

# Charge storage at Pt/YSZ interface as the origin of ‘permanent’ electrochemical promotion of catalysis

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## Abstract

Tuning of the catalytic reaction rate by electric polarization of the interface between an electron conducting catalyst and an ion conducting support, called electrochemical promotion of catalysis (EPOC), is most often fully reversible. Its state-of-the-art model regards the gas-exposed catalyst surface as the unique location of charge storage via backspillover of electrochemically generated species, responsible for promotion. After long-lasting anodic polarization, a permanent effect (P-EPOC) was observed in ethylene combustion with oxygen over Pt/YSZ catalyst. Double step chronoamperometric and linear sweep voltammetric analysis revealed delayed oxygen storage, located presumably at the vicinity of the catalyst/electrolyte interface. It is proposed that oxygen stored at this location, hence hidden for the reactants and then released during relaxation, was at the origin of the observed P-EPOC. The effect of this ‘hidden’ promoter on the catalytic reaction rate was found to be highly non Faradaic.

## Keywords

EPOC · Permanent promotion · Pt/YSZ catalyst · Oxygen storage

## Acknowledgement

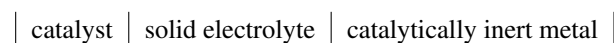
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## 1 Introduction

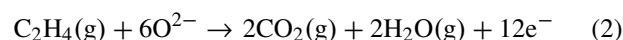
Controlled tuning of catalytic activity has been a long-sought goal in heterogeneous catalysis. In their pioneering work in the early 1980s Vayenas et al. reported the control of catalytic reactions via electrochemical polarization [1]. They found that the catalytic activity of thin porous metal catalyst films could be tuned in a controlled manner by polarization of the catalyst/solid electrolyte interface in an electrochemical cell of the type:



where the catalyst film is the working electrode and the catalytically inert metal (typically gold) is the counter electrode. Take the example of ethylene combustion as catalytic reaction:



occurring at an open-circuit reaction rate of  $r_o$  (mol O s<sup>-1</sup>). Using an oxide ion (O<sup>2-</sup>) conducting material (e.g. yttria-stabilized-zirconia, YSZ) as solid electrolyte, application of an anodic current between the counter and the working electrode (now the solid electrolyte is the source of O<sup>2-</sup> ions and the working electrode is the collector of electrons) may result in the electrochemical oxidation of ethylene at the working electrode:

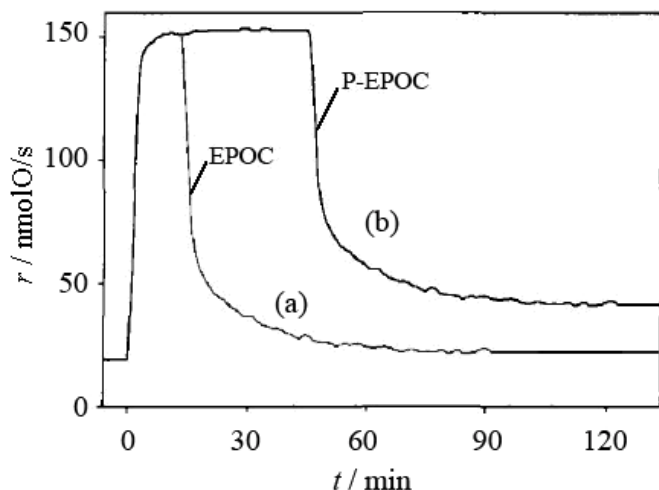


Supposing a current efficiency of 100%, the maximum possible electrochemical reaction rate,  $r_{el}$  (mol O s<sup>-1</sup>), is calculated with Faraday’s law:

$$r_{el} = I/zF \quad (3)$$

where  $I$  is the electric current,  $z$  is the charge number of the transported ions (for O<sup>2-</sup>,  $z = 2$ ), and  $F$  is the Faraday constant. If open-circuit and Faradaic reactions would be simply added, Eq. (3) would give the maximum expected increase in reaction rate due to polarization.

Fig. 1 shows, in a schematic way, the evolution of the experimentally observed reaction rate,  $r$ , in a stepwise anodic polarization cycle, i.e. before, during, and after galvanostatic polarization of the catalyst/YSZ interface. It is seen, that the experimental rate increase,  $r - r_o$ , is by orders of magnitude higher



**Fig. 1.** Polarization and relaxation transients of the rate of ethylene combustion on IrO<sub>2</sub>/YSZ catalyst due to anodic current application (300 μA) with two different polarization times: (a) short polarization of 15 min resulting in reversible EPOC and (b) long polarization of 50 min resulting in P-EPOC.  $T = 380^{\circ}\text{C}$ ,  $p_{\text{O}_2} = 17 \text{ kPa}$ ,  $p_{\text{C}_2\text{H}_4} = 140 \text{ Pa}$ . [8]

than the maximum possible rate increase ( $1.6 \text{ nmol O s}^{-1}$ ) calculated from Faraday's law. Obviously, polarization of the catalyst/electrolyte interface causes a dramatic alteration in catalytic activity rather than simply contribute to the reaction rate by adding the electrochemical (Faradaic) reaction. The highly non-Faradaic character of electrochemical promotion originates its currently used synonym: non-Faradaic electrochemical modification of catalytic activity (NEMCA effect) [2].

