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Electrochemical Promotion of a Pt catalyst supported on $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ hollow fibre membranes

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Abstract

The use of wireless electrochemical promotion of catalysis (EPOC) of a Pt catalyst supported on a mixed ionic electronic conducting hollow fibre membranes is investigated. This reactor configuration offers high surface areas per unit volume and is ideally suited for scaled-up applications. The MIEC membrane used is the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ perovskite (LSCF) with a Pt catalyst film deposited on the outer surface of the LSCF membrane. Experimental results showed that after initial catalyst deactivation (in the absence of an oxygen chemical potential difference across the membrane) the catalytic rate can be enhanced by using an oxygen sweep and wireless EPOC can be used for the in situ regeneration of a deactivated catalyst.

Keywords: *catalyst remote control, MIEC support, EPOC, hollow fibre membranes, ethylene oxidation, LSCF.*

1. Introduction

The non-Faradaic electrochemical modification of catalytic activity (NEMCA effect) was discovered and developed by Vayenas et al. [1, 2]. This phenomenon is based on the modification of the chemisorption properties of the catalyst, by an applied potential, as a consequence of the electrochemical pumping of ions (promoters) from a solid electrolyte to the catalyst film. This

phenomenon allows improving the catalytic performance of a metal catalyst in a very pronounced and controlled way[3].

More recently EPOC has been demonstrated on catalysts supported on mixed ionic and electronic conducting membranes (wireless EPOC)[4, 5] and a model has been proposed to explain the promotional behaviour of these systems[6]. In this work, we propose a novel configuration for wireless EPOC where the platinum catalyst is supported on an LSCF hollow fibre(HF) membrane. Compared to the disk membranes that have been used as the catalyst support in earlier studies, HF membrane reactors provide an increased surface area per unit volume and can be easily scaled up for practical application. Therefore, the successful use of this reactor configuration in EPOC experiments constitutes a significant step towards practical utilisation of the phenomenon of electrochemical promotion of catalysis.

The MIEC membrane employed in this study is the perovskite $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\alpha}$ (LSCF) with a platinum catalyst film deposited on the outer surface of the membrane. LSCF was chosen as the catalyst support because it is a well studied mixed oxygen ion and electronic conductor that shows significant oxygen permeation rates at high temperatures (750-1000°C) [7-10] and has good chemical and mechanical stability due to its modest Sr doping and high Fe content[11]. At the temperatures employed in this work (500 °C) the oxygen flux is expected to be adequate to provide the oxygen promoter supply on the catalyst surface as has been shown in our previous work [5, 6].

2. Experimental

LSCF hollow fibres were prepared using the phase inversion method described in detail elsewhere [12]. Viscosity was measured with a rotary viscometer (NDJ-79, Sance, China) at 20 °C. Ultrafiltrated water at 20 °C was used as external coagulant and DMAc/water was used as internal coagulant. A tube-in orifice spinneret was used for the membrane formation. The dope suspension was extruded into the annulus of the spinneret and the internal coagulant was fed into

the inner tube of the spinneret using two different syringe pumps. Then, the nascent hollow fibre was allowed to enter the external coagulant bath freely. The as-spun hollow fibres were stored in fresh water for at least one day to leach out the residual solvent and subsequently sintered to 1250 °C for 12 hours. The resultant sintered HFs used in this work had an outer diameter of 1 mm, an inner diameter of 0.2 mm and a nominal length of 23 cm.

