

Charge storage in the $O_{2(g)}$,Pt/YSZ system

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Abstract

The $O_{2(g)}$,Pt/YSZ system was characterized at 450 °C by using various electrochemical techniques such as single- and double-step chronoamperometry, chronocoulometry and chronopotentiometry. The response to these experiments gives evidence for the presence of pseudocapacitive processes related with charge storage. Linear sweep voltammetric measurements after prolonged anodic polarization have shown that these charges are located at three different locations.

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1. Introduction

Solid electrolyte cells are commonly used for numerous applications including gas sensors [1], gas pumps [1], solid oxide fuel cells [2] and electrochemically promoted catalysts [3]. The most widely used solid electrolyte is yttria-stabilized zirconia (YSZ), which is an O^{2-} ion-conducting material at temperature above 300 °C. Out of a variety of metals and composite materials employed as electrode, platinum has always been of particular interest due to its electrocatalytic properties. In fact, the platinum/YSZ system is the most widely studied example of catalyst electrodes deposited on YSZ [4–6]. Nevertheless, numerous aspects of the electrochemical reactions occurring in an $O_{2(g)}$,Pt/YSZ system are still under discussion due to the complexity of the system.

In an $O_{2(g)}$,Pt/YSZ system, various interfaces exist where electrochemical reactions may take place: three binary interfaces (Pt/YSZ, YSZ/ $O_{2(g)}$ and Pt/ $O_{2(g)}$) and the triple phase boundary (tpb) where the three binary interfaces meet (Fig. 1). The electrochemical couples playing a role in the overall charge transfer reaction are PtO_x /Pt and $O_{2(g)}/O^{2-}$. The PtO_x /Pt couple

corresponds to the redox reaction (1) [7–9]:



where use of the symbol PtO_x is due to the ill-defined stoichiometry of the electrochemically formed oxide [10]. The other electrochemical reaction, involving the couple $O_{2(g)}/O^{2-}$, consist of electron exchange between gaseous oxygen and O^{2-} ion of the solid electrolyte:



where V_O is an oxygen vacancy in the lattice of the electrolyte. It should be emphasized, that the two electrochemical reactions are not independent of each other, and the first may strongly influence the second. For instance, it is well established that the presence of an oxide film at the metal/electrolyte interface affects the mechanism and kinetics of various anodic processes by changing the electronic properties of the metal surface and by imposing a barrier to charge transfer across the surface oxide film [11].

In a recent work [12] it was found by cyclic voltammetry, that different sorts of oxidized species formed under prolonged anodic oxidation are consumed subsequently during a linear cathodic potential scan resulting in three distinct reduction peaks. The coexistence of three electrochemical processes is explained with the extension of the triple phase boundary. The rapid first process is assumed to be formation of a PtO_x mono-

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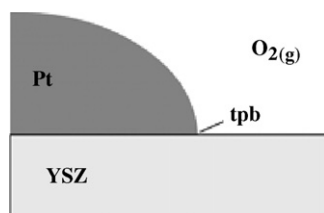


Fig. 1. Schematic representation of an $O_2(g)$ /Pt/YSZ solid electrolyte cell indicating the triple phase boundary (tpb).

layer at the electrode/metal interface, the second process – a much slower, parallel one – is related to the phenomenon of oxygen backspillover at the metal/gas interface, and the slowest third process – consecutive to the first one – is attributed to progressive metal oxidation extending from the electrode/metal interface toward the bulk of the metal controlled by solid diffusion.

In the present work, cyclic voltammetry and chronometric methods are used to study the prolonged anodic polarization effect on the electrochemical behavior of Pt/YSZ electrodes. Chronometric methods highlight the pseudocapacitive behavior and the kinetics of the system while voltammetry allows distinguishing three processes of charge storage.

2. Experimental

2.1. Experimental settings

In previous works, Pt/YSZ electrodes prepared by different methods, namely Pt sputtering, thermal decomposition of a Pt salt and screen-printing of a paste composed of Pt and YSZ particles, have been investigated [13,14]. The results evidenced significant dependence of the cyclic voltammetric response on the method of preparation, hence on the resulted microstructure revealed by SEM. Electrodes prepared by sputtering and thermal decomposition appeared to be highly sensitive to sintering under working conditions, leading to a progressive loss of the pseudocapacitive behavior, hence suggesting that the oxygen exchange reaction became favored over charge storage processes. On the contrary, electrodes prepared by

