

Charge storage at the Pt/YSZ interface

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Received: 13 March 2007 / Accepted: 15 October 2007 / Published online: 7 November 2007
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Abstract The electrochemical behavior of Pt/YSZ electrodes in oxygen containing atmosphere at 450 °C has been investigated by double-step chronoamperometry and programmed linear sweep cyclic voltammetry. The response of the O₂(g),Pt/YSZ system in these experiments could be separated into a time dependent and a steady state contribution, the former being dominated by pseudocapacitive processes. It is proposed that Pt–O type species were stored via different processes at three different locations in the O₂(g),Pt/YSZ system: (1) Build-up of a platinum oxide monolayer at the Pt/YSZ binary interface. (2) Formation of Pt–O species at the triple phase boundary and their spreading-out along the Pt/gas interface. (3) Growth of the platinum oxide layer from the binary Pt/YSZ interface toward the bulk of the platinum electrode.

Keywords Platinum electrode · YSZ · Charge storage · Pseudocapacitance

1 Introduction

Among solid electrolyte cells, commonly used for numerous applications including gas sensors, gas pumps, solid oxide fuel cells and electrochemically promoted catalysts, platinum electrode deposited on yttria stabilized zirconia (YSZ) is one of the most widely studied examples [1–3]. Nevertheless, due to the complexity of the system, the

electrochemical behavior of Pt/YSZ cells in oxygen containing atmosphere is still not fully understood.

In an O₂(g),Pt/YSZ system, the two redox couples involved in the overall charge transfer reaction are PtO_x/Pt and O_{2(g)}/O²⁻. The PtO_x/Pt couple corresponds to the redox reaction (Eq. 1) [4–6]:



where use of the symbol PtO_x is due to the ill-defined stoichiometry of the electrochemically formed oxide [7]. The other electrochemical reaction, involving the couple O_{2(g)}/O²⁻, consists of electron exchange between gaseous oxygen and O²⁻ ion of the solid electrolyte:



where V_O is an oxygen vacancy in the lattice of the electrolyte.

In recent works [8, 9] it was found that prolonged anodic polarization leads to formation of different oxidized species which are consumed subsequently during a linear cathodic potential scan resulting in three distinct reduction peaks. The coexistence of three electrochemical processes indicates charge storage at three different locations in the O₂(g), Pt/YSZ system. In the present work, double-step chronoamperometry and programmed cyclic voltammetry are used to study the effect of prolonged anodic polarization on the electrochemical behavior of Pt/YSZ electrodes.

2 Experimental

The electrochemical behavior of Pt/YSZ electrodes prepared by platinum sputtering, thermal decomposition of a platinum salt and screen-printing of a paste containing Pt

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and YSZ particles was found to be dependent of the method of preparation, hence on the resulted microstructure revealed by SEM [9]. While 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, the electrodes prepared by screen-printing exhibited superior pseudocapacitive behavior without any sign of degradation under the same conditions, so they are the best suited for studying charge storage phenomena.

In this work, platinum deposition was made by screen-printing of a paste composed of 65%_w of 1 μm particle size platinum powder (Fluka), 11%_w of 1 μm particle size YSZ (8 mol% Y₂O₃ in ZrO₂, Tosoh) and 24% of a polyvinyl pyrrolidone solution (2% in isopropanol, Fluka) on a 1.3 mm thick YSZ (8 mol%) pellet, followed by sintering at 1400 °C in air to give a film thickness of 15 μm. The resulting deposit of 0.08 cm² geometric surface area is composed of 62%_{vol} of platinum and 38%_{vol} of YSZ and it is highly porous. No morphological change has been observed due to prolonged use and/or polarization during working months. The three-electrode electrochemical cell was of single-pellet type; all electrodes were made of platinum and prepared simultaneously via the above screen-printing method. Details on the electrochemical cell and the experimental setup including a single-chamber type atmospheric reactor and units for temperature, gas atmosphere and potential control are given in previous papers [8, 9]. All electrochemical measurements were made in 20 kPa O₂ (in He) at 450 °C.

