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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_x species over the Pt/gas interface. The polarization time and O₂ pressure show strong influence on the relaxation transient upon current interruption. We propose that during anodic polarization, PtO_x is first formed at the Pt/YSZ interface. With prolonged polarization time, the formed PtO_x 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. Y₂O₃-stabilized ZrO₂, 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^{δ-}, 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_x is formed at both the Pt/YSZ and the Pt/gas interface according to two different mechanisms [11]. The PtO_x species on the Pt/gas interface acts as oxygen promoter and induces the EP effect. At the Pt/YSZ interface, PtO_x formation is an electrochemical process following a parabolic growth law, while the presence of PtO_x at the Pt/gas interface is related to the diffusion of PtO_x formed at the triple phase boundary (TPB) towards the Pt/gas interface [12]. However, the stability of PtO_x is thermodynamically not favored at 400 °C under HV conditions restraining the appearance of EP [11]. In order to investigate the influence of PtO_x on EP, decreasing the operation temperature to stabilize PtO_x 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 $1\ \mu\text{m}$ thick Pt electrode was deposited with a deposition rate of $0.09\ \text{nm s}^{-1}$ 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 $7\ \text{mm} \times 5\ \text{mm}$ giving a geometric surface of $0.35\ \text{cm}^2$. 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 spectroscopy (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 gauge.

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

- Perturbation of the Pt/YSZ interface with an applied current of $10\ \mu\text{A}$ at 300°C and 400°C in the absence of reactive gas.
- Measurements of electrochemical promotion at an applied current of $4\ \mu\text{A}$ 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 $10\ \mu\text{A}$ 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

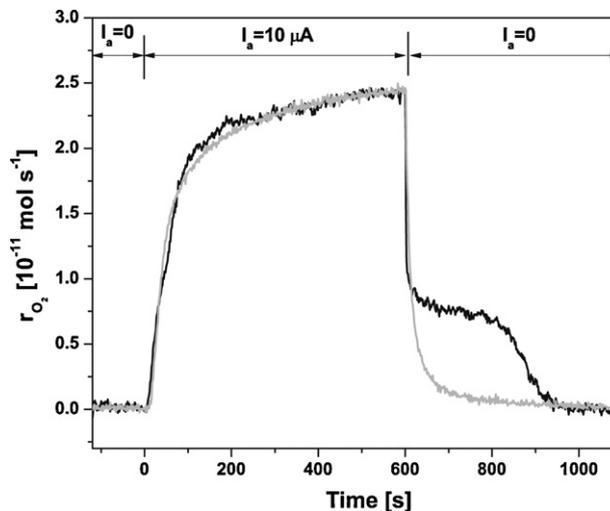


Fig. 1. The transient effect of anodic polarization on the oxygen evolution over Pt/YSZ cell at 300°C (gray) and 400°C (black) at a background pressure of 10^{-6} Pa.

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 $4\ \mu\text{A}$ on the catalytic rate of CO combustion at 300°C ($P_{\text{CO}} = 1.5 \times 10^{-3}$ 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, ρ , and the Faradaic efficiency, Λ , as defined by Eqs. (1) and (2):

$$\rho = \frac{r_{\text{CO}_2}}{r_{\text{CO}_2}^0} \quad (1)$$

and

$$\Lambda = \frac{(r_{\text{CO}_2} - r_{\text{CO}_2}^0)}{(I/2F)} \quad (2)$$

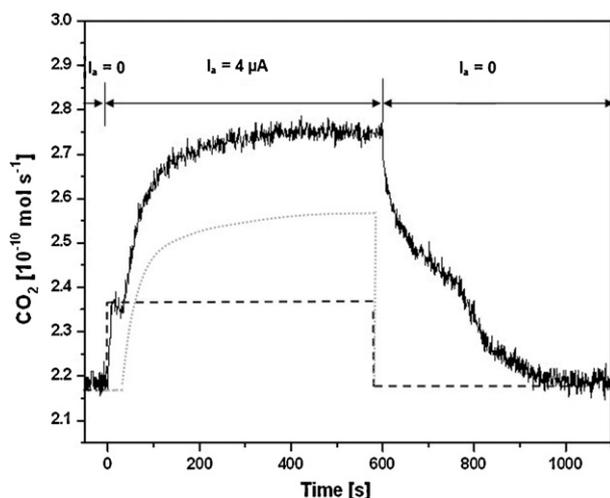


Fig. 2. The transient effect of an applied current of 4 μA on the catalytic rate of CO combustion at 300 °C ($P_{\text{CO}} = 1.5 \times 10^{-3}$ Pa, $P_{\text{O}_2} = 4.4 \times 10^{-4}$ Pa). (---) Faradaic rate, (...) non-Faradaic rate.

where r_{CO_2} and $r_{\text{CO}_2}^0$ are the electropromoted and the initial open circuit rate, respectively, of CO combustion (R5) expressed in mol s^{-1} and F is Faraday's constant.



