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ORIGINAL PAPER

Comparative studies between classic and wireless electrochemical promotion of a Pt catalyst for ethylene oxidation

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Abstract A comparative study between a classic and a wireless electrochemical promotion experiment was undertaken as a tool towards the better understanding of both systems. The catalytic modification of a platinum catalyst for ethylene oxidation was studied. The catalyst was supported on yttria-stabilised-zirconia (YSZ), a known pure oxide ion conductor, for the classic experiment and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$—a mixed oxide ion electronic conductor—was used for the wireless experiment. The two systems showed certain similarities in terms of the reaction classification (in both cases electrophobic behaviour was observed) and the promotion mechanism. Significant difference was observed in the time scales and the reversibility of the induced rate modification.

Keywords Electrochemical promotion · Mixed conductor · Catalysis remote control

1 Introduction

Electrochemical Promotion of Catalysis (EPOC), namely the modification of the activity of a metal catalyst (supported on an ionic conductor) by the electrochemically induced spillover of the promoting species onto the catalyst surface is a phenomenon that has attracted a lot of interest in the last 25 years. Several reactions, catalyst and supports have been studied and some recent examples can be found in [1–6]. It appears that the backspillover of the promoting species onto the catalyst surface creates a double layer that changes the chemisorptive bond strength of the reactants on the catalyst, thereby modifying the catalytic reaction rate. This has been supported by the use of different analytical techniques, such as in situ TPD [7], work function measurements [8], and models exist to predict the behaviour of model systems [9–11].

Recently, a novel configuration using a mixed ionic-electronic conducting (MIEC) support has been developed for use in electrochemical promotion experiments [12]. The mixed conductivity of the support eliminates the need for an external circuit. In this system the use of an appropriate sweep gas can create a chemical potential difference across the membrane that induces the promoter supply towards the reaction side. The principle of operation of this wireless configuration can be seen in Fig. 1. The use of the oxygen sweep on one side of the reactor creates the necessary driving force for oxygen migration across the membrane and ensures the supply of the promoter to the catalyst, in an analogy with classic EPOC experiments where the promoter is driven by the application of overpotential across the electrolytic membrane.

Initial results on mixed oxide-ion-electronic and protonic-electronic conductors have shown the feasibility of the wireless configuration of EPOC experiments. Significant rate changes were obtained [12, 13]. In this work a comparative study between classic and wireless EPOC experiments is performed.

2 Materials and methods

The reaction investigated in this study was ethylene oxidation on a metallic platinum catalyst. For the classic EPOC experiment the catalyst was supported on an oxide ion conducting membrane (yttria-stabilised-zirconia, YSZ) and

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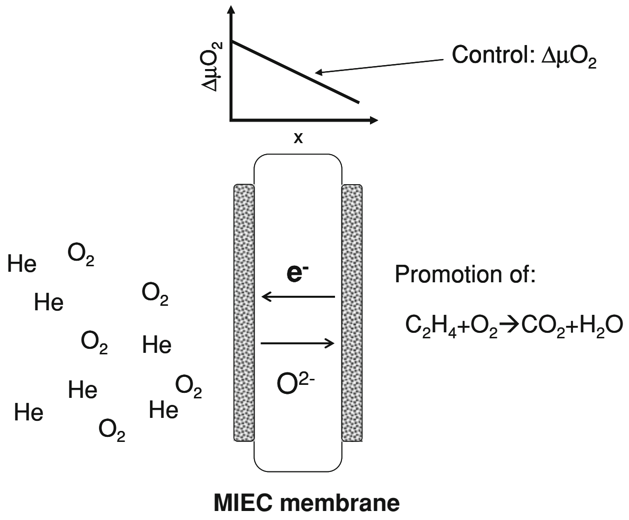

Fig. 1 Promotional mechanism of wireless electrochemical promotion

for the wireless experiment on a mixed oxide ion and electronic conductor ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, LSCF). Two pellets were prepared from the starting materials (YSZ and LSCF powders, purchased by Praxair) and catalysts of the same geometric projected area (1 cm^2) were deposited on the working / reaction side of the membrane by painting of a Pt paste and then sintering to 850 °C. The reaction rate was monitored by the composition of carbon dioxide in the outlet of the reactor and is expressed in $\mu mol\ cm^{-2}\ s^{-1}$. The flow rates used throughout these experiments were approximately 100 ml min^{-1} (all volumetric flow rates are quoted at STP) on either side of the dual chamber reactor and 250ml min^{-1} for the single chamber reactor. The reaction temperature was 400°C and the reactors were operated at 101 kPa. Gas analysis was performed by gas chromatography (Varian CP-3800, molsieve 5 A, Haysep Q), infrared spectroscopy (Binos 100 CO/CO_2 analyser) and mass spectroscopy (MKS-Cirrus). The testing rig has been described in detail in our previous communication [12].