The experiments were performed on a one-fibre reactor module in order to study the promotion of ethylene oxidation. A schematic of the reactor module can be seen in Fig. 1. A platinum catalyst film (5542 Pt ESL-Europe resin) was deposited on the outer surface of a LSCF HF membrane by brush painting and then calcined at 980 °C for 10 min at 10 °C min⁻¹. The platinum catalyst film covered approximately 5 cm in the middle of the HF membrane. The mass of the platinum film supported on the hollow fibre was 16 mg. No catalyst was deposited on the inner surface of the HF. The geometric projected surface area of the platinum catalyst film (used for the area specific reaction rate calculations) was approximately 3 cm² and the geometric surface area of the inner and outer sides of the HF in the isothermal heated zone of the furnace (10 cm) were 8.2 cm² and 9.5 cm² respectively. Carbon monoxide titration (with oxygen) was explored in order to calculate the number of active sites on the platinum catalyst deposited on the outer side of the HF membrane. In addition the same technique was used on a bare LSCF membrane to determine the number of active sites on the LSCF membrane (known to have some catalytic activity due to the presence Co and Fe in the perovskite structure). This technique has been described in detail elsewhere[6]. It must be noted that the accuracy of the CO titration technique for the system used in this work (where low surface areas and low catalyst dispersions are used) is limited and was only used in order to provide order-of-magnitude estimation of the platinum catalyst and LSCF membrane surface active sites.

The reactants used, provided by BOC, were 20% O₂/He and 10% C₂H₄/He. Helium (CP grade) was used as the balance gas. A mixture of 5% H₂/He (BOC) was also used during the catalyst activation step prior to the kinetic experiments (CO titration measurements were conducted on the

platinum catalyst and LSCF membrane surface both pre- and post the activation step). Analysis of the products was carried out by gas chromatography (Varian CP3800). In addition, the CO₂ concentrations on both sides of the membrane were simultaneously monitored using two infra-red CO₂ analysers (Binos 100 CO/CO₂ and X-Stream CO₂ analyser by Emerson) in order to calculate the reaction rates (calculated based on the CO₂ concentration measured at the outlet of each stream). A custom built quantum cascade laser (QCL) CO₂ analyser [13] was used for some measurements of the CO₂ outlet concentration (when stated). All volumetric flowrates are reported at STP.

The probe reaction (ethylene oxidation) took place in the outer side, while on the inner side the gas composition was varied in order to control the oxygen chemical potential difference across the fibre membranes and drive the promoter supply to the platinum catalyst. By using a 20% O₂/He gas mixture on the inner side (oxygen sweep) we create a driving force for oxygen migration to the outer side platinum catalyst and can thus modify its activity. Initially, the reactor is operated under nominally symmetrical conditions (with the same reaction mixture fed to both sides of the membrane) with no oxygen chemical potential difference across the membrane. We must note here that due to the lack of catalyst on the lumen side these measurements were not performed under truly symmetrical conditions as the reaction rates are different and some driving force for oxygen migration may exist. Experiments took place at 500 °C. The reaction mixture composition was set to 1.5 kPa O₂ and 0.5 kPa C₂H₄ (a stoichiometric ratio of the reactants). In order to measure reaction rates accurately the reactor was operated under differential conversion (less than 10%). The flow rate (measured at the exit of each reactor chamber) was 110ml min⁻¹. We must note that O₂ mass balance for the experiments described here closed to within more than 5% accuracy indicating that no measurable gas phase O₂ transfer occurred across the membrane. The carbon mass balance closed to approximately 7% accuracy.

3. Results and discussion

Initial kinetic results on ethylene oxidation at 500 °C using an as-prepared Pt-LSCF HF module showed very low catalytic activity under symmetrical conditions, and no electrochemical promotion of the platinum catalyst was observed even after several days of operation under an O₂ sweep. Fig. 2 shows the reaction kinetics with respect to oxygen at 500 °C for an ethylene partial pressure of $p_{\text{C}_2\text{H}_4} = 0.5$ kPa. The CO₂ concentrations for this experiment were measured using the QCL CO₂ analyser. We can see that the rate on the reaction side (where the platinum catalyst was deposited) is very low and very close to that of the sweep side (where there is no catalyst); the reaction rate observed on the sweep side is possibly due to the inherent catalytic activity of the LSCF support and possibly also some gas phase reaction¹. In fact the observed reaction rate was close to three orders of magnitude lower than the rates observed in previous studies using Pt-LSCF catalysts for ethylene oxidation [5, 6, 14] and in the rest of the kinetic experiments shown here. The low reaction rates observed on the reaction side were indicative of poisoning of the platinum catalyst. It is possible that Pt oxides were formed on the surface of the catalyst during the sintering step (performed in air). In order to address this issue the platinum catalyst was pre-reduced under a flow of 5 kPa H₂/He for 4 hours at 800 °C. During this activation step the membrane was operated under symmetrical conditions (i.e. a flow of 5 kPa of H₂/He was also introduced in the sweep side of the reactor) to avoid creating a chemical potential difference across the membrane that could result in membrane failure. Carbon monoxide titration indicated a significant (almost 50-fold) increase in the number of platinum active sites after the reduction step. No significant difference in the activity of the LSCF membrane surface (within the accuracy of the CO titration measurements) was observed as a result of the reduction step. After the successful activation of the platinum catalyst significant deactivation took place