EPOC is usually quantified by two parameters,  $\rho$  and  $\Lambda$ . The rate enhancement factor,  $\rho$ , is defined as the ratio of the steady-state promoted catalytic rate,  $r$ , to the initial open-circuit reaction rate,  $r_o$ , and is a measure of the level of promotion:

$$\rho = r/r_o \quad (4)$$

The Faradaic efficiency,  $\Lambda$ , is defined as the ratio of the observed rate increase to the maximum possible electrochemical rate:

$$\Lambda = (r - r_o)/(I/zF) \quad (5)$$

so  $|\Lambda| > 1$  is the criterion of non-Faradaic behavior. For the example seen in Fig. 1, the approximate values are  $\rho \approx 7$  and  $\Lambda \approx 85$ .

Since its discovery [1], the non-Faradaic character of EPOC promotion has been demonstrated for more than 70 catalytic reactions, and it is now well established that EPOC is not limited to any particular class of catalysts, electrolytes or reactions [3]. The current understanding of the physicochemical origin of the phenomenon, based on numerous spectroscopic and electrochemical techniques and reviewed thoroughly [3, 4], attributes the effect of electrochemical promotion to transport of ionic species through the solid electrolyte support, their discharge at the triple phase boundary (tpb) and subsequent migration of the

discharged species to the catalytically active catalyst/gas interface. The discharged species act as promoters but are also consumed by the catalytic reaction and/or desorption. The resulting steady-state population of promoters at the gas exposed catalyst surface causes a potential-controlled change in the work function of this latter. According to this concept, EPOC is reversible and the catalyst restores its initial activity, typically within a few tens of minutes, after potential or current interruption.

In our laboratory, several cases of irreversible EPOC have been reported. Such effect, termed 'permanent' electrochemical promotion (P-EPOC), was first observed with IrO<sub>2</sub> catalyst for ethylene combustion [5], and later also with RuO<sub>2</sub> [6] and Rh [7] catalysts, all interfaced with YSZ. Recently, it was found that reversibility of EPOC may depend strongly on the duration of polarization [8]. In fact, as illustrated in Fig. 1, in the same catalytic system short (15 min) polarization causes reversible promotion, see curve (a), while after prolonged (50 min) polarization the open-circuit catalytic reaction rate after current interruption remains significantly higher than its initial value before current application, see curve (b). Such behavior can not be interpreted with the current model of EPOC.

In this paper, recent studies are reviewed on the phenomenon of P-EPOC with Pt/YSZ catalyst combining reaction rate measurements in ethylene combustion [8] and electrochemical analysis [9]-[11], aiming at getting a deeper insight to the origin of P-EPOC.

## 2 Experimental

In the single-pellet type three-electrode Pt/YSZ electrochemical cell used for catalytic measurements, the working electrode was a platinum film deposited onto a 1 mm thick YSZ (8 mol%) pellet by non-reactive magnetron sputtering of platinum at ambient temperature in argon atmosphere followed by heat treatment at  $700^{\circ}\text{C}$  in air, while counter and reference electrodes were pasted gold films (Gwent C70219R4) fired at  $550^{\circ}\text{C}$  in air. The size of the electrodes was  $7 \times 5 \text{ mm}$ , giving a geometric surface of  $0.35 \text{ cm}^2$ . More details on cell preparation are given elsewhere [12]. In the cell used for electrochemical characterization, all three electrodes were platinum films deposited onto a 1.3 mm thick YSZ (8 mol%) pellet by screen-printing of a paste, composed of 65%<sub>w</sub> of  $1 \mu\text{m}$  particle size platinum powder (Fluka), 11%<sub>w</sub> of  $1 \mu\text{m}$  particle size YSZ (8 mol% Y<sub>2</sub>O<sub>3</sub> in ZrO<sub>2</sub>, Tosoh) and 24%<sub>w</sub> of a polyvinyl pyrrolidone solution (2% in isopropanol, Fluka), followed by sintering at  $1400^{\circ}\text{C}$  in air to give a film thickness of  $15 \mu\text{m}$ . The resulting deposits of  $0.08 \text{ cm}^2$  geometric surface area each are composed of 62%<sub>vol</sub> of platinum and 38%<sub>vol</sub> of YSZ and they are highly porous. No morphological change has been observed due to prolonged use and/or polarization during working months.

The reactor for both catalytic and electrochemical measurements 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, and it worked un-

der atmospheric pressure. The electrochemical cells were suspended in the reactor with three gold wires serving as electrical contacts to the electrodes. The reactor was put into a furnace (XVA271, Horst) equipped with a heat control system (HT30, Horst), and the temperature was measured with a K-type (NiCr-Ni) thermocouple placed in proximity of the surface of the working electrode. Constant gas flow of  $200 \text{ ml min}^{-1}$  STP was fed by mass flow controllers (E-5514-FA, Bronkhorst). Catalytic measurements were conducted in a slightly oxidizing reactive gas mixture containing  $0.25 \text{ kPa C}_2\text{H}_4$  and  $1 \text{ kPa O}_2$ , while electrochemical characterization was made at  $20 \text{ kPa O}_2$  partial pressure. The gas sources were Carbagas certified standards of  $\text{O}_2$  (99.95%) and  $\text{C}_2\text{H}_4$  (99.95%) supplied, respectively, as 20% and 1% mixture in He (99.996%). Balance was helium of 99.996% purity.