Two reactor configurations shown in Fig. 2 were used. A single chamber reactor (Fig. 2a) was used for the classic EPOC experiment and a dual chamber reactor (Fig. 2b) for the wireless EPOC experiment.

For the classic EPOC, gold reference and counter electrodes were deposited on the counter side of the YSZ pellet. When using the single chamber reactor configuration both sides of the electrolytic membrane are exposed to the same gas atmosphere (i.e. the reaction mixture) so the use of catalytically inert counter and reference electrodes can eliminate any contribution to the reaction rate that could corrupt the experimental results. In the polarisation experiments polarisation was achieved using a potentiostat/glavanostat. Working under galvanostatic mode currents of 120 μA and −120 μA (corresponding to a current density of ±120 $\mu A\ cm^{-2}$) were applied. The equivalent overpotential η was ±1 V approximately.

The wireless EPOC experiments were conducted in the dual chamber reactor (clearly wireless EPOC experiments cannot be performed in a single chamber). In this case a platinum catalyst was deposited on either side of the MIEC membrane. The equivalent of polarisation in this system was simulated by the use of appropriate sweep gas on the sweep chamber of the reactor (while the composition of the reaction mixture on the reaction chamber remained constant). Open circuit conditions correspond to symmetrical

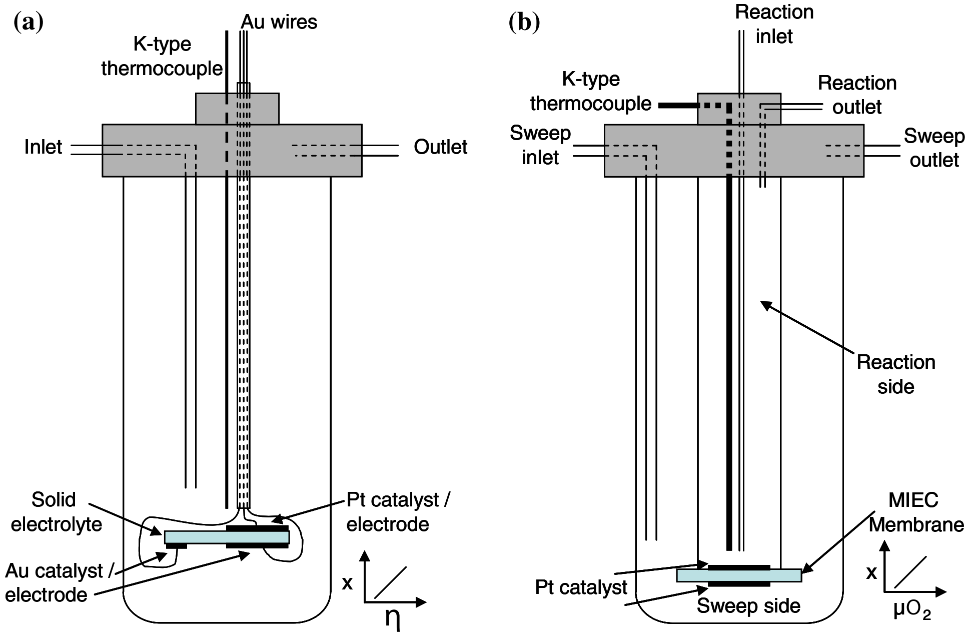

Fig. 2 Reactor schematics: (**a**) single chamber reactor—classic EPOC and (**b**) dual chamber reactor—wireless EPOC

operation (i.e. the use of the same reaction mixture on both reactor chambers). Positive polarisation, i.e pumping of oxygen towards the reaction side catalyst was achieved by the use of an oxygen sweep (20% O_2/He, BOC) that creates an oxygen chemical potential difference across the membrane driving oxygen towards the reaction side. Some experiments were conducted with an oxygen sweep of the following composition, 19.5% O_2, 0.5% C_2H_4 in helium as it was found that presence of ethylene in the sweep gas enhanced the stability of the membrane. Negative polarisation (oxygen removal from the reaction catalyst) was represented by the use of a hydrogen sweep (5%H_2/He BOC) that creates a driving force for oxygen removal from the reaction side. The use of a platinum catalyst on the sweep side of the reactor plays a dual role. It acts as a catalyst under symmetrical operation and it facilitates oxygen dissociation during the oxygen sweep, thus improving the rate of promoter supply to the reaction side catalyst.