3 Results and discussion

Double-step chronoamperometric measurements were made using a potential program composed of a pretreatment step and two measurement steps (see the insert in Fig. 1). The cathodic pretreatment step (A) aims to reduce any residual oxidized species and guarantee identical reproducible initial state before each experiment. It consisted of a polarization at a constant potential of $E_{pre} = -400$ mV during $t_{pre} = 60$ s. 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 chronoamperometric transients of the anodic polarization step 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

in 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, attributed mainly to the oxygen evolution reaction (Eq. 2), may be contributed also from other Faradaic reactions related to charge storage (see later). There is a clear evidence of a Faradaic contribution also to the transient current. In fact, the experimentally found time constant is several orders of magnitude higher than that of double layer charging 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 ($C_{dl} = 50 \mu\text{F}/\text{cm}^2$ [10]) and with the geometric surface of the electrode ($S = 0.08 \text{ cm}^2$) to give $\tau = R_{el} \cdot C_{dl} \cdot S = 4$ ms. Even by taking into account a surface roughness factor as high as ten, the time constant of double layer charging would remain by at least two orders of magnitude below the experimentally obtained value. This indicates contribution from an other 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 orders of magnitude higher than the electrostatic double layer capacity.

Figure 1 shows the current transients during cathodic discharge 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 ($-30 \mu\text{A}$) 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

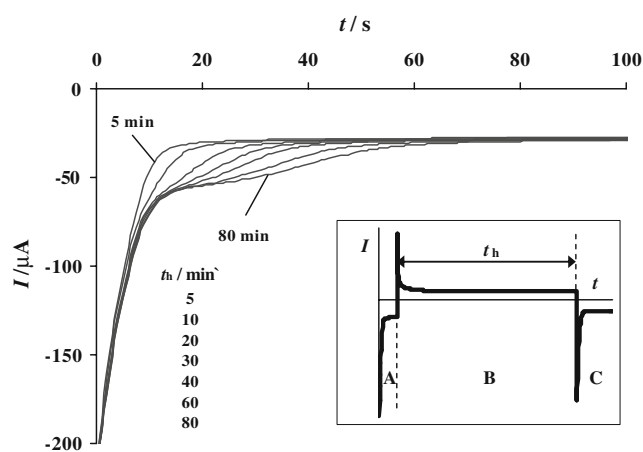


Fig. 1 Double step chronoamperometric measurements. Effect of the holding time, t_h , at the anodic potential of $E_h = 100$ mV on the current transients obtained during the cathodic discharging step. $E_{dis} = -300$ mV, $T = 450$ °C, $p_{O_2} = 20$ kPa. The insert illustrates schematically the subsequent steps: (A) cathodic pretreatment, (B) anodic polarization, and (C) cathodic discharge

time is needed to reach the steady state current. In particular, after a long polarization time ($t_h=80$ min), 80 s 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_{charging} and $Q_{\text{discharging}}$ in the anodic and the cathodic step, respectively. The value of $Q_{\text{discharging}}$ is considered as the charge effectively stored during the anodic step. Figure 2 shows the values of Q_{charging} and $Q_{\text{discharging}}$, as a function of the anodic holding time in the range of 5 to 80 minutes, obtained by integration of the $I-t$ curves of Fig. 1. Contrary to Q_{charging} , which is independent of t_h , $Q_{\text{discharging}}$ 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, $Q_{\text{discharging}}$ exceeds Q_{charging} , meaning that the electrode has stored more charge than expected from the anodic $I-t$ curve. The difference between these two charges, called extra charge, $Q_{\text{extra}} (=Q_{\text{discharging}} - Q_{\text{charging}})$ was found to be a linear function of $t_h^{1/2}$ (see insert in Fig. 2), 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 $Q_{\text{extra}}=0$. This means that there is a delay of roughly 100 s after the onset of the anodic polarization before extra charge is stored with a $t_h^{1/2}$ kinetic rule. Then this storage process goes on during the totality of anodic polarization