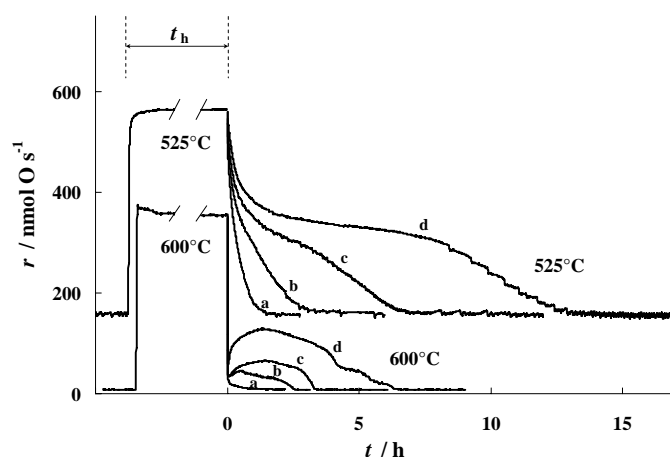
Electrochemical promotion experiments were realized in potentiostatic mode of operation using a potentiostat (EG&G PAR, Model 362), and  $\text{CO}_2$  production of the catalytic oxidation of ethylene was monitored on-line using an IR analyzer (Horiba PIR 2000). Chronoamperometric and voltammetric measurements were made with a scanning potentiostat (Autolab, Model PGSTAT30, EcoChemie).

### 3 Results

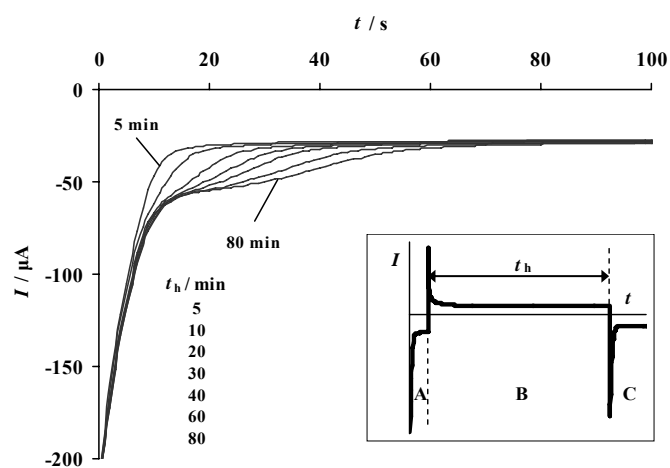
Used as catalyst and working electrode at the same time, the catalytic activity of Pt deposited onto YSZ was measured under both open-circuit and anodically promoted conditions, the model catalytic reaction being the combustion of ethylene with oxygen [8]. Electrochemical characterization of the Pt/YSZ electrode was made using chronoamperometry [10, 11] and linear sweep voltammetry [9]-[11] in  $\text{O}_2$ -containing atmosphere.

The reaction rate of the catalytic combustion of ethylene with oxygen over the Pt/YSZ catalyst was measured at two different temperatures in an ethylene/oxygen mixture of slightly oxidizing composition. Potentiostatic anodic polarization at  $E_{WR} = 400 \text{ mV}$  was applied for varying holding times,  $t_h$ , and polarization and relaxation transients of the catalytic reaction rate were recorded, shown in Fig. 2. Initially the catalyst is under open-circuit conditions and the non-promoted rate is about  $r_o = 150 \text{ nmol O s}^{-1}$  at  $525^\circ\text{C}$ , while it equals only about  $15 \text{ nmol O s}^{-1}$  at  $600^\circ\text{C}$  due to known desactivation of Pt catalyst above  $550^\circ\text{C}$ . Once a positive catalyst potential is applied, the rate immediately starts increasing. The time needed for the catalytic rate to reach its new electropromoted steady-state value is approximately 1 hour. At 525 and  $600^\circ\text{C}$ , respectively, the rate enhancement ratio is  $\rho = 3.5$  and 24, and the Faradaic efficiency is  $\Lambda = 160$  and 40, showing strong non-Faradaic effect even at  $600^\circ\text{C}$  which is quite exceptional at such high temperature. It is seen, that once the steady-state rate is reached, it remains constant whatever is the duration of prolonged anodic polarization. The relaxation transients, however, are strongly dependent of the polarization time,  $t_h$ . After short polarization ( $t_h = 1 \text{ h}$ ) the open-circuit catalytic activity drops abruptly and

reaches quickly its initial values like in any typical (reversible) EPOC experiment. In contrast, by increasing the polarization time, longer and longer relaxation is required to attain the initial catalytic activity. At the higher temperature the relaxation, just like any kinetics, is faster but also passing through a maximum. As seen, the effect of polarization time,  $t_h$ , is only observed once the circuit is opened, but it has apparently no effect on the electropromoted steady-state reaction rate during the polarization step. Obviously, long-lasting polarization must alter a part of the system which is not exposed to the catalytic reaction. After current interruption this hidden influence becomes visible, so the species implicated must reach somehow the active catalytic surface of the system.



