].

To our knowledge no complete survey of literature on CV studies of the system Pt(O_2)|YSZ has been published so far. Hence, we prefix a compact commented review, emphasising open issues and disagreements in literature.

2. Commented survey of CV literature

2.1. Investigated systems

2.1.1. Electrodes

As working electrodes (WE) mostly sintered ($T_{max}=1073$ K – 1573 K, sintering time $t=10$ min–2 h) Pt pastes [4–8,10,11,13,15,16,18,20–24,35] and screen printed Pt pastes [9,30] were investigated, respectively. In two of these studies the electrodes were polarised during sintering [5,9]. Often point electrodes [1,2,12,14,19,29,31] or sputtered electrodes [10,13,16,32,34] were used, and rarely other preparation techniques like spray pyrolysis [27] or microlithography [13,22] were applied. More recently a cermet electrode has been studied [32–34].

The counter (CE) and reference electrode (RE) were usually made up of Pt paste [1–5,7,10,15,21,22,24,31,36] or prepared by the same method as the WE [10,30,32,34], alternatively Pt foil [14] or gauze was used [21]. Frequently the electrode was made of Ag [11,13,17,18,25,27] or Au [6,20,23] paste. Especially Ag with its low melting point is much more mobile at high temperature compared to Pt which may influence the results. A solid state Me|MeO_x reference electrode has been reported by Shoemaker et al. [9].

2.1.2. Electrolyte

Mostly 8 mol% [4,6,7,9,11–14,17–21,23,24,27,31,32] or higher ((9.0 [3], 9.5 [36], 12.3–13.3 [11,13,17]) mol%) yttria-doped zirconia, i.e. fully stabilised cubic YSZ was investigated. Only in one case 4 mol% doped material was used [1]. If there is a comment on that at all in the majority of studies the electrode was polycrystalline [1,2,6,11–13,17,18,20,23,25,31–34], rarely single crystalline [7,11,13,16,17,36].

2.2. (Ex situ) electrode characterisation

Only in a few cases additional information on the electrodes was presented or referred to: the electrode microstructure as obtained by SEM [4,27,32–34,36], the size of electrode crystallites by XRD [27], the electrode composition by XPS [4], the gas exposed WE surface area determined by an isothermal surface titration technique [4] or an estimation of the tpb length and contact area by reflecting optical microscopy [7]. The majority of the available studies rely only on electrochemical methods. Therefore, correlations between sample characteristics and CV behaviour cannot be formulated in retrospect reviewing the literature.

2.3. Electrode geometry

Except in a few studies [15,26,28] a three electrode—WE, CE and RE—configuration was used. The relative size and the geometrical arrangement of the three electrodes influence the electrochemical measurement [44,45], and thus the resulting CV [10,21]. Once not a point contact WE is used, a symmetrical arrangement of WE and CE on both sides of the solid electrolyte ensures a uniform current density at the WE. The RE should be placed close to the WE [44,45], which was realised in many studies [7,11,17,21,27,36]. However, very coften the RE was placed on the backside next to the CE [3,4,6,8,13,16,20,22–25,30,32–35] or even other arrangements were chosen [5,9,15] so that these results have to be compared with care.

2.4. Influence of sweep rate

The sweep rate v influences the shape of the CV in two ways: Firstly, a vertical shift of the forth and backward scan—in the following named vertical hysteresis ΔI (see Fig. 19a)—occurs due to the (un)charging of the electrochemical double layer capacity c_d. This hysteresis is proportional to the sweep rate ($\Delta I \sim v c_d$). Secondly, also the peak currents I_p increase with increasing v and—depending on the reversibility of the system—the peak potentials may shift. In addition, at higher sweep rates usually different peaks in close vicinity cannot be resolved which results in one broad and less well defined peak. A vanishing sweep rate $v \rightarrow 0$ Vs^{-1} finally corresponds to a steady state measurement [19] and thus at very small sweep rates ((0.05 [12], (0.001–0.1) [31], 0.01 [29]) mVs^{-1}) no peaks appear. However, slow changes in the electrochemical performance, e.g. due to electrode activation or slow morphology changes, can be observed at low sweep rates. In general, peaks are recorded at higher v values, typically between 1 mVs^{-1} and 200 mVs^{-1} [1–7,9,11,13,14,16,18,20,22,23,25,30,32,34,36]. The effect of the sweep rate on the shape of the CVs or the peak currents was investigated in a number of experiments [4–6,13,16,19,22,30–32,34]. However, conclusions out of these studies are not very clear as I_p was found to be proportional to v [4] as well as proportional to $v^{1/2}$ [5,6,30] or even a relation in between [22]. By choosing only one sweep rate it has to be assured that the required information is really obtained. In general, a systematic variation of the sweep rate is recommended.

2.5. Influence of temperature

Studies have been performed at temperatures between 473 K and 1273 K, either at one fixed temperature or in a temperature range [4–7,9,10,14–16,21,22,25,35,36]. The effect of T on CV has also been studied in detail [4–6,9,14,15] and the area of the peaks (in oxygen atmosphere) usually passes a maximum and vanishes with increasing T. The reported temperatures differ extremely ($T_{max}=700$ K–935 K, $T_{vanish}=845$ K–1170 K) and some authors report peaks even at temperatures as high as 1273 K [1–3]. However, the observed behaviour has been explained by spillover oxygen [4] as well as by the stability of Pt oxide [5] and thus is no evidence for one of these alternatives. Therefore, in this study we chose $T=723$ K which results in clear peaks, assures oxygen ion conductivity of YSZ and avoids temperature induced morphology changes of the Pt electrode. In addition, 723 K allows a direct comparison to recent studies [30,32–34].

2.6. Influence of pressure

CVs were measured in air (or $p(O_2) \sim 2 \cdot 10^4$ Pa) [1,2,4–6,11–13,16,19,21,24,29,30–34] or at a reduced oxygen partial pressure ($p(O_2)^{min}=1 \cdot 10^{-7}$ Pa) [3,4,6–10,13,14,16,18–20,22,23,25,30,35], in N_2 [5,9,14–16], He [4], or pure O_2 [5,7,9,14,19,27]. The influence of $p(O_2)$ on CV and the cathodic peak current was investigated in several studies [4–9,13,16,19,20,22,23,30,34]. In general, it was found that the main cathodic peak shifted to more negative potentials as $p(O_2)$ was increased [5,7,9,22].

2.7. Reversal potentials

The anodic and cathodic reversal potentials $V_{r,a}$, $V_{r,c}$ strongly influence the shape of the recorded CVs. The maximum voltage range