Control of Spillover Processes in Catalysis

-Porous and Patterned Electrodes

By

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ABSTRACT

Electrochemical promotion of catalysis (EPOC) is a result of backspillover phenomena which involves the migration of backspillover (oxygen ionic) species through the tpb onto the catalyst surface under the influence of electrical potential application. The present work studies the occurrence and the role of the backspillover species and also the mechanisms of the related processes including factors controlling this phenomenon in a Pt/YSZ system which utilises a model catalyst or sputtered patterned electrodes. In comparison to the electrodes prepared by painting the commercially available Pt catalysts on YSZ, the geometric characteristics and the type and amount of impurities on the Pt surface should not vary significantly among the samples except the tpb length (of the 3rd batch samples). Therefore, the electrochemical processes at the tpb can be studied systematically and the electrochemical data should be reproducible which are not the case when electrodes prepared by using the commercially available catalysts are involved. The variability in the electrochemical behaviour (charge transfer reaction) of the Pt/YSZ system, as depicted by CV results under a nonreactive condition at 400 °C, of the Pt electrodes prepared by using the commercially available catalysts is demonstrated in the first part of the study. The three commercially available catalysts provided by ESL, Heraeus and Metalor are shown to contain different type and amount of impurities and to have different Pt surface morphology. The impurities were analysed by ICP-OES while the surface morphology was investigated by SEM. In the second part of the study, the focus was on the Pt/YSZ system utilising the patterned electrodes where the correlations between the oxygen charge transfer (oxygen activity) and the tpb length were investigated by CV, EIS and current overpotential experiments under a nonreactive condition at temperatures between 300 °C and 450 °C. The term oxygen activity in this thesis refers to the kinetics of the oxygen charge transfer reaction. A proportional relationship between the oxygen charge transfer and the tpb length was not observed and this is explained by the changes in Pt surface morphology throughout the experimental works and most important the formation of surface oxides at the tpb which blocks the charge transfer processes. However, the changes in the oxygen activity at the tpb can be observed from the correlation between the current density and the peak current from the CV results. Another interesting observation is the appearance of additional peak in CV after exposure to hydrogen which can be associated with either the decomposition of impurity oxides or
Pt oxides of different oxidation state at the binary interface. In the third part of the study, the catalytic and electrochemical behaviour of the system utilising the patterned electrodes was investigated during CO oxidation at temperatures between 300 °C and 450 °C. The Pt/YSZ system was found to exhibit (i) EPOC at 0.10 V, 0.20 V and 1.0 V, (ii) permanent EPOC and (iii) permanent poisoning effect. The backspillover species was found not only to enhance the catalytic rate but also to stop the open circuit rate oscillations and, at a high pO₂, to restore the rate due to the permanent poisoning effect. Furthermore, five types of oxygen species are suggested to present at the tpb and on the Pt surface during the experimental works where the coverage of these species controls the amount of oxygen ionic species which can migrate through the tpb onto the Pt surface.
Nomenclature

List of acronyms

<table>
<thead>
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<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>EPOC</td>
<td>Electrochemical promotion of catalysis</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma-optical emission spectroscopy</td>
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<tr>
<td>MIEC</td>
<td>Mixed ionic-electronic conducting membranes</td>
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<tr>
<td>NEMCA</td>
<td>Non-faradaic electrochemical modification of catalytic activity</td>
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<tr>
<td>OCP</td>
<td>Open circuit potential</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>SMSI</td>
<td>Strong metal-support interactions</td>
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<td>STM</td>
<td>Scanning tunnelling microscopy</td>
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<td>Tpb</td>
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Chapter 1. Introduction

1.0 Research Background

The current work focuses on the electrochemical promotion of catalysis (EPOC) or non-faradaic electrochemical modification of catalytic activity (NEMCA) which has been studied and applied quite successfully for many catalytic systems (the term EPOC will be used in this thesis from now on). In EPOC, catalytic activity and selectivity of metal films in contact with electrolytes, both solid state and aqueous, can be varied in situ in a very pronounced and reversible manner via electrical potential application between the catalyst film and a counter electrode also in contact with the electrolyte. Vayenas and co-workers discovered this EPOC phenomenon in early 1980s and many types of reactions and systems have been studied today by many research groups. One of the practical utilisation of EPOC is in environmental catalysis, particularly in automotive pollution control. Recent investigations include implementation of EPOC on $O^{2-}$ ionically conducting ceramics for automotive post-treatment (e.g., NO reduction, CO oxidation, hydrocarbons oxidation) and air cleaning (e.g., Volatile organic compounds oxidation) applications [1].