**Fig. 2.** Electrochemical promotion of ethylene oxidation on Pt/YSZ catalyst at two different temperatures ( $525^\circ\text{C}$  and  $600^\circ\text{C}$ ). Effect of the anodic polarization time ( $t_h$ ), a: 1 h, b: 2 h, c: 4 h, d: 11 h, on the rate transients observed during open-circuit relaxation. Potentiostatic mode of operation with  $E_{WR} = +400 \text{ mV}$ , the resulting current is about 0.5 and 1.6 mA at  $525^\circ\text{C}$  and  $600^\circ\text{C}$ , respectively. Feed composition:  $p_{\text{C}_2\text{H}_4} = 0.25 \text{ kPa}$ ,  $p_{\text{O}_2} = 1 \text{ kPa}$ .

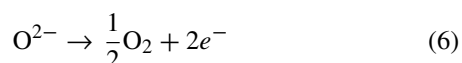


**Fig. 3.** Double step chronoamperometry in the  $\text{O}_2(\text{g})/\text{Pt}/\text{YSZ}$  system [10]. Effect of the holding time,  $t_h$ , at the anodic potential of  $E_h = 100 \text{ mV}$  on the current transients obtained during the cathodic discharging step (C).  $E_{dis} = -300 \text{ mV}$ ,  $T = 450^\circ\text{C}$ ,  $p_{\text{O}_2} = 20 \text{ kPa}$ . Insert: schematic illustration of the current response to the subsequent potential steps: cathodic pretreatment (A), anodic polarization (B), and cathodic discharge (C).

Double-step chronoamperometric measurements [10] were

made at 450°C using a potential program composed of a pretreatment step and two measurement steps (see the inset in Fig. 3). The cathodic pretreatment step (A), polarization at a constant potential of  $E_{pre} = -400$  mV for  $t_{pre} = 60$  s, aims to reduce any residual oxidized species and so providing a well-defined initial state. In the first measurement step (B) a constant anodic holding potential,  $E_h$ , was applied for varying holding times,  $t_h$ . Then, in the second measuring step (C), the cell was discharged by setting the potential to a constant cathodic potential,  $E_{dis} = -300$  mV, held for  $t_{dis} = 150$  s. This step aims to reduce the species formed during the preceding anodic potential holding step. During the two measuring steps, the current passing through the cell was recorded as a function of time.

The observed chronoamperometric transients of the anodic polarization step (B) were composed of two parts. In the first transient part, the current decreased with a time constant of a few tens of seconds to reach a non-zero steady-state value characteristic to the second part. The time constant and the current, both transient and steady-state, depended on the anodic holding potential. The non-zero steady-state current indicates clearly the existence of an anodic Faradaic process under positive polarization, which persists at infinite time. This process is attributed mainly to the oxygen evolution reaction (Eq. 6), which is the discharge of  $O^{2-}$  ion from the solid electrolyte:



However, one can not exclude that the observed finite steady-state current is contributed also from other Faradaic reactions related to charge storage, as it will be shown below.

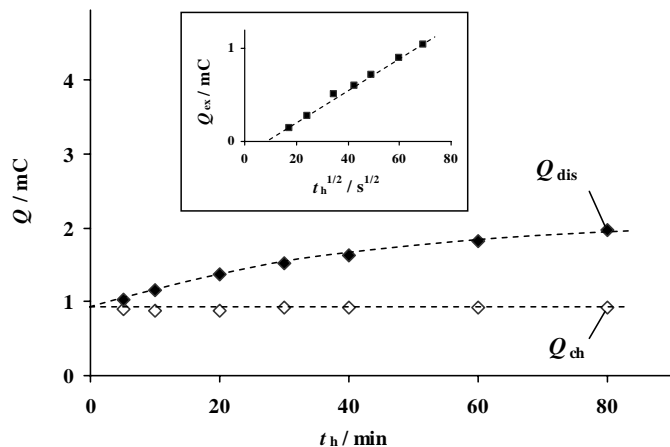
On the other hand, there is a clear evidence of a Faradaic contribution also to the transient current. In fact, the experimentally found time constant is by several orders of magnitude higher than that of double layer charging of a blocking Pt/YSZ interface in the given cell, estimated with the ohmic resistance of the electrolyte ( $R_{el} = 980 \Omega$  measured by impedance spectroscopy), with the capacitance of the double layer ( $C_{dl} = 50 \mu F cm^{-2}$  [13]) and with the geometric surface area of the electrode ( $S = 0.08 cm^2$ ) to give  $\tau = R_{el} C_{dl} S = 4$  ms. Even with a roughness factor (meaning here the ratio of the Pt/YSZ interface area to the geometric area) estimated to be as high as 10, the time constant of double layer charging would remain by at least two orders of magnitude below the experimentally obtained value. This indicates a contribution from another phenomenon, which is not only much slower than the electrostatic double layer charging but it is also at the origin of the pseudocapacity of the electrode which is by orders of magnitude higher than the electrostatic double layer capacity.

Fig. 3 shows the current transients during cathodic discharge, step (C), subsequent to anodic polarization at  $E_h = +100$  mV for varying holding time,  $t_h$ . For short holding time ( $t_h = 5$  min), a relatively fast decay of the cathodic current is observed, approaching a steady-state value ( $-30 \mu A$ ) after about 10 s. The

other curves also show a rapid decay in the initial stage of the cathodic current ( $t < 10$  s), but as  $t_h$  increases, more and more time is needed to reach the steady-state current. In particular, after a long polarization time of  $t_h = 80$  min, 80 seconds are necessary to reach the steady-state. This suggests that, during anodic polarization, charge is stored via a Faradaic process, and this is not limited to the period of anodic current decay but is extended to the region of steady-state, in parallel to the main reaction of  $O_2$  evolution.