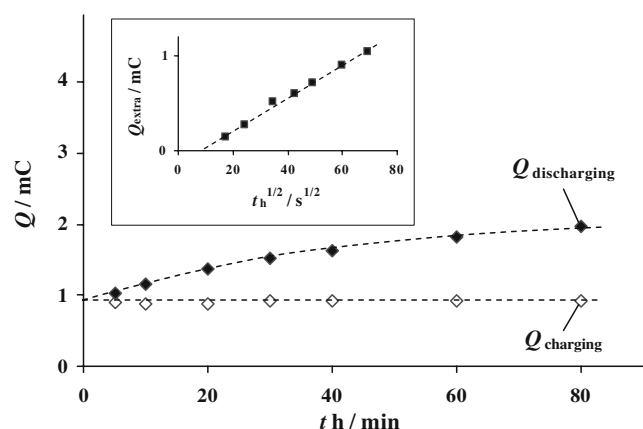


Fig. 2 Effect of the anodic holding time, t_h , on Q_{charging} (open diamond) and $Q_{\text{discharging}}$ (filled diamond). $T=450$ °C, $pO_2=20$ kPa. $E_h=100$ mV, $E_{\text{dis}}=-300$ mV. The insert shows the Q_{extra} vs $t_h^{1/2}$ plot, where $Q_{\text{extra}}=Q_{\text{discharging}}-Q_{\text{charging}}$

step, including the period of steady state current. Hence, a certain fraction of the apparent steady state current is in fact stored as extra charge.

These observations are in full agreement with cyclic voltammetric measurements, analogous to those of a previous work [8], but performed with very long anodic potential holding. The measurements consisted of a cathodic pretreatment step identical to that of the chronoamperometric experiments discussed above, an anodic potential holding step at $E_h=+100$ mV for different holding times between 1 and 2,000 min, followed by a linear potential sweep down to a cathodic potential of -800 mV (first cathodic scan) and subsequent continuous cycling between these two potential limits with the same scan rate of 10 mV/s. Figure 3 shows a typical voltammetric response of the Pt/YSZ electrode. At a very short holding time (1 min), two distinct reduction peaks at about -150 and -250 mV, respectively, appear with comparable sizes. By increasing t_h , the second peak increases more rapidly than the first peak. By further increasing the holding time, a third peak – 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. 4 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 (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 of PtO_x in the first peak increases from the beginning and reaches a saturation value in about 10 min. Similarly, the second peak starts to grow from the beginning suggesting two parallel processes. Also the area of

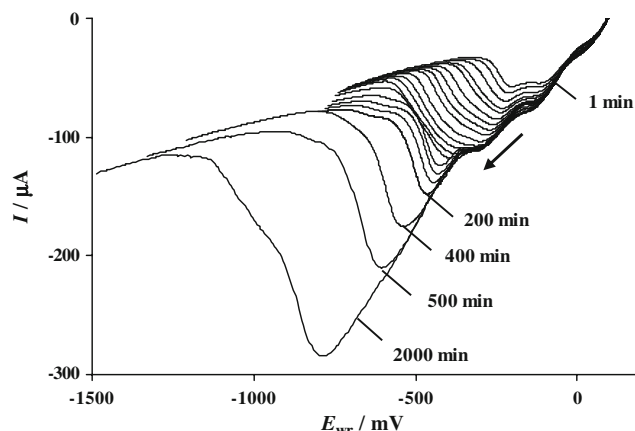


Fig. 3 Linear sweep voltammetric measurements. Effect of the holding time, t_h , at $E_h=100$ mV on the first cathodic scan. $T=450$ °C, $pO_2=20$ kPa, $v=10$ mV/s