¹We must note that the rates shown in this plot correspond to CO₂ concentrations are very close to the detection limit of the analytical equipment used so significant error may be associated with these measurements.

within several hours of operation. However, it was still possible to promote the reaction by the supply of oxygen promoting species to the platinum catalyst as will be discussed later.

Next, kinetic experiments on three pre-reduced membranes will be discussed. In Fig. 3a we can see an experiment performed on a bare membrane (no catalyst) during one cycle of symmetrical- O_2 -symmetrical sweeps. As can be seen from this figure there is a small reaction rate (due to the catalytic properties of the LSCF membrane) that is similar on both sides of the membrane and no rate modification is observed during the O_2 sweep or upon return to symmetrical operation for more than 120 hours of operation. The results show that while the LSCF possesses some catalytic activity, no modification can be observed by the supply of oxygen species to the LSCF surface. In Fig. 3b we can see a reaction rate transient of the Pt-LSCF membrane during one cycle of symmetrical- O_2 -symmetrical sweeps. As can be seen, during the first 50 hours of the first symmetrical sweep the platinum catalyst slowly deactivates and the reaction rate decreases from 0.2 to just under 0.01 $\mu\text{mol cm}^{-2} \text{s}^{-1}$. The final rate of 0.01 $\mu\text{mol cm}^{-2} \text{s}^{-1}$ is very close to the rate of the bare membrane shown in Fig. 3a. The high catalytic activity after the H_2 activation step could be explained either by a simple reduction of the oxides formed on the Pt catalyst surface during sintering, or by a synergistic effect between the Pt and the surface of LSCF perovskite membrane that catalyses the reduction of the perovskite surface (no such activity modification was observed on the bare LSCF membrane as shown in Fig. 3a). Therefore the subsequent deactivation could in turn be due to the re-oxidation of either the Pt or the perovskite surface. After 30 hours of operation under an O_2 sweep the rate showed an increase of a factor of two (approximately to 0.02 $\mu\text{mol cm}^{-2} \text{s}^{-1}$). In addition, upon return to symmetrical operation the reaction rate continues to increase reaching a final rate of 0.06 $\mu\text{mol cm}^{-2} \text{s}^{-1}$ at the end of the experiment (one order of magnitude higher than the deactivated rate during the first symmetrical sweep). This rate increase could be due to the modification of the catalytic properties of either the Pt catalyst or the reduced perovskite surface

(produced during the activation step), or a combination of the two, as a result of the introduction of the oxygen spillover species during the oxygen sweep. It may not be possible to differentiate between the activity and modification of the Pt and the LSCF support at this stage, but we can see that in absence of the Pt no rate modification is obtained (as discussed in Fig. 3a), therefore the observed effect may be a synergy between the Pt, the reduced perovskite surface and the spillover oxygen species. An increase on the reaction rate of the sweep side around 150 hours (to $0.01 \mu\text{mol cm}^{-2} \text{s}^{-1}$) of operation indicated the presence of a cross-chamber leak and the experiment was stopped at that point. We must note that a smaller leak rate may have also been present during the last part of the O_2 sweep (around 100 hours) as a small reaction rate in the sweep side is observed. However, the experiment was only stopped when the intra-chamber leak began to have a pronounced effect on the reaction rate side.