One important parameter of the reactor setup is the minimisation of intra-chamber leaks for the work on the dual chamber reactor; as such an occurrence could lead to false rate modification upon introduction of the oxygen sweep. However, it should be mentioned here that any rate change due to intra-chamber leaks would be observed at a gas phase oxygen reaction time scale (i.e. approximately 1min after introduction of the oxygen sweep), while rate modification due to EPOC would be observed at a much slower time scale (in excess of 2 hours) as will be discussed in the following paragraph. Therefore, it would be possible to separate the two different contributions, even in the case where intra-chamber leaks occurred. For the experiments discussed here the intra-chamber leak was measured (by GC analysis in an experiment with air in one chamber and helium in the other) to be approximately 0.02 μmol s^{-1}. We would therefore expect that under reaction conditions with a partial pressure of oxygen of up to 20 kPa on the sweep side that the oxygen leak rate would be of the order of 0.004 μmol s^{-1} or lower. This oxygen leak rate is at least one order of magnitude lower than the measured reaction rates. Moreover, no gas phase oxygen contribution to the rate modification was observed.

3 Results and discussion

3.1 Pre-operation analysis

The two catalyst-support systems employed in this work (namely Pt-YSZ-Au and Pt-LSCF-Pt were examined by scanning electron microscopy (SEM) prior to the kinetic experiments, in order to compare the morphology of the different catalysts employed. Some representative SEM micrographs can be seen in Fig. 3.

As can be seen from Fig. 3a, where the platinum catalyst deposited on the YSZ pellet is shown, the catalyst shows significant porosity.

Figures 3b, c show the platinum catalyst deposited on the reaction and sweep sides of the LSCF membrane respectively. In both cases the platinum film shows significant porosity. Moreover, the two films exhibit a similar degree of porosity indicating that the two catalysts should have similar catalytic activity. This is an important observation as it shows that under symmetrical operation the catalytic rates should be of the same range and therefore, the reactor is operated under truly symmetrical conditions.

When comparing the catalyst films of deposited on the two different membranes it becomes apparent that the catalyst film deposited on the YSZ membrane has higher porosity (i.e. higher surface area) than the ones deposited on the LSCF membrane. Given the fact that in both cases the geometric projected surface area of the deposited catalysts was the same we may expect the catalyst deposited on the YSZ membrane to exhibit slightly higher catalytic activity. This variation in porosity is probably only due to the method of deposition (painting and sintering the catalyst) and is of small significance for this work, where only a qualitative comparison between the two systems is attempted.

3.2 Kinetic data analysis

Next we will discuss the kinetic results obtained from the two systems. First the reversibility of the two systems was compared. Figure 4 shows the reaction rate transients for the classic (Fig. 4a) and wireless (Fig. 4b) experiment. For the classic experiment the system was polarised by using a current density of $I = 120\ \mu A\ cm^{-2}$ and after the rate reached the new steady state, the system returned to open circuit. As seen from Fig. 4a upon depolarisation the rate returns to the original open circuit value, as expected. For the equivalent experiment on the wireless system we can see that when moving from symmetrical to oxygen sweep the rate increases but upon return to the symmetrical conditions the phenomenon is not reversed. This behaviour has been discussed in detail in previous communications [12, 14] and one possible explanation may be that, due to its mixed ionic and electronic conductivity, the LSCF support can incorporate oxygen from the reaction side to sustain the induced promotion. This phenomenon has been termed "surface oxygen capture". It is clear that in the case of the wireless system the catalyst shows a memory effect and the history of the catalyst system is very important for the interpretation of its behaviour.