EPOC has been shown to be due to the catalytically promoting properties of ionic species which migrate onto the catalyst surface under the influence of the applied potential. These species accompanied by their compensating charge in the metal establish an overall neutral double layer on the gas exposed catalyst surface. The effective double layer affects the binding strength of chemisorbed reactants and reaction intermediates and thus affects the catalytic rate in a very pronounced and reversible manner [2]. After current interruption, the catalytic rate usually returns to the initial open circuit value, however, there are also cases where the rate remained at the highly active steady state [3,4] and at a value lower than the initial condition [5,6].

The migration of the ionic species and the formation or the stabilisation of the effective double layer are influenced by catalyst surface microstructure and surface impurities. For a case of commercial catalysts, impurities may pre-exist on the catalyst surface and
catalyst surface characteristics may also be different as a result of the differences in catalyst manufacturing processes. The resulting catalyst films of different providers, therefore, may have different impurities [7, 8] and microstructure or morphology [8, 9] which can result to significant differences in the number of the available active sites (three phase boundary (tpb) interface) for the charge transfer reactions and hence exhibit different transient responses in EPOC. Furthermore, impurities cause changes in the catalyst work function and also can directly interact with the gas phase reactants and reaction intermediates and promoter or backspillover species [10]. Addition of an impurity (such as sodium) onto Pt catalyst has been shown to affect the catalyst catalytic and electrocatalytic activity, however, there was no evidence of the effect of such species on causing EPOC [10].

The effect of impurity and morphology on the catalyst catalytic and electrocatalytic behaviour interact and hence a special focus on either the contamination [8] or the morphology is necessary to obtain a clear evidence of the effect of each of these two factors on EPOC. A focus on the influence of impurities on EPOC can be obtained by adding a known amount of impurity onto a catalyst surface where the catalytic and electrocatalytic behaviour can be studied by analysing several samples with different amount of added impurities [10, 11]. However, for cases where the electrode is prepared by brushing or painting (manually), there should also a variation in the catalyst film thickness and amount among the electrodes (although using the same catalyst) where the morphology effect cannot simply be neglected. Besides that, impurities such as Si can also be introduced onto the catalyst surface during electrode preparation. A focus on the morphology, on the other hand, requires a clean sample or at least samples with a controlled amount and type of impurities. In other words, the samples should be similar in terms of the type and amount of impurities present on the Pt surface.

The variations or complexity in the electrode geometric (film thickness) and surface (morphology and impurities) characteristics of the porous electrodes prepared by using the commercially available catalysts led to difficulties in carrying out a systematic study on the geometric (such as tpb) dependence of the charge transfer reactions. These problems which also resulted to the experimental data which was not reproducible however can be solved through the application of model catalysts such as those prepared
by sputtering with known geometric tpb length [12-14]. Model catalysts prepared by sputtering have a controlled geometric characteristics and amount of impurities and are usually of a thin and dense electrode. However, there are limitations when this model catalyst was used where

(i) significant changes in the morphology were observed as a result of anodic polarisation and heat treatment [15]

(ii) surface oxidation at the catalyst active sites or tpb was unavoidable and was usually discussed in the literature as a cause of catalyst or electrode deactivation [15,16]

The electrode deactivation phenomenon is associated with a decrease in the oxygen activity at the tpb where the charge transfer reactions are hindered by the passive oxide layer at this interface [15]. For a case of a dense electrode, this decrease in the oxygen activity at the tpb causes an increase in the activity at other interfaces in the Pt/YSZ system such as at the Pt/YSZ (or binary) interface. In other words, oxygen activity at each of the interfaces in the system influence each other [8]. Since the deactivation phenomenon is particularly important in terms of the performance of the electrode, such as in EPOC where the processes occurring at the tpb is highly important, detail understanding of the processes occurring at each of these interfaces are therefore necessary.

### 1.1 Problem Statements

Variability in the electrochemical behaviour of a Pt/YSZ system are often reported in the literatures which could be due to the presence of different types of impurities in the raw materials used for the preparation of different samples [10]. To date, very little information is available on the possible influence of impurities on the charge transfer reactions and EPOC in a Pt/YSZ system. The presence of impurities on the catalyst surface requires a complex model to predict and explain the electrochemical behaviour of such a system [10]. As demonstrated by Ibrahim et al.[10], at high sodium (impurity) coverage, (i) sodium effect on the open circuit catalytic rate was more pronounced and (ii) the interaction between the sodium and oxygen (promoter) under the polarisation became significant. In order to simplify the model describing the electrochemical
behaviour of a Pt/YSZ system, (i) impurities should present (if there any) on the catalyst surface at the lowest possible amount so that the assumption of the negligible interaction with the promoter under the polarisation is valid or (ii) the type and amount of impurities present on the catalyst surface should not vary significantly among the samples so that the variables associated with impurities are minimised and a focus on the morphology or geometric characteristics can be obtained.

However, the commercially available catalysts should contain impurities and the manual preparation of the electrodes also can cause variation in the electrode geometric characteristics and hence the electrochemical data