The charges involved in the storage process were determined by integration of the chronoamperometric transients using the final steady-state currents as baseline to give values of  $Q_{ch}$  and  $Q_{dis}$  in the anodic (charging) and the cathodic (discharging) step, respectively. The value of  $Q_{dis}$  is regarded as the charge effectively stored during the anodic step. Fig. 4 shows the values of  $Q_{ch}$  and  $Q_{dis}$  obtained by integration of the  $I - t$  curves in Fig. 3 as a function of the anodic holding time in the range of 5 to 80 minutes. Contrary to  $Q_{ch}$ , which is independent of  $t_h$ ,  $Q_{dis}$  increases with increasing  $t_h$ . At short holding time ( $t_h = 5$  min) the two charges are comparable, meaning that the charge apparently stored during the anodic charging step represents the totality of the stored charge measured by its release during the discharging step. However, as  $t_h$  increases,  $Q_{dis}$  exceeds  $Q_{ch}$ , meaning that the electrode has stored more charge than expected from the anodic  $I - t$  curve. The difference between these two charges, a sort of excess charge,  $Q_{ex} (= Q_{dis} - Q_{ch})$  was found to be a linear function of  $t_h^{1/2}$  (see the inset of Fig. 4), suggesting a diffusion-controlled process. The linear extrapolation, however, does not pass through the origin of the plot, having an intersection of  $t_h^{1/2} = 10 s^{1/2}$  at  $Q_{ex} = 0$ . This means that there is a delay of roughly 100 s after the onset of the anodic polarization before excess charge is stored with a  $t_h^{1/2}$  kinetic rule. Then this storage process goes on during the totality of the anodic polarization step, including the period of steady-state current. Hence, a certain fraction of the apparent steady-state current is in fact stored as excess charge. One can define a charge storage yield as the ratio between  $Q_{ex}$  and the total charge passing as steady-state current. In the present case, the obtained yield lies between 1.5 and 6% and tends to decrease with increasing  $t_h$ .

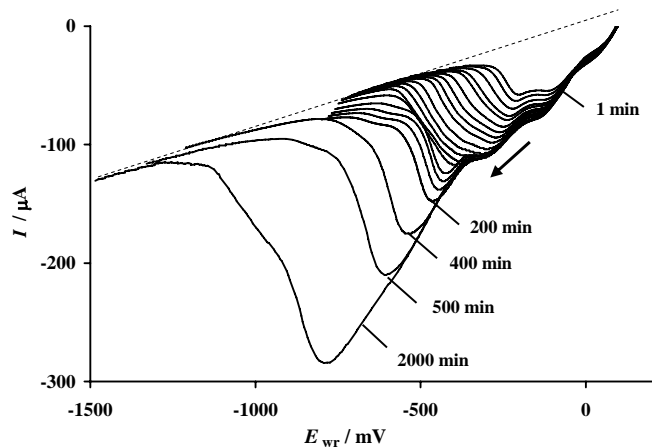
These observations are in good agreement with linear sweep voltammetric measurements, made first with moderate [9] and later with very long anodic potential holding [10]. The measurements consisted of a cathodic pretreatment step, identical to that of the above chronoamperometric experiments, and an anodic potential holding step at  $E_h = +100$  mV for different holding times between 1 and 2000 minutes, followed by a linear potential sweep down to a cathodic potential of -800 mV with a scan rate of  $10 mV s^{-1}$  (first cathodic scan). Fig. 5 shows a typical voltammetric response of the Pt/YSZ electrode. At a very short holding time (1 min), two distinct reduction peaks appear with comparable sizes at about -150 and -250 mV, respectively. By increasing  $t_h$ , the second peak increases more rapidly than the first peak. By further increasing the holding time, a third peak



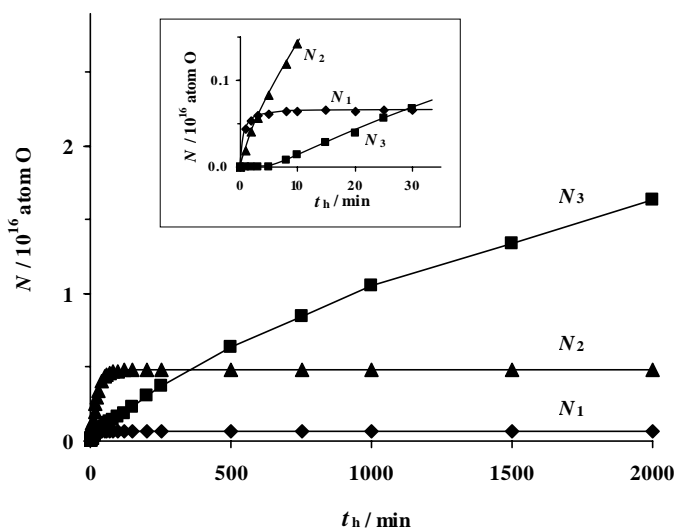
**Fig. 4.** Double step chronoamperometry in the  $O_2(g)$ ,Pt/YSZ system [10]. Effect of the anodic holding time,  $t_h$ , on  $Q_{ch}$  ( $\diamond$ ) and  $Q_{dis}$  ( $\blacklozenge$ ). The inset shows the  $Q_{ex}$  vs  $t_h^{1/2}$  plot, where  $Q_{ex} = Q_{dis} - Q_{ch}$ . Experimental conditions as in Fig. 3.