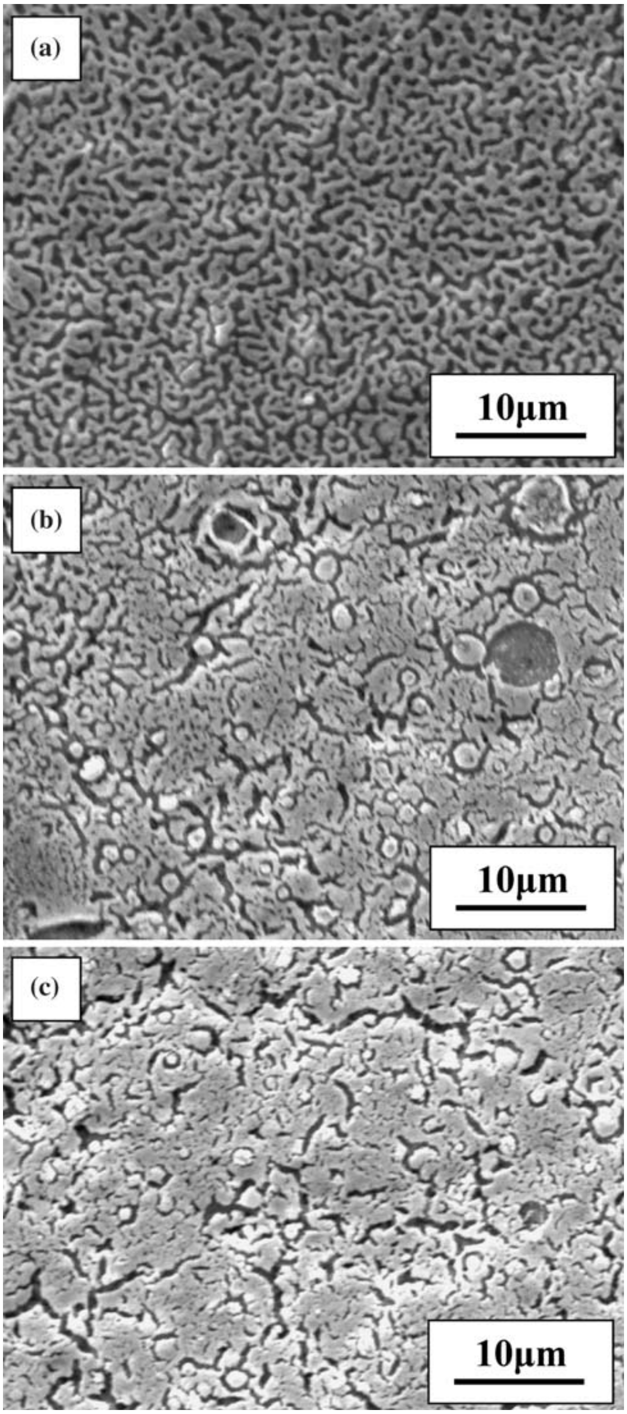

Fig. 3 SEM micrographs of the three catalyst films (scale shown on the bottom of the micrographs)—(**a**) working platinum electrode/catalyst on YSZ pellet (**b**) reaction side platinum catalyst on LSCF pellet (**c**) sweep side platinum catalyst on LSCF pellet

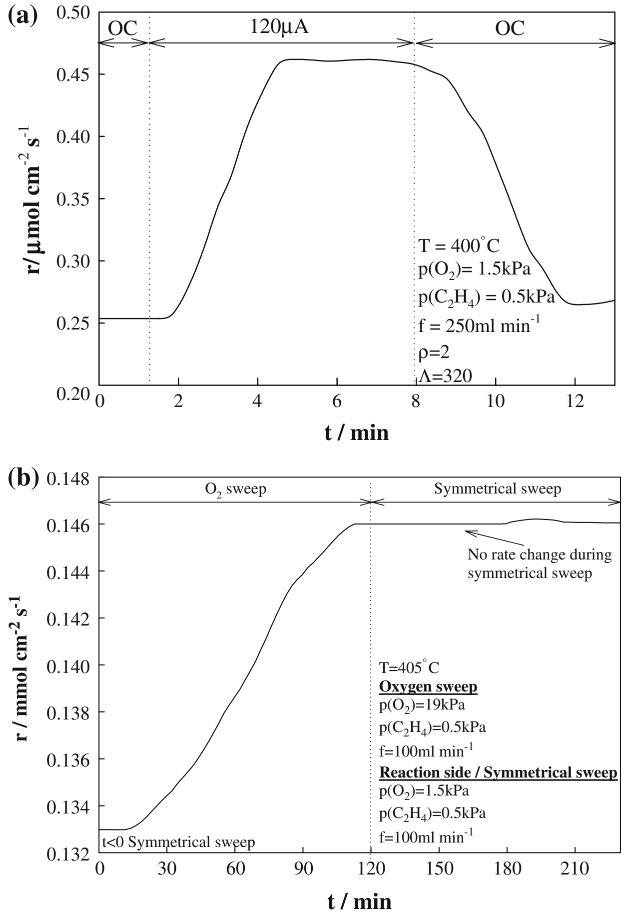

Fig. 4 Reaction rate transients at 400°C (**a**) classic EPOC experiment (**b**) wireless EPOC experiments

