



## Electrochemical promotion of CO combustion over Pt/YSZ under high vacuum conditions

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### ABSTRACT

Electrochemical promotion of CO combustion over Pt/YSZ was investigated under high vacuum conditions. A galvanostatic step was coupled to mass spectrometric gas analysis using an electrochemical mass spectrometric monitoring device. Non-Faradaic electrochemical promotion of catalysis took place at 300 °C while only electrochemical oxidation was observed at 400 °C. Oxygen evolution measurements revealed that electrochemical promotion is related to the thermodynamically stable PtO<sub>x</sub> species over the Pt/gas interface. The polarization time and O<sub>2</sub> pressure show strong influence on the relaxation transient upon current interruption. We propose that during anodic polarization, PtO<sub>x</sub> is first formed at the Pt/YSZ interface. With prolonged polarization time, the formed PtO<sub>x</sub> either migrates over the Pt/gas interface inducing electrochemical promotion or diffuses into the Pt bulk leading to the oxygen storage. After polarization, the stored O species is released and acts as sacrificial promoter causing the persistent electrochemical promotion effect.

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### 1. Introduction

The catalytic activity of metal and metal oxide catalysts, deposited on solid electrolytes (e.g. Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub>, YSZ), can be increased in a pronounced manner by current or potential application between the catalyst and a gold electrode in an electrochemical cell of the type:

Gaseous reactants, catalyst|solid electrolyte|Au electrode, gaseous reactants

This is reported in the literature as electrochemical promotion (EP) or as non-Faradaic electrochemical modification of catalytic activity (NEMCA). It has been studied during the last few years for several reactions using different catalysts and solid electrolytes [1–3].

The commonly proposed model of EP over Pt/YSZ attributes this phenomenon to electrochemically formed species, i.e. O<sup>δ-</sup>, migrating from the solid electrolyte to the surface of catalyst inducing a work function (WF) change on the metal surface. These oxygen promoters weaken the catalyst–O bond of chemisorbed oxygen atoms which leads to an increase in catalytic rate [4]. Numerous analytical probe techniques, e.g. X-ray photoelectron spectroscopy

(XPS), photoelectron emission microscopy (PEEM), scanning tunneling microscopy (STM), temperature programmed desorption (TPD) coupled to an electrochemical perturbation have been used to monitor (qualitatively and quantitatively) the oxygen species [5–8]. However, few papers reveal the relation between the detected O species and EP effect. Due to the complexity of the system, the electrochemical behavior of a metal/YSZ cell in EP is still not fully understood [9].

In order to shed more light on these processes, a high vacuum (HV) setup was built to perform the electrochemical investigation over Pt/YSZ at 400 °C as described recently [10]. Under anodic polarization, oxygen evolution reactions are identified. We assume that PtO<sub>x</sub> is formed at both the Pt/YSZ and the Pt/gas interface according to two different mechanisms [11]. The PtO<sub>x</sub> species on the Pt/gas interface acts as oxygen promoter and induces the EP effect. At the Pt/YSZ interface, PtO<sub>x</sub> formation is an electrochemical process following a parabolic growth law, while the presence of PtO<sub>x</sub> at the Pt/gas interface is related to the diffusion of PtO<sub>x</sub> formed at the triple phase boundary (TPB) towards the Pt/gas interface [12]. However, the stability of PtO<sub>x</sub> is thermodynamically not favored at 400 °C under HV conditions restraining the appearance of EP [11]. In order to investigate the influence of PtO<sub>x</sub> on EP, decreasing the operation temperature to stabilize PtO<sub>x</sub> seems an alternate way according to thermodynamic data [13].

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In this work, a galvanostatic step is imposed to the Pt/YSZ interface in the presence of reactants ( $O_2$  and CO) at lower temperature (e.g. 300 °C) under HV conditions and the products are analyzed online by mass spectrometry (MS). Based on the assumption that  $PtO_x$  is formed during polarization, the influence of electrochemically formed  $PtO_x$  on the EP at various operation conditions (temperature, polarization time and  $O_2$  pressure) is discussed. A dynamic model of EP over a Pt/YSZ cell is proposed based on these experimental facts.

## 2. Experimental

A commercial zirconia pellet stabilized by 8 mol%  $Y_2O_3$  (Technox 802, Dynamic Ceramic Ltd.) was used as substrate on which a platinum electrode was deposited by magnetron sputtering in Ar at room temperature. The magnetron operates in the direct current (dc) mode maintaining a discharge of 330 V at an Ar pressure of 1 Pa. Under these conditions, a 1  $\mu m$  thick Pt electrode was deposited with a deposition rate of 0.09  $nm s^{-1}$  on the YSZ pellet as determined by profilometric measurements (Alphastep, Model 500) of the film deposited on smooth silicon samples processed simultaneously. The size of Pt working electrode is 7 mm  $\times$  5 mm giving a geometric surface of 0.35  $cm^2$ . The Pt working and Au counter electrodes were located in a symmetrical face-to-face arrangement on the opposite side of the YSZ pellet with the Au reference electrode lying next to the counter electrode. This geometry ensured a symmetrical current and potential distribution in the cell [14]. Before using, the sample has been treated at 700 °C in 20 kPa  $O_2$  during 4 h in order to stabilize the porous platinum electrode films [15].