– not observed at very low  $t_h$  – appears progressively. One can discern the third peak from about  $t_h = 10$  min. At higher holding times ( $t_h > 80$  min), the first and second peaks have stopped growing, but the third peak shows no sign of saturation. This appears clearly in Fig. 6 which reports the charge for each peak as a function of the holding time. The charges were obtained by peak integration and given in terms of equivalent amount of oxygen atoms ( $\text{atom O cm}^{-2}$ ) for the three peaks ( $N_1$ ,  $N_2$  and  $N_3$ , respectively), calculated with the exchange of two electrons and referred to unit geometrical surface area of the deposit. The amount involved in the first peak increases from the beginning and reaches saturation in about 10 minutes. Similarly, the second peak starts to grow from the beginning suggesting two parallel processes. Also the area of the second peak tends to saturation, at a value of about seven times higher than that of the first peak, in about 80 minutes of holding time. As seen in the inset of Fig. 6, the third peak starts growing when the first peak has reached its saturation. Therefore this process seems to be consecutive to that of the first peak. The third peak then grows continuously and, during holding times as long as 2000 min, there is no clear sign of any tendency to peak area saturation.

Similarly to the accumulation of the excess charge in the double-step chronoamperometric experiments (see the inset of Fig. 4), also the increase in the area of the third voltammetric peak ( $N_3$ ) follows  $t_h^{1/2}$  kinetics, suggesting again a diffusion mechanism [10]. Supposing that  $N_1$  corresponds to the formation of an oxide monolayer at the Pt/YSZ interface and  $N_3$  to the formation of multilayer, one can estimate the diffusion length  $L_t$  at a given time from  $L_t = d N_3(t_h) / N_1$ , where  $N_3(t_h)$  is the amount of oxygen atoms in the multilayer at time  $t_h$ ,  $N_1$  is the amount of oxygen atoms in the monolayer at the Pt/YSZ interface ( $6.6 \times 10^{14}$  atom) and  $d$  is the average thickness of an oxide layer ( $2.7 \times 10^{-10}$  m, estimated with the Pt-Pt atomic distance [14]). Knowing the diffusion length as a function of time, a diffusion coefficient of  $D = 3 \times 10^{-22} \text{ m}^2 \text{ s}^{-1}$  is calculated. This



**Fig. 5.** Linear sweep voltammetry in the  $O_2(g)$ ,Pt/YSZ system [10]. Effect of the holding time,  $t_h$ , at  $E_h = 100$  mV on the first cathodic scan.  $T = 450^\circ\text{C}$ ,  $p_{O_2} = 20$  kPa,  $v = 10 \text{ mV s}^{-1}$ . Dashed line shows the baseline used for peak area integration.

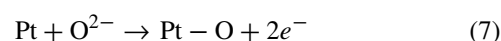


**Fig. 6.** Linear sweep voltammetry in the  $O_2(g)$ ,Pt/YSZ system [10]. Effect of holding time,  $t_h$ , at  $E_h = 100$  mV on the amount of stored oxygen reduced in the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> peaks. The amount of oxygen atoms,  $N$ , is calculated assuming the exchange of two electrons. The inset shows a zoom on the domain of short holding time. Experimental conditions as in Fig. 5

value is typical for a diffusion process in a solid phase and is in good agreement with prediction [15] for the diffusion of oxygen inside platinum at the experimental temperature of  $450^\circ\text{C}$ .

#### 4 Discussion

The pseudocapacitive behavior of the  $O_2(g)$ ,Pt/YSZ system reveals that Faradaic processes contribute to both the time dependent and the steady-state current observed in chronoamperometry. A possible reaction scheme involving two anodic Faradaic processes is proposed. One of them is oxygen evolution via electrochemical oxidation of  $O^{2-}$  ions (Eq. 6), responsible for the main part of the steady-state current, while the other is electrochemical oxidation of platinum to form Pt–O type species (Eq. 7), responsible for charge storage:



where use of the symbol Pt–O is due to the unknown stoichiometry of the electrochemically formed oxide [16]. The two reaction paths share the same reactant  $O^{2-}$ , the charge carrier in the solid electrolyte YSZ.

Charge storage may take place at different locations in the  $O_2(g), Pt/YSZ$  system. First,  $O^{2-}$  originating from the YSZ lattice gets in contact with the Pt electrode to form a platinum-oxygen compound by releasing two electrons. The formation of this first oxide layer at the Pt/YSZ binary interface is believed to be at the origin of the first peak observed by linear sweep voltammetry. The process is fairly reversible, and the completion of this oxide layer is rapid requiring about 10 minutes of holding time at the anodic potential of +100 mV (see the inset of Fig. 6). The saturation amount of the oxide species is  $8 \times 10^{15}$  atom O  $cm^{-2}$  of geometrical surface area. Comparison with the surface density of Pt ( $\sim 1 \times 10^{15}$  atom O  $cm^{-2}$ ) gives a roughness factor of about 8.