In order to understand better the nature of the observed catalytic modification we will calculate the faradaic efficiency of the reaction rate promotion during this experiment. The faradaic efficiency Λ is defined as:

$$\Lambda = \frac{\Delta r}{i/zF} \quad \text{Eq. 1}$$

Where, Δr is the difference in the promoted and unpromoted catalytic rate, i is the polarisation current density, $z=2$ in the case of oxygen ion conductors and F is Faraday's constant. It is obvious that we cannot directly calculate Λ for this system as no direct electrical polarisation was used to drive the promoter supply. We can however estimate the equivalent current based on a predicted O_2 flux across the membrane. No flux data exist for LSCF at 500°C , but it is possible to calculate a value of $j_{\text{O}_2} = 1 \pm 0.5 \text{nmol cm}^{-2} \text{s}^{-1}$ by using values reported in the literature for LSCF HF membranes operating under the same oxygen partial pressures [8] at $600\text{-}1000^\circ\text{C}$ and extrapolating to 500°C . This flux corresponds to an equivalent current density of $i=200 \pm 100 \mu\text{A cm}^{-2}$. Using the two extremes of the estimated current density (i.e. 100 and $300 \mu\text{A cm}^{-2}$) we can

calculate that the faradaic efficiency, Λ , at the end of the O_2 sweep should range from 20 to 60.

This suggests that modest non-faradaic rate modification is observed..

Another interesting feature shown in Fig. 3b is that during the second symmetrical sweep the reaction rate does not return to the initial (deactivated) value at the beginning of the O_2 sweep as is the case for classic EPOC experiments and it does not remain at the new promoted value at the end of the O_2 sweep as has been observed in the past with wireless EPOC experiments on pellet membranes [15]. This behaviour could be possibly due to the fact that the LSCF membrane provides oxygen storage during the O_2 sweep and then slowly releases the oxygen during the second symmetrical sweep. The higher surface area of the membrane and the finger-like porous structures on either side of the middle dense layer may also contribute to this effect in comparison to work on dense pellets. It has been found in the past that at high temperatures of operation (when significant oxygen fluxes can be measured) LSCF HF membranes periodically release pulses of oxygen after prolonged operation under an oxygen chemical potential difference [7]. It is possible that this still happens at lower temperatures enabling the promoter supply to the platinum catalyst even under symmetrical operation. The same behaviour is also shown in Fig. 3c (only the reaction side rate is shown here) where a rate transient under prolonged post-oxygen-sweep symmetrical operation (of more than 150 hours) was recorded. We can see that after approximately 180 hours of operation (100 hours after the beginning of the second symmetrical sweep) the rate periodically shows an almost five-fold increase (from $0.05 \mu\text{mol cm}^{-2} \text{s}^{-1}$ to $0.25 \mu\text{mol cm}^{-2} \text{s}^{-1}$). In the experiments conducted in this work this oscillating behaviour was only seen under post- O_2 sweep symmetrical operation.

As seen from the results presented here it is possible to use a wireless EPOC configuration for the *in situ* regeneration of a platinum catalyst via the introduction of short pulses of oxygen on the sweep side of the membrane reactor. This finding represents a very important step forward in practical applications of EPOC.

4. Conclusions

A single HF reactor module was used for the study of wireless EPOC of ethylene oxidation using a platinum catalyst film. It was found that the platinum catalyst required an activation step under a flow of H₂. Under symmetrical operation a slow deactivation of the platinum catalyst was observed while the rate increased by almost one order of magnitude (compared to the deactivated rate) during one O₂ and one subsequent symmetrical sweep. The results presented here show that wireless EPOC can be used for the *in situ* regeneration of a platinum catalyst without the need to stop the reaction for the regeneration step to take place.