The open circuit rate yields $r_{\text{CO}_2}^0 = 2.2 \times 10^{-10} \text{ mol s}^{-1}$. The application of a 4 μA current causes a 1.3-fold increasing of the catalytic rate, i.e. $\rho = 1.3$. The Faradaic efficiency, Λ , equals to 2.7 indicating a non-Faradaic process. Worth to note that a small plateau in the CO_2 production with a length of 60 s is observed before the catalytic rate reaches steady state. The value of this CO_2 plateau equals the Faradaic rate, $I/2F$. This is an important observation as it implies that electrochemical oxidation of CO takes place at the TPB before electrochemical promotion occurs. Therefore, the transient reaction under polarization can be easily divided into two processes, i.e. the Faradaic process (reaction (R6)) and the non-Faradaic process (reaction (R5)), as shown in Fig. 2.



Upon current interruption, the catalytic rate decreases and a 400 s relaxation time is needed to obtain the initial open circuit rate. Such reaction relaxation is reported as persistent-EP (*pers-EP*) which is related to the oxygen storage during polarization [17,18].

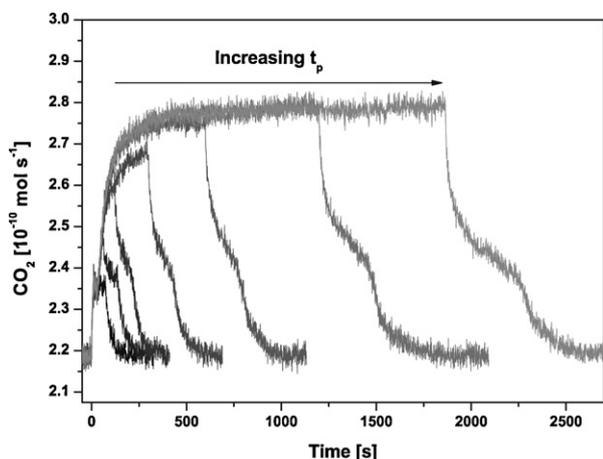


Fig. 3. The influence of holding time, t_p , at 4 μA on the EP performance. t_p increases from 30 s to 1800 s. Conditions: idem Fig. 2.

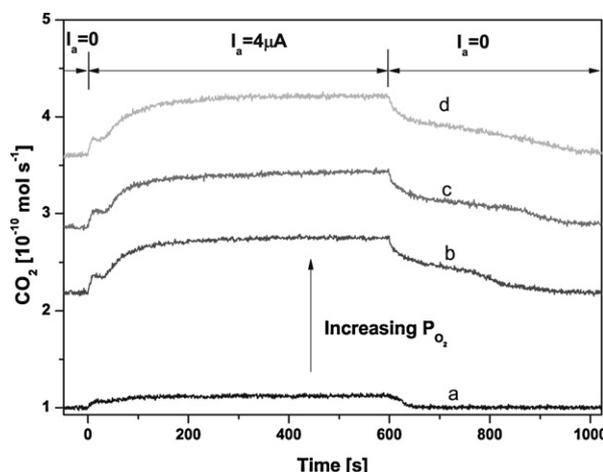


Fig. 4. The influence of O_2 pressure on the EP transient effect of CO oxidation at an applied current of 4 μA . O_2 pressure, P_{O_2} (a) 4.8×10^{-5} Pa, (b) 4.4×10^{-4} Pa, (c) 9×10^{-4} Pa, (d) 1.5×10^{-3} Pa. $P_{\text{CO}} = 1.5 \times 10^{-3}$ Pa. $T = 300^\circ\text{C}$.