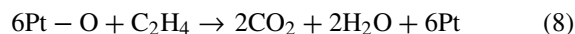
Due to the formation of a compact and poorly conducting oxide layer, the Pt/YSZ binary interface gets a blocking character, which renders any further charge transfer through this interface difficult. However, due to build-up of a strong concentration gradient, the accumulating oxygen species may diffuse slowly away from the electron exchange site, following  $t^{1/2}$  kinetics. The third peak observed by linear sweep voltammetry may be correlated with this slow process, apparently consecutive to the first process, without showing any tendency to saturate even after anodic polarization as long as 2000 minutes. It is believed that this process consists of progressive growth of the platinum oxide layer formed at the metal/electrolyte interface during the first process. However, there is no direct experimental evidence about the location of oxygen stored in this solid diffusion-controlled step. One can not exclude the possibility that oxygen is stored in the YSZ at the vicinity of the anodically polarized Pt electrode, and not in the Pt electrode itself.

Charge may be stored in form of oxygen species also at the Pt/gas interface via spillover mechanism. Atomic oxygen released at the tpb does not desorb necessarily to the gas phase as molecular oxygen but may be stuck on the metal, the resulting oxygen species spreading out over the gas-exposed surface. This process is well known in heterogeneous catalysis and considered as the origin of EPOC [3]. The second peak observed in linear sweep voltammetry may well correspond to the reduction of oxygen species populating the gas exposed surface via the inverse reaction of (Eq. 6). In fact, the second process of charge storage has a time constant of a few tens of minutes, in good agreement with that commonly observed in EPOC experiments. The area of the second peak tends to saturation at about  $6 \times 10^{16}$  atom O  $cm^{-2}$ , which corresponds to partial steady-state coverage of the highly porous Pt/gas interface.

This picture is in good agreement with the sacrificial promoter mechanism of electrochemical promotion [3] presented in the Introduction. As postulated, the electrochemically produced species populate progressively the catalyst/gas interface where

they are consumed both by reaction with the reactant (ethylene) and by desorption. When balance between electrochemical production and consumption is reached, the electropromoted rate of the catalytic reaction (ethylene oxidation in the present case) reaches a steady-state and it remains constant during the whole polarization period, meaning that no more alteration of the catalyst/gas interface occurs. However, as revealed by electrochemical techniques, during this apparent steady-state period the polarization still alters the system, without concerning directly the gas-exposed catalyst surface. The alteration must then occur at another location of the system, ‘hidden’ from the gas phase. It only affects the catalytic activity once the circuit is opened. The very long characteristic times of this effect indicate that the hidden alteration is linked to very slow processes, even at high temperatures.

Now a mechanism is proposed for the persistent enhancement of catalytic activity after current interruption, involving oxygen storage under polarization (Eq. 7) and consumption of stored oxygen by the hydrocarbon during relaxation at open-circuit (Eq. 8).



A hypothetical maximum amount of Pt–O,  $N_F$ , stored via Eq. (7) can be calculated with Faraday’s law from the total electric charge passed through the cell during the whole polarization period,  $t_h$ . Obviously, the effective oxygen storage represents only a minor fraction of  $N_F$  because the majority of the electrogenerated oxygen either desorbs into the gas phase as  $O_2$  (Eq. (6) or, in the presence of a reactant like ethylene, is consumed in the catalytic reaction. On the other hand, the amount of oxygen consumed in the catalytic reaction in excess to the non-promoted rate during relaxation,  $N_r$ , can be calculated by integrating the area between the relaxation transient curve and the base line given by the non-promoted catalytic rate. One can then define an oxygen storage efficiency,  $\Lambda_{OS} = N_r / N_F$ , as the ratio between the amount of oxygen consumed by reaction with ethylene,  $N_r$ , and the maximum amount of electrochemically stored oxygen [8]. Values of  $\Lambda_{OS}$  higher than unity would mean that the effect of stored oxygen on the catalytic reaction rate is non-Faradaic. Obviously, when calculated with  $N_F$ ,  $\Lambda_{OS}$  is highly underestimated. Even so, for the example of experiments at 525 °C in Fig. 2, values of  $\Lambda_{OS}$  between 40 and 70 are found, exceeding significantly the critical value of one. This reveals that the rate enhancement after current interruption is not simply due to the consumption of the stored oxygen species by ethylene (Eq. 8), but the effect of stored oxygen on the catalytic reaction rate is highly non-Faradaic.

## 5 Conclusions

In reactive atmosphere, the catalytic activity of Pt/YSZ may be enhanced strongly by application of anodic potential (EPOC). After prolonged anodic polarization, an unusual long-lasting relaxation of the reaction rate of ethylene oxidation was observed

(P-EPOC). For the interpretation of this phenomenon, a model is attempted relating EPOC with oxygen storage at various locations in the  $O_2(g)$ , Pt/YSZ system. In fact, in  $O_2$ -containing atmosphere, prolonged anodic polarization of Pt/YSZ causes, in excess to the main reaction of oxygen evolution, storage of Pt–O species at various locations of the electrode. This takes place not only at the gas-exposed platinum surface but also at other hidden phases and/or interfaces. These charging/discharging processes are responsible for the pseudocapacitive behavior of the electrode. Linear sweep voltammetric measurements indicated that, upon anodic polarization, at least three types of Pt–O species were stored, following distinct kinetics. Based on the effect of the polarization time on the amount of the stored Pt–O species, they were attributed to three different locations on the electrode: i) at the Pt/YSZ interface, ii) diffusing from the tpb toward the Pt/gas interface, iii) diffusing from the Pt/YSZ interface toward the bulk of the platinum electrode.

