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Oxygen storage in O_2/Pt/YSZ cell

Cyril Falgairette *, György Fóti

Ecole Polytechnique Fédérale de Lausanne (EPFL), Institute of Chemical Sciences and Engineering, CH-1015 Lausanne, Switzerland

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The phenomenon of electrochemical promotion of catalysis (EPOC) was initially characterized as fully reversible, i.e. the catalyst restores its initial activity after current interruption. However, it has been recently demonstrated that after prolonged anodic polarization an unusual promoted activity is observed for a certain time after current interruption. This phenomenon has been reported as permanent electrochemical promotion of catalysis (P-EPOC).

In this work the oxygen storage reported as responsible of P-EPOC has been investigated by transient electrochemical techniques using an O_2(g)Pt/YSZ cell. A model has been proposed involving place interchange of Pt and O species in Pt/YSZ system. This seems to be induced by the strong lateral interaction of Pt–O surface dipoles and by increasing electric field at the Pt/YSZ interface. Such a rearranged oxide, so-called "phase oxide" can have a lower free energy than the initial monolayer oxide. This cooperative interaction of Pt and O species can lead to further thickening of this "phase oxide" especially at high temperature and potentials (currents). Furthermore, as the charge involved in this oxide thickening shows a $t^{1/2}$ dependency, the process seems to be diffusion controlled.

1. Introduction

Electrochemical promotion of catalysis (EPOC) denotes electrochemically controlled modification of heterogenous catalytic activity and selectivity. This phenomenon discovered by Vayenas et al. [1] has made a strong impact on solid state electrochemistry, catalysis and surface science. The EPOC phenomenon has been initially characterized as reversible, i.e. the catalyst restores its initial activity after current interruption [2,3]. Indeed, this is the case for short polarization times (few minutes). However, it has been demonstrated in our laboratory that after prolonged polarization (few hours) of the catalyst/YSZ interface, an unusual promoted activity is observed for a certain time after current interruption. This intriguing phenomenon, observed with IrO_2 [4], RuO_2 [5], Rh [6] and Pt [7,8] catalysts, is known as permanent electrochemical promotion of catalysis (P-EPOC). It has been reported that the phenomenon is linked to oxygen storage at different locations of the catalyst Pt/YSZ system during a prolonged anodic polarization [9]. This stored oxygen is believed to act as sacrificial promoter after current interruption [10].

In this work oxygen storage in the Pt/YSZ system has been investigated in a wide temperature range (425–550 °C) by means of different electrochemical techniques like cyclic voltammetry, chronoamperometry, chronopotentiometry and chronocoulometry using the O_2(g),Pt/YSZ cell. These techniques have been widely applied in liquid electrochemistry for the investigation of the Pt/liquid electrolyte interface, however, their application to solid state electrochemistry is very scarce [11–13].

2. Experimental

A three-electrode electrochemical cell was used. All three electrodes were platinum films deposited onto a 1.3 mm thick YSZ pellet (yttria-stabilized zirconia 8 mol%) by screen-printing of a paste, composed of 65 wt% of 1 μm particle size YSZ (8 mol% Y_2O_3 in ZrO_2, Tosoh) and 24% of a polyvinyl pyrrolidone solution (2% in isopropanol, Fluka), followed by sintering at 1400 °C in air to give a film thickness of 15 μm. Working, counter and reference electrodes, having a geometrical surface area of 0.08 cm^2 each, are composed of 62 vol% of platinum and 38 vol% of YSZ. This single-pellet three-electrode cell was suspended in a single-chamber type reactor with three gold wires serving as electrical contacts to the electrodes. A K-type (NiCr–Ni) thermocouple placed in proximity of the surface of the working electrode was used to measure the temperature of the system. The reactor was put into a furnace (XVA271, Horst) equipped with a heat control system (HT30, Horst). A mass flow controller (E-5514-FA, Bronkhorst) was used to keep the gas flow constant at 200 ml/min. The gas source was a Carbagas certified standard of O_2 (99.95%) supplied as a 20% mixture in He (99.996%). All the electrochemical measurements and data acquisition were made using a scanning potentiostat (Autolab, Model PGSTAT30, EcoChemie).

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* Corresponding author. Tel.: +41 216936164.
E-mail address: cyril.falgairette@epfl.ch (C. Falgairette).

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Before each electrochemical measurement, the cell has been pretreated by cathodic polarization at −600 mV for 10 min, this is in order to assure the same initial electrode state before measurements.

As both working (W) and reference (R) electrodes are in contact with the same gas composition (20 kPa O_2), the measured potential difference between the W and R electrode gives directly the electrode overpotential (η) at the working electrode.

3. Results and discussion

3.1. Chronoamperometric measurements

Fig. 1 shows chronoamperometric curves obtained at different anodic overpotentials (η_a). Initially the current decreases ($t < 10$ s) then starts to increase reaching a maximum (10 s $< t < 100$ s). This maximum seems to be visible only for high overpotentials application ($\eta_a > 0.2$ V). For longer polarization ($t > 100$ s) the current reaches a steady state value which depends on the applied overpotential.

Furthermore, Fig. 1 shows that the time involved between starting potential application and the appearance of the current peak (lag time t_{lag}) decreases as the applied potential increases. The appearance of a current peak in the chronoamperometric measurements is a strong indication of sites regeneration, on the YSZ/Pt system, induced by the anodic polarization.