This behaviour of permanent rate modification constitutes the first main difference between classic and wireless EPOC. On a wireless EPOC experiment the supply of the promoter is only necessary in order to achieve the required promotion but not to sustain it, as is the case for classic EPOC. This permanent rate modification has so far been observed only in cases where mixed oxygen-ion and electron conducting materials have been used as the catalyst support as is the case examined here. In a previous study conducted on a mixed protonic and electronic conducting support [13] (where the promoting species are protons) the rate modification of ethylene oxidation induced by the use of a hydrogen sweep was fully reversible upon return to symmetrical operation. It should be noted that a 'surface hydrogen capture' mechanism would not on first inspection be expected to occur in the case of a mixed protonic and electronic conductor acting as a catalyst support for a hydrocarbon oxidation as there is no gas phase hydrogen present.

From Fig. 4 we can also see that the time required to reach the new steady state for the wireless experiment (approximately 120 min) is higher by a factor 20 when compared to the time required for the classic experiment (approximately 6 min). Moreover, the magnitude of the promotion as demonstrated by the rate enhancement factor

$$\rho = \frac{r_{\text{modified}}}{r_{\text{initial unmodified}}}$$

is significantly lower for the wireless experiment ($\rho_{\text{wireless}} = 1.1$, $\rho_{\text{classic}} = 2$). In fact the rate enhancement ratio observed here is up to two orders of magnitude lower than in other classic EPOC studies on ethylene oxidation on Pt-YSZ [11]. The low enhancement factor observed for the classic EPOC experiment may be, at least partially, a result of the high initial catalytic activity. As far as the wireless experiment is concerned, both the time scale and magnitude of the effect in the wireless experiment may be a consequence of the low oxygen flux of LSCF at the temperature of operation [15]. Studying different reactor geometries that utilise thinner membranes may lead to increased fluxes. As can be seen from Figure 4 the unmodified catalytic rate of the classic experiment is double the one measured for the wireless experiment. This was expected from the SEM pre-operation analysis as discussed earlier due to the higher surface area expected for the catalyst deposited on the YSZ pellet.

In an attempt to control reaction rate during the wireless experiment a hydrogen sweep was used following the oxygen sweep that induced the rate change. To simulate this on the classic experiment, we used a negative current density of -120 μA cm^{-2} to follow the positive current. Figure 5 shows the obtained reaction rate transients.

So we can better compare the two systems we have plotted reaction rate versus dimensionless time (where time is normalised with respect to the duration of the experiment, 1,500 s for the classic experiment and 90,000 s for the wireless experiment) in Fig. 5. We can see a more pronounced effect in the case of the wireless experiment with $\rho = 1.4$. This may be due to the fact that slightly different oxygen sweep gas compositions were used in the experiments shown in Figs. 4 and 5. However, for the purpose of this qualitative study this difference if not crucial.

As seen from Fig. 5, in the classic EPOC experiment the reaction rate is fully reversible (i.e. the reaction rate under open circuit conditions is the same both at the start of the experiment and the end). In the case of the wireless experiment we do not see full reversibility. The hydrogen sweep decreases the reaction rate (possibly due to a reverse in the direction of the promoter flux) but a new reaction rate (lower than the starting symmetrical reaction rate) is achieved. Upon return to symmetrical conditions this rate is unchanged. In both cases the reaction shows electrophobic behaviour as the rate increases when we are pumping oxygen ions towards the catalyst surface (either by electrical or chemical potential difference) and decreases by pumping oxide ions away from the catalyst surface. This behaviour has been repeatedly observed for earlier EPOC studies on ethylene oxidation on Pt-YSZ [11]. It is expected that both systems should exhibit the same behaviour as in both cases the support is an oxide ion conductor.

The kinetics of the reaction as a function of the oxygen partial pressure in the reaction mixture are shown for both systems in Fig. 6. Figure 6a corresponds to the classic and Fig. 6b to the wireless experiment. As can be seen, in both cases the reaction rate is positive order towards oxygen, while for high oxygen partial pressures it becomes almost zero order. The catalytic rates of the classic experiment remain higher than the rates of the wireless experiment.