According to the proposed model of P-EPOC, anodic polarization produces Pt–O species. The majority of these species is released at the tpb, spills over the catalyst/gas interface and promotes the catalytic activity to reach a promoted steady-state as it is done in any reversible EPOC experiment. In parallel, Pt–O species are continuously formed at the Pt/YSZ interface to be stored at two distinct locations, both being hidden from the reactive gas phase. One of these hidden locations is the Pt/YSZ interface itself, where Pt–O storage is quickly saturated due to the limited amount of available storage sites. The other hidden location is the neighboring Pt phase reached by solid state diffusion, consecutive to saturation of the Pt/YSZ interface, and indicating a very large storage capacity and obeying  $t^{1/2}$  kinetic law. When the polarization is switched off, these hidden oxygen species reappear at the tpb, spread out over the gas-exposed surface and cause non-Faradaic promotion, as any electrochemically formed backspillover oxygen does. The large amount of stored charge and its slow diffusion-controlled emergence causes the rate enhancement to last for hours.

## References

- 1 **Stoukides M, Vayenas CG**, *The Effect of Electrochemical Oxygen Pumping on the Rate and Selectivity of Ethylene Oxidation on Polycrystalline Silver*, Journal of Catalysis **70** (1981), 137-146, DOI 10.1016/0021-9517(81)90323-7.
- 2 **Vayenas CG, Bebelis S, Neophytides**, *Non-Faradaic Electrochemical Modification of Catalytic Activity*, Journal of Physical Chemistry **92** (1988), 5083-5085, DOI 10.1021/j100329a007.
- 3 **Vayenas CG, Bebelis S, Pliangos C, Brosda S, Tsiplakides D**, *Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion and Metal-Support Interactions*, Kluwer Academic/Plenum Publishers, 2001.
- 4 **Fóti G, Bolzonella I, Comninellis C**, *Electrochemical Promotion of Catalysis*, Modern Aspects of Electrochemistry (Vayenas G C, Conway B E, White R E, eds.), 2003, pp. 191-254. Plenum Publishers.
- 5 **Nicole J, Tsiplakides D, Wodiunig S, Comninellis C**, *Activation of Catalyst for Gas-Phase Combustion by Electrochemical Pretreatment*, Journal of the Electrochemical Society **144** (1997), 312-314, DOI 10.1149/1.1838143.
- 6 **Wodiunig S, Patsis V, Comninellis C**, *Electrochemical Promotion of*

- RuO<sub>2</sub>-Catalysts for the Gas Phase Combustion of C<sub>2</sub>H<sub>4</sub>*, Solid State Ionics **136-137** (2000), 813-817, DOI 10.1016/S0167-2738(00)00505-1.
- 7 **Fóti G, Lavanchy O, Comninellis C**, *Electrochemical Promotion of Rh Catalyst in Gas-Phase Reduction of NO by Propylene*, Journal of Applied Electrochemistry **30** (2000), 1223-1228, DOI 10.1023/A:1026505829359.
- 8 **Falgairette C, Jaccoud A, Fóti G, Comninellis C**, *The Phenomenon of "Permanent" Electrochemical Promotion of Catalysis (P-EPOC)*, Journal of Applied Electrochemistry **38** (2008), 1075-1082, DOI 10.1007/s10800-008-9554-y.
- 9 **Jaccoud A, Fóti G, Comninellis C**, *Electrochemical Investigation of Platinum Electrode in Solid Electrolyte Cell*, Electrochimica Acta **51** (2006), 1264-1273, DOI 10.1016/j.electacta.2005.06.026.
- 10 **Jaccoud A, Falgairette C, Fóti G, Comninellis C**, *Charge Storage in the O<sub>2</sub>(g), Pt/YSZ System*, Electrochimica Acta **52** (2007), 7927-7935, DOI 10.1016/j.electacta.2007.06.046.
- 11 **Fóti G, Jaccoud A, Falgairette C, Comninellis C**, *Charge Storage at the Pt/YSZ Interface*, Journal of Electroceramics, posted on 2009, DOI 10.1007/s10832-007-9352-7, (to appear in print).
- 12 **Jaccoud A, Fóti G, Wüthrich R, Jotterand H, Comninellis C**, *Effect of Microstructure on the Electrochemical Behavior of Pt/YSZ Electrodes*, Topics in Catalysis **44** (2007), 409-417, DOI 10.1007/s11244-006-0133-3.
- 13 **Hendriks MGHM, ten Elshof JE, Bouwmeester HJM, Verweij H**, *The Electrochemical Double-Layer Capacitance of Ytria-Stabilised Zirconia*, Solid State Ionics **146** (2002), 211-217, DOI 10.1016/S0167-2738(01)01017-7.
- 14 **Markusse AP, Kuster BFM, Koningsberger DC, Marin GB**, *Platinum Deactivation: In Situ EXAFS during Aqueous Alcohol Oxidation Reaction*, Catalysis Letters **55** (1998), 141-145, DOI 10.1023/A:1019007601442.
- 15 **Velho LR, Bartlett RW**, *Diffusivity and Solubility of Oxygen in Platinum and Pt-Ni Alloys*, Metallurgical and Materials Transactions B **3** (1972), 65-72, DOI 10.1007/BF02680586.
- 16 **Berry RJ**, *Study of Multilayer Surface Oxidation of Platinum by Electrical Resistance Technique*, Surface Science **76** (1978), 415-442, DOI 10.1016/0039-6028(78)90106-1.