Electrochemical measurement were carried out under high vacuum (HV) conditions with a background pressure of  $10^{-6}$  Pa by solid electrochemical mass spectrometry (EMS) using a setup described in detail elsewhere [10]. This electrochemical technique involves the imposition of an electrochemical perturbation (Autolab, Metrohm, and PGSTAT30) to the system while monitoring directly by mass spectrometry (QMS, Pfeiffer, Prisma200) the formation of products released into the gas phase. If needed, the reactants i.e.  $O_2$  (46 purity Carbagas certified) and CO (60 purity Carbagas certified), are introduced into the reactor via HV leak valves and capillary stainless steel gas lines. Total pressure is monitored by a cold cathode pressure gage.

In this work, the EMS technique is used under the following conditions:

- Perturbation of the Pt/YSZ interface with an applied current of 10  $\mu A$  at 300 °C and 400 °C in the absence of reactive gas.
- Measurements of electrochemical promotion at an applied current of 4  $\mu A$  in the presence of CO and  $O_2$  at 300 °C. In addition, a galvanostatic step was imposed to Pt/YSZ cell for a variety of polarization time and at different  $O_2$  pressure.

During the measurements, all gas products are monitored online. The response time of the system is 0.5 s.

## 3. Results

### 3.1. Anodic polarization in the absence of reactive gas

Fig. 1 shows the transient effect on the oxygen evolution over Pt/YSZ at 300 °C and 400 °C in the absence of reactive gas at a background pressure of  $10^{-6}$  Pa. When a current of 10  $\mu A$  is applied between the Pt working electrode and the counter electrode, oxygen evolution is observed by MS at both temperatures. During the galvanostatic step, zirconia is electrochemically reduced at the cathode to release  $O^{2-}$  which migrates to the anode across YSZ

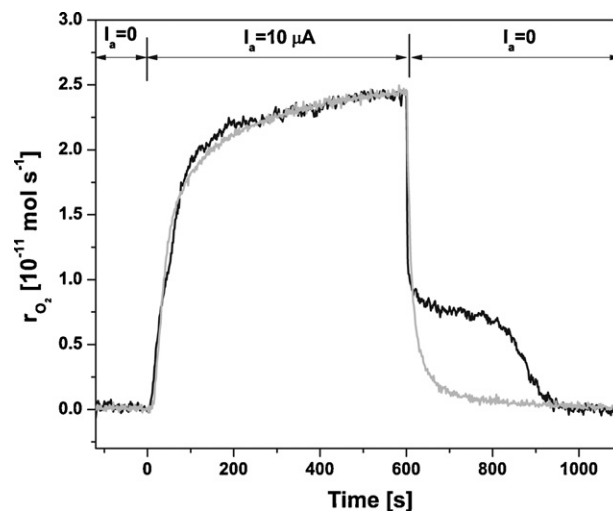


Fig. 1. The transient effect of anodic polarization on the oxygen evolution over Pt/YSZ cell at 300 °C (gray) and 400 °C (black) at a background pressure of  $10^{-6}$  Pa.

according to reaction (R1) [16]. When the potential of Pt electrode (vs. gold reference) is higher than 300 mV [11], oxygen evolution takes place at the triple phase boundary (TPB) of the anode according to reaction (R2):



Upon current interruption, the flux of evolved  $O_2$  decreases back to zero within 1 min at 300 °C while at 400 °C a plateau is observed before returning to the initial open circuit value. This unexpected plateau also occurred in both MS–cyclic voltammetry (MS–CV) and MS–double step chronopotentiometry (MS–DSCP) measurements at the same conditions [11]. During anodic polarization, a fraction of  $PtO_x$  forms at the TPB according to reaction (R3) and diffuses to the Pt/gas interface. However, the thermodynamic instability of  $PtO_x$  under high vacuum conditions at 400 °C results in  $O_2$  release (reaction (R4)).



In contrast, the stabilization of  $PtO_x$  becomes thermodynamically favored at 300 °C under the same atmosphere, which limits  $PtO_x$  decomposition after polarization which explains the behavior as depicted in Fig. 1.

### 3.2. Anodic polarization in the presence of reactive gases

Fig. 2 presents the transient effect of an applied current of 4  $\mu A$  on the catalytic rate of CO combustion at 300 °C ( $P_{CO} = 1.5 \times 10^{-3}$  Pa and  $P_{O_2} = 4.4 \times 10^{-4}$  Pa). In EP experiments, two important parameters are commonly used to quantify the magnitude of the phenomenon, the rate enhancement ratio,  $\rho$ , and the Faradaic efficiency,  $\Lambda$ , as defined by Eqs. (1) and (2):

$$\rho = \frac{r_{CO_2}}{r_{CO_2}^0} \quad (1)$$

and

$$\Lambda = \frac{(r_{CO_2} - r_{CO_2}^0)}{(I/2F)} \quad (2)$$

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