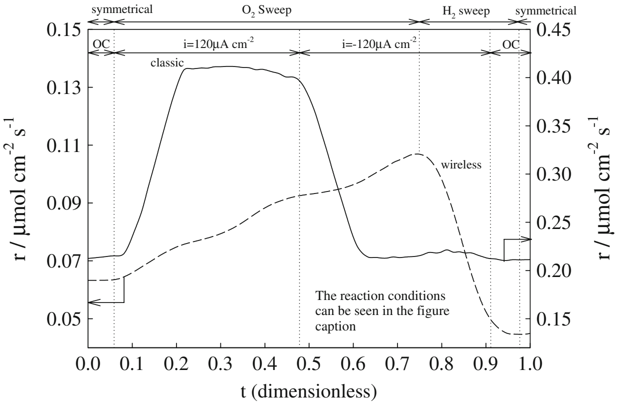

Fig. 5 Reaction rate transients for classic (continuous line) and wireless (dashed line) EPOC at 400 °C for $p(O_2) = 1.5$ kPa and $p(C_2H_4) = 0.5$ kPa. Classic experiment: f = 250 ml min^{-1}, Wireless experiment: $f_{\text{reaction}} = 100$ ml min^{-1}, $f_{\text{sweep}} = 100$ ml min^{-1}, $p(O_2)_{\text{sweep}} = 20$ kPa, $p(H_2)_{\text{sweep}} = 5$ kPa. The left y-axis corresponds to the wireless experiment and the right y-axis to the classic experiment

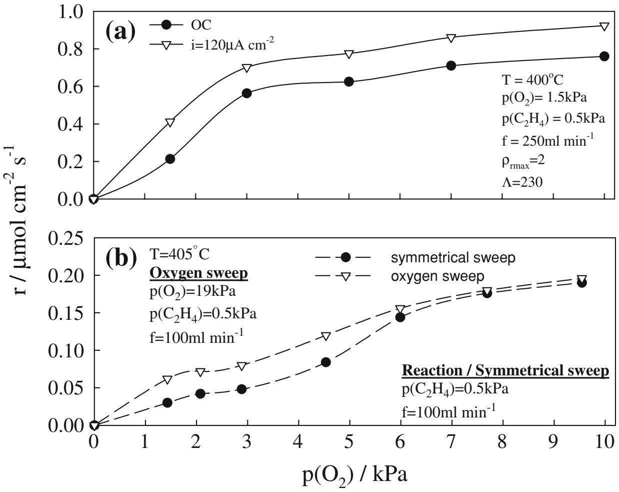

Fig. 6 Reaction kinetics, (**a**) classic experiment, $p(C_2H_4) = 0.5$ kPa, f = 250 ml min^{-1}, (**b**) wireless experiment, $f_{\text{reaction}} = 100$ ml min^{-1}, $f_{\text{sweep}} = 100$ ml min^{-1}, $p(O_2)_{\text{sweep}} = 20$ kPa, $p(H_2)_{\text{sweep}} = 5$ kPa

For the classic experiment the change in reaction rate on polarisation does not depend significantly on the oxygen partial pressure. In the case of the wireless experiment, for oxygen partial pressures higher than 6 kPa the observed promotion becomes insignificant. This behaviour is expected, as in this system by increasing the oxygen partial pressure in the reaction chamber we decrease the oxygen chemical potential difference across the membrane and thus the driving force for oxygen migration that consequently affects the promoter supply to the catalyst. While for classic EPOC high rate enhancement ratios of ethylene oxidation on platinum have generally been reported under highly oxidising conditions [16], in the case of wireless EPOC higher rate enhancement ratios have so far been obtained under stoichiometric or mildly oxidising conditions [12, 14]. Work is currently in progress to study wireless EPOC under reducing conditions (i.e. high ethylene partial pressures). We expect that this may have a positive effect on the rate enhancement as it should help increase the driving force for oxygen migration across the membrane.

4 Conclusions

Preliminary comparative experimental results between a classic and a wireless EPOC experiment for the promotion of a platinum catalyst for ethylene oxidation indicate that in both cases the reaction shows electrophobic behaviour indicating that the promotional mechanism may be the same. However, in the case of the LSCF support (i.e. mixed conductor) cessation of the promoter supply did not reverse the induced promotion as is the case for classic EPOC. This suggests that for wireless EPOC supply of the promoter via an oxygen sweep is only necessary in order to initiate the promotion. The use of a hydrogen sweep in the wireless experiment resulted in reduction of the reaction rate to a new rate, lower than the initial unpromoted rate. Following a symmetrical sweep the rate decrease was not reversed. The time scale observed for the wireless experiment was longer by at least a factor of 60 compared to the classic experiment.

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