5. Acknowledgements

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Figure Captions:

Fig. 1: Schematic of HF reactor module

Fig. 2: Kinetic data as a function of p_{O_2} at 500 °C prior to catalyst activation under a H_2 flow at 800 °C. The data was recorded under symmetrical operation, the partial pressures of the reactants were $p_{O_2}=1.5$ kPa, $p_{C_2H_4}=0.5$ kPa. The flow rate on both sides of the membrane was 110 ml min^{-1} (STP)

Fig. 3: Reaction rate transients at 500 °C for a Symmetrical- O_2 -Symmetrical experimental cycle. The partial pressures of the reactants were $p_{O_2}=1.5$ kPa, $p_{C_2H_4}=0.5$ kPa. The flow rate on both sides of the membrane was 110 ml min^{-1} (STP). During the O_2 sweep the gas composition of the sweep side was 20kPa O_2 in He at 110 ml min^{-1} .

a) LSCF bare membrane (no catalyst)

b) Pt-LSCF membrane (Pt catalyst deposited on the shell side)

c) Long term experiment on a Pt-LSCF membrane (Pt catalyst deposited on the shell side), rate oscillations are observed after prolonged operation

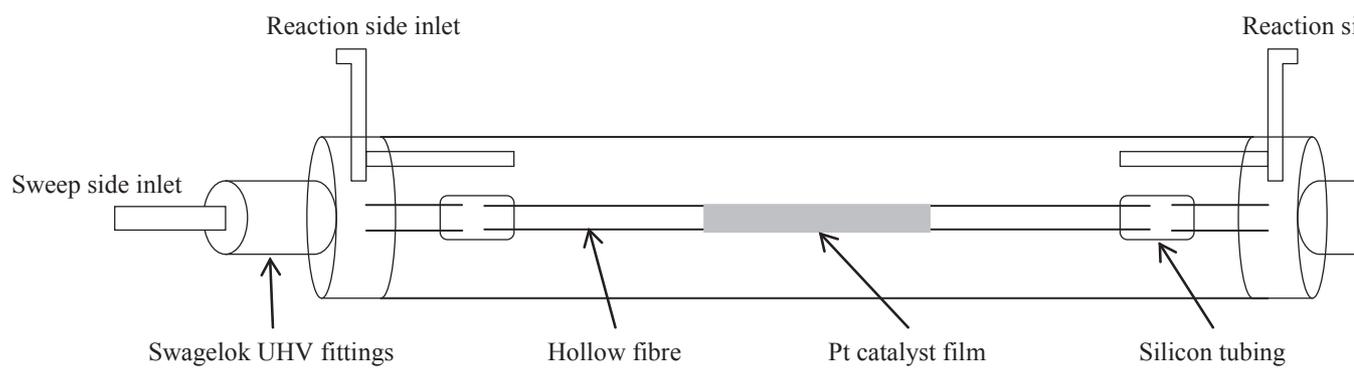


Fig. 1

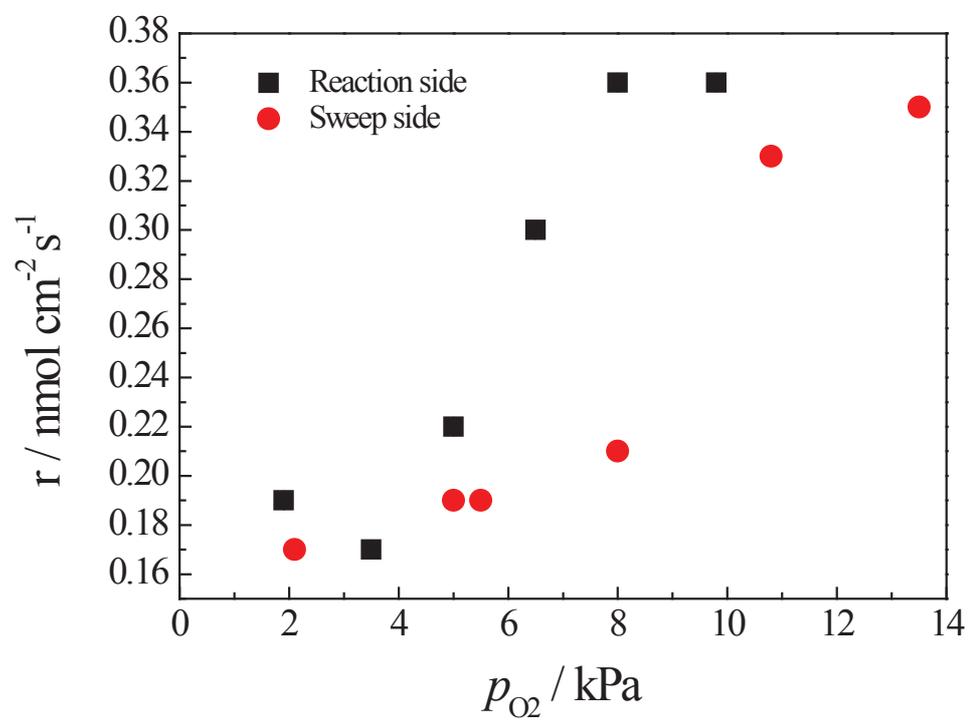
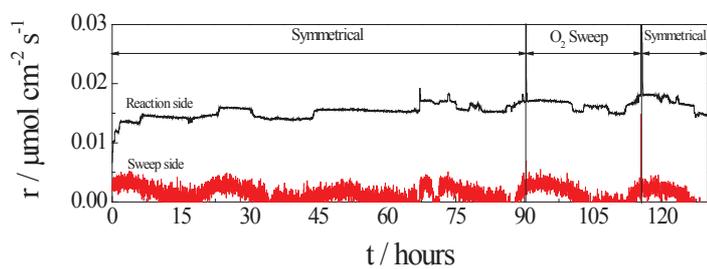
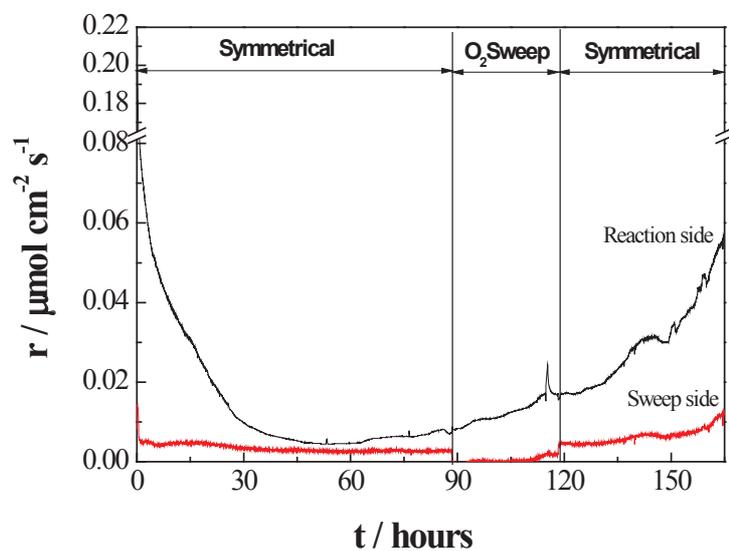


Fig 2

a)



b)



c)

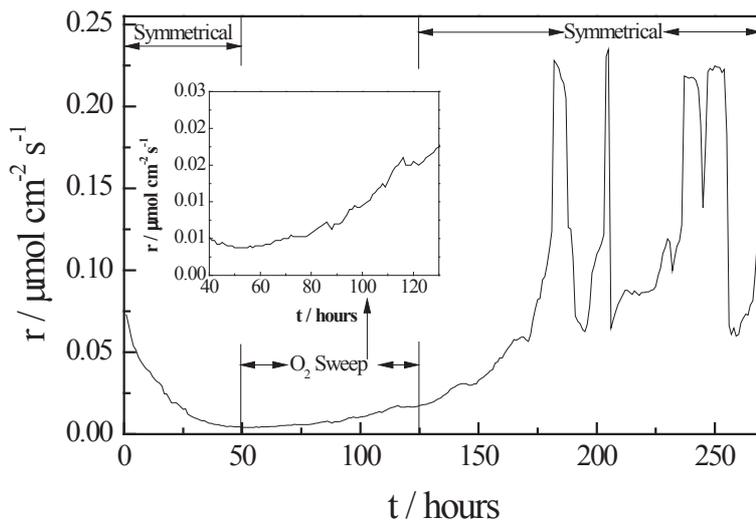


Fig. 3