Fig. 3 presents the influence of polarization time, t_H , on the transient effect of catalytic rate at 300 °C in the presence of reactive gases. A galvanostatic step of 4 μA was applied for various holding times from 30 s to 1800 s. It is observed that the initial CO_2 plateau is independent on the polarization time. In addition, once the steady state catalytic rate is reached at $t = 400$ s, it remains constant independent on the duration of prolonged anodic polarization. In contrast, longer and longer relaxation times are required to attain the initial open circuit rate upon current interruption by increasing the polarization time. Indeed, the shape of the relaxation transient strongly depends on t_p , but it has no effect on the electropromoted steady state rate during polarization. This strongly indicates that the polarization at long t_p must influence a part of the system which is not exposed to the catalytic reaction. At current interruption, this “hidden” influence becomes visible, so the species implicated must reach the active catalytic surface of the system [19].

The reaction rate transients during application of a constant anodic current on the CO_2 catalytic rate for varying O_2 pressure are presented in Fig. 4. At low O_2 pressure (4.8×10^{-5} Pa), the polarization of the Pt/YSZ cell only causes predominantly a Faradaic increase of the catalytic rate ($\Lambda < 1$). Most of the CO_2 product forms due to the electrochemical oxidation of CO at the TPB.

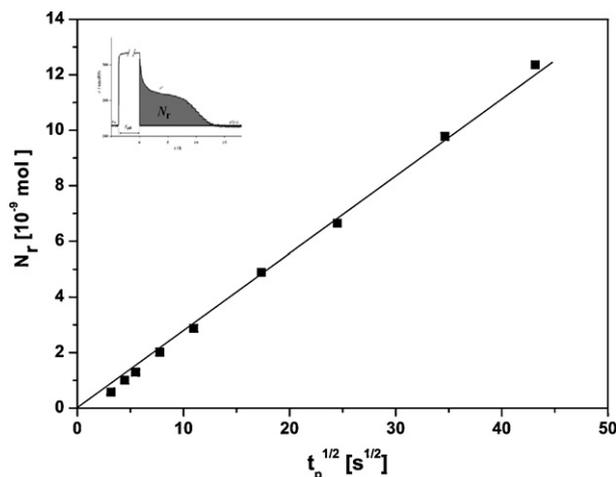


Fig. 5. Integrated amount of oxygen species, N_r , consumed via CO combustion after current interruption as a function of the square root of polarization time, $t_p^{1/2}$, in Fig. 3.

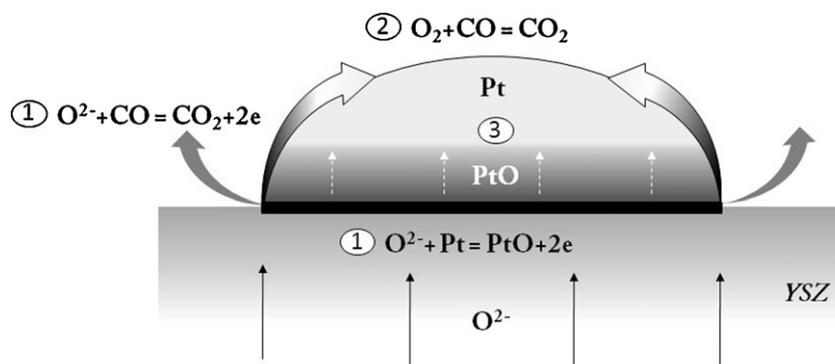


Fig. 6. Schematic representation of reaction processes during anodic polarization. The kinetic processes involved in electrochemical promotion. (1) PtO electrochemical formation at the Pt/YSZ interface and CO electrochemical oxidation at the TPB. (2) Migration of O promoter to the Pt/gas interface inducing EP effect. (3) Growth of platinum oxide from the Pt/YSZ interface into Pt bulk leading to *pers*-EP after polarization.

With increasing O_2 pressure, the promoted rate strongly increases, evidencing both the CO_2 plateau at the beginning of polarization and the independence or saturation of the promoted rate. In contrast, the variation of O_2 pressure has an important influence on the *pers*-EP, i.e. longer relaxation time under higher O_2 pressure.

4. Discussion

In our previous paper, the electrochemical measurements were carried out over a Pt/YSZ cell at $400^\circ C$ under a background pressure of 10^{-6} Pa. The polarization only caused a Faradaic increase of the catalytic rate with $\Lambda = 0.1$ [11]. The lack of non-Faradaic processes is attributed to the thermodynamic instability of PtO_x under operation conditions according to [13]. The unstable PtO_x species either reacts with CO forming CO_2 or to desorb in the form of O_2 (Fig. 1). In contrast, when the cell temperature decreases to $300^\circ C$, a non-Faradaic rate is observed as depicted in Fig. 2. Under this condition, the stabilization of surface PtO_x is thermodynamically favored. PtO_x species stabilized on the Pt surface lead to the appearance of EP which is in agreement with HV results reported by Katsaounis et al. [20].