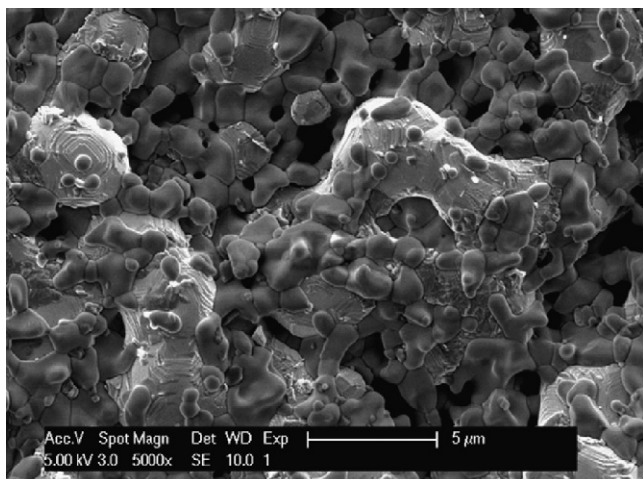


Fig. 2. SEM micrograph of the Pt/YSZ electrode prepared by screen-printing.

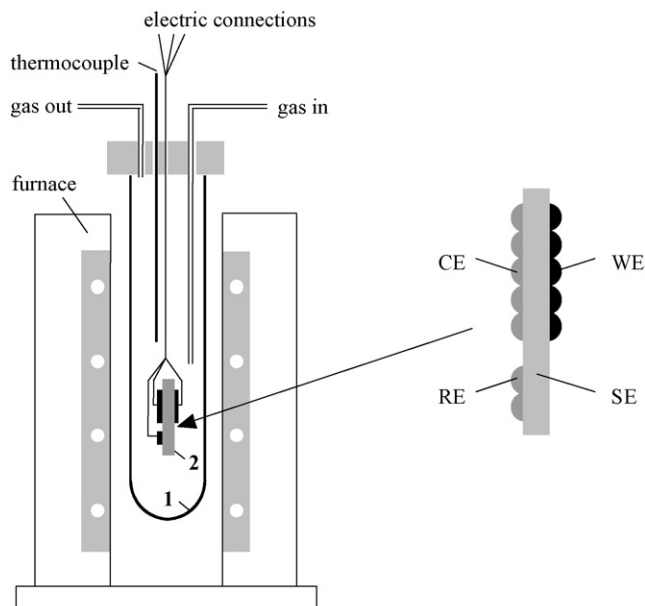


Fig. 3. Scheme of the experimental setup. 1: quartz tube; 2: electrochemical cell. WE: working electrode; CE: counter electrode; RE: reference electrode; SE: solid electrolyte (YSZ).

screen-printing featured superior pseudocapacitive behavior without any sign of degradation under working conditions, so they are the best suited for studying charge storage phenomena.

In this work, platinum deposition was made using a paste composed of 65 (wt%) of $1\ \mu\text{m}$ particle size platinum powder (Fluka), 11 (wt%) of $1\ \mu\text{m}$ particle size YSZ (8 mol% Y_2O_3 in ZrO_2 , Tosoh) and 24% of a polyvinyl pyrrolidone solution (2% in isopropanol, Fluka). The paste was screen printed on a $1.3\ \text{mm}$ thick YSZ pellet in the shape of $2\ \text{mm} \times 4\ \text{mm}$ rectangles and sintered at $1400\ ^\circ\text{C}$ in air to give a film thickness of $15\ \mu\text{m}$. The resulting deposit of $0.08\ \text{cm}^2$ geometric surface area is composed of 62%_{vol} of platinum and 38%_{vol} of YSZ and it is highly porous as seen on the SEM micrograph in Fig. 2. No morphological change has been observed due to prolonged use and/or polarization during working months.

The three-electrode electrochemical cell used in this work was of single-pellet type shown in Fig. 3. All electrodes were made of platinum and prepared simultaneously via the screen-printing method described above. Working and counter electrodes were located in a symmetrical face-to-face arrangement on the opposite sides of the YSZ pellet, while the reference electrode was located nearby the counter electrode at a distance of 2 mm. This geometry ensured a symmetrical current and potential distribution in the cell [15]. The electrical contacts were made by using gold wires ($d=0.15\ \text{mm}$, *Cendres & Métaux*) glued onto the electrode surfaces with a tiny dot of gold paste (*Gwent C70219R4*) then fired at $550\ ^\circ\text{C}$.

The reactor for electrochemical measurements, shown in Fig. 3, was of single-chamber type where all electrodes were exposed to the same atmosphere. It consisted of a quartz tube of 90 ml volume closed with a stainless steel cap. The single-

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