3.2. Chronopotentiometric measurements

Fig. 2 shows chronopotentiometric curves obtained at different applied anodic currents (I_a). For short times ($t < 10$ s) and for all applied currents (I_a) the potential increases rapidly with time. At intermediate times (10 s $< t < 50$ s), the potential starts decreasing reaching a minimum value which is visible only for high I_a (>300 mA). At longer times ($t > 50$ s) the potential starts to increase again reaching a steady value. The potential minimum observed at intermediate times in the chronopotentiometric measurements can be related with the liberation of new sites, as discussed in the chronoamperometric measurements.

Fig. 3 shows double step chronopotentiometric curves: application of an anodic current of 30 μA for a given holding time (t_h) followed by application of a cathodic current of −30 μA for the same holding time t_h.

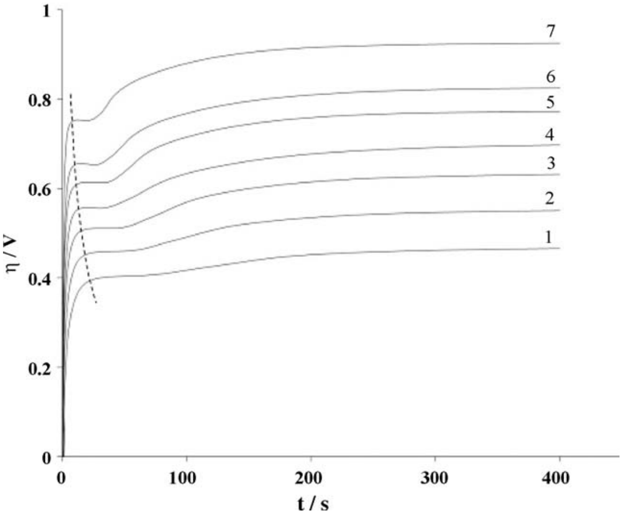

Fig. 2. Chronopotentiometric curves obtained at various applied anodic current I_a. Increasing anodic current step of 50 μA from 300 μA (1) to 600 μA (7), T = 450 °C; $P_{O_2} = 20$ kPa. Dashed line represents the evolution of lag time before the onset of the Pt site regeneration.

The anodic chronopotentiometric curves show a single plateau even after polarization as long as 1000 s, however, the cathodic chronopotentiometric curves shows at least two shoulders which are visible only for high anodic holding times ($t_h > 200$ s).

3.3. Chronocoulometric measurements

This is a two step process: in the first step, a constant anodic overpotential (η_a) was applied on to the O_2(g)Pt/YSZ cell for varying holding times (charging of the cell). In the second step a constant cathodic overpotential (η_c) was applied for 150 s (discharging of the cell). During discharging, the current (I) passing through the cell was recorded as a function of time (t) as is shown in Fig. 4a for the case of η_a = 100 mV and η_c = 300 mV at T = 450 °C. From this figure the involved stored charge (Q_{stor}) has been determined by integration, taking the discharging curve obtained after 5 min as base line.

Fig. 5 shows Q_{stor} as a function of anodic holding time (t_h) at 100 mV and the inset shows the dependence of Q_{stor} on $t_h^{1/2}$. The

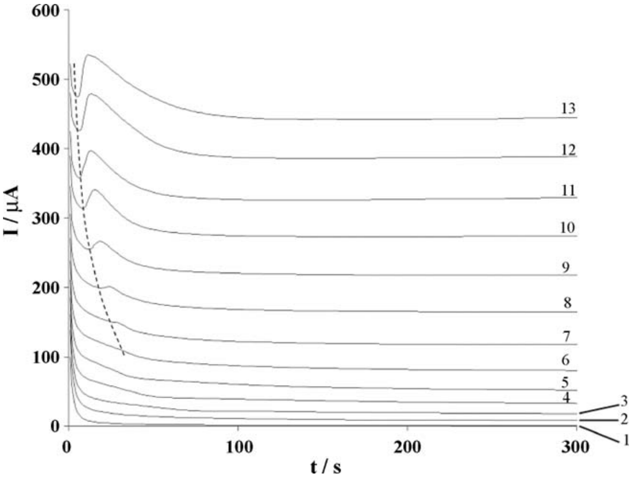

Fig. 1. Chronoamperometric curves obtained at various anodic overpotentials η_a. Increasing overpotential step of 50 mV from open circuit (1) to 600 mV (13), T = 450 °C; $P_{O_2} = 20$ kPa. Dashed line represents the evolution of lag time before the onset of the Pt site regeneration.

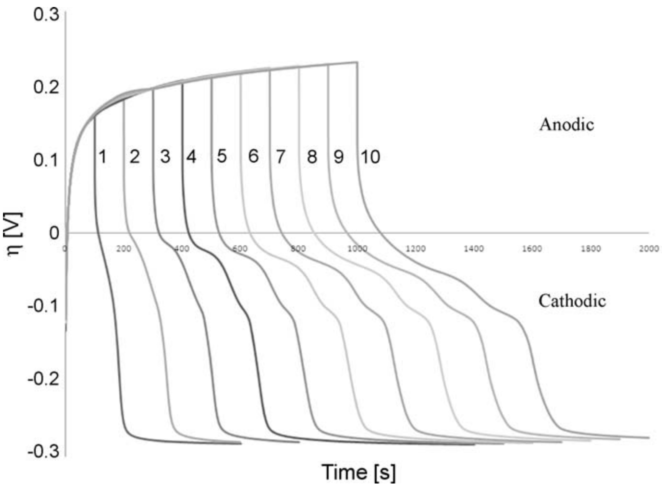

Fig. 3. Double step chronopotentiometry of the O_2(g), Pt/YSZ system. An anodic current (I_a = 30 μA) is applied during 10 different holding times, from 100 s (1) to 1000 s (10), followed by application of a cathodic current (I_c = −30 μA) during 1000 s. $P_{O_2} = 20$ kPa, T = 475 °C.