In the literature, either the EP effect on the catalytic rate or the existence of surface O species under polarization is discussed. Here we give evidence that the EP effect is determined by the electrochemically formed O species over the Pt/gas interface as in the “sacrificial” promoter mechanism of EP proposed by Vayenas et al. [4].

The phenomenon of *pers*-EPOC after polarization was first observed in the C_2H_4 combustion over Pt/YSZ at high temperature (500 – $600^\circ C$) under ambient pressure [21]. For a better understanding, a series of techniques such as single and double step chronoamperometry, chronocoulometry and programmed cyclic voltammetry were performed as reported in [22]. They indicated that application of an anodic polarization on the Pt/YSZ system caused short and long term oxygen storage in the working electrode. Upon current interruption, the stored O species are released to the catalytic Pt surface and act as the sacrificial promoters leading to *pers*-EPOC. In Fig. 3, prolonged polarization presents significant influence on *pers*-EPOC rather than on electropromoted steady state rate indicating that stored oxygen species are hidden in the non-gas exposed location, i.e. Pt/YSZ interface and Pt bulk [15]. By integration of the relaxation part as shown in Fig. 5, the total amount of consumed O atoms, N_r , is found to be proportional to $t_H^{1/2}$. According to the oxygen storage model, upon current interruption, the stored oxygen species is released over the Pt surface and act as sacrificial promoter inducing *pers*-EPOC. Actually, the relaxation part N_r is composed of two parts, i.e. consumption of stored oxygen promoter N_p and absorbed oxygen from gas phase

N_o as Eq. (3). The amount of the latter is directly determined by former as Eq. (4). Thus, the integration of the transient part is a reasonable way to characterize the change of the stored oxygen promoter as a function of polarization time.

$$N_r = N_p + N_o \quad (3)$$

$$N_o = A \times N_p \quad (4)$$

where A is termed as persistent constant.

From Eqs. (3) and (4)

$$N_r = N_p(1+A) \quad (5)$$

According to Fig. 5 and Eq. (5), the amount of stored oxygen promoter, N_p , also obeys the $t_H^{1/2}$ kinetic law as N_r , typical for diffusion controlled processes [21]. This supports the idea of oxygen diffusion from the Pt/YSZ interface into the Pt bulk under prolonged polarization. The amount of deposited Pt can be considered as an infinite reservoir. Furthermore, the increase of P_{O_2} has a dramatic impact not only on EPOC but also on *pers*-EPOC. Higher O_2 pressure is in favor of *pers*-EP leading to longer relaxation time as depicted in Fig. 4.

The dynamic model of electrochemical promotion over Pt/YSZ cell is schematically shown in Fig. 6. In reactive atmosphere, O^{2-} ions are formed in the cathode (reaction (R1)) and diffuse through YSZ to the anode under anodic polarization. A monolayer of PtO is formed at the Pt/YSZ (reaction (R3)) while electrochemical oxidation of CO takes place at TPB (reaction (R6)) as (1). Once the TPB and Pt/YSZ interface are saturated, the electrochemically formed PtO_x species migrate to the Pt/gas interface as back-spillover promoters inducing the EP effect (2) and simultaneously diffuse through the Pt bulk as oxygen storage (3) leading to *pers*-EP after polarization as illustrated in Fig. 3.

5. Conclusion

A galvanostatic step is applied to Pt/YSZ in the presence of O_2 and CO at $300^\circ C$ and $400^\circ C$ under high vacuum conditions. The catalytic rate presents the electrochemical promotion effect at $300^\circ C$ while only electrochemical oxidation is observed at $400^\circ C$. The measurement of oxygen evolution in the absence of reactive gas is assumed to be a consequence of the instability of electrochemically formed PtO_x species at higher temperature. This means that thermodynamically stable PtO_x over the Pt/gas interface has to be present to induce the electrochemical promotion.

The polarization time has an important influence on the performance of *pers*-EP while it has no effect on the promoted steady state rate. Such relaxation transient is attributed to the oxygen storage hidden in the non-gas exposed places, i.e. Pt/YSZ interface and Pt

bulk. Upon current interruption, the stored O species are released to the Pt/gas interface keeping the catalytic rate at the promoted state. In addition, the behavior of *pers*-EP is affected by the O₂ pressure, i.e. longer relaxation time under higher O₂ pressure.

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