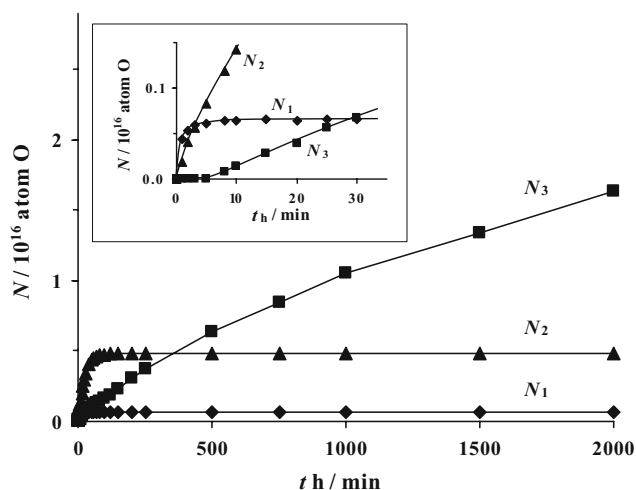


Fig. 4 Effect of holding time, t_h , at $E_h=100$ mV on the amount of injected oxygen related to the first, second and third peaks. The amount of oxygen atoms, N , is calculated assuming the exchange of two electrons. $T=450$ °C, $p_{O_2}=20$ kPa, $\nu=10$ mV s $^{-1}$. The insert shows a zoom on the domain of short holding time

the second peak tends to saturation at a value of about seven times higher than that of the first peak in about 80 min of holding time. As seen in the insert of Fig. 4, 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 2,000 min, there is no clear sign of any tendency to peak area saturation.

Similarly to the accumulation of the extra charge in the double-step chronoamperometric experiments (Fig. 2), also the increase in the area of the third voltammetric peak (N_3) follows a $t_h^{1/2}$ kinetics, suggesting again a diffusion mechanism. Considering 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 ($6.6 \cdot 10^{14}$ atom) and d is the average thickness of an oxide layer ($2.7 \cdot 10^{-10}$ m, estimated with the Pt–Pt atomic distance [11]), a diffusion coefficient of $D=3 \cdot 10^{-22}$ m 2 /s is calculated. This value is typical for a diffusion process in a solid phase and is in good agreement with prediction [12] for the diffusion of oxygen inside platinum at the experimental temperature of 450 °C.

The pseudocapacitive behavior of the O $_2$ (g),Pt/YSZ system lets think that both the time dependent and the steady state current regions are governed by Faradaic processes. A possible reaction scheme involving two anodic Faradaic processes is proposed. One of them is electrochemical oxidation of platinum to form PtO $_x$ type species

(Eq. 1), responsible for charge storage, while the other is oxygen evolution via electrochemical oxidation of O $^{2-}$ ions (Eq. 2), responsible for the main part of the steady state current. 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 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 Fig. 4). The saturation amount of the oxide species is $8 \cdot 10^{15}$ atom O cm $^{-2}$ of geometrical surface area. Comparison with the surface density of Pt ($\sim 1 \cdot 10^{15}$ 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 a strong concentration gradient, the accumulating Pt–O species may diffuse slowly away from the electron exchange site, following a $t^{1/2}$ kinetics. The third peak observed by cyclic 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 2,000 min. 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.

Finally, charge may be stored in form of Pt–O 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 Pt–O species spreading out over the gas exposed surface. This process, well known in heterogeneous catalysis and considered as the origin of the phenomenon of electrochemical promotion of catalysis (EPOC) [13], may correspond to the second peak observed in cyclic voltammetry. In fact, the second process 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 $6 \cdot 10^{16}$ atom O cm $^{-2}$, which corresponds to partial steady state coverage of the highly porous Pt/gas interface.

4 Conclusion

Based on the double-step chronoamperometric and cyclic voltammetric experiments, charge storage in the $O_2(g)$, Pt/YSZ system under prolonged anodic polarization is proposed to take place via different processes at three different locations: (1) Build-up of a platinum oxide monolayer at the Pt/YSZ binary interface. This process rapidly reaches saturation and causes partial blocking of the Pt/YSZ interface. (2) Formation of Pt–O species at the triple phase boundary and their spreading-out along the Pt/gas interface (spillover via surface diffusion). This process is parallel to process 1 and it reaches slowly an apparent steady-state. (3) Growth of the platinum oxide layer from the binary Pt/YSZ interface toward the bulk of the platinum electrode. This process is consecutive to process 1, it is very slow and follows a $t^{1/2}$ kinetics without showing any apparent saturation.

Acknowledgement Financial support from the Fonds National Suisse de la Recherche Scientifique is gratefully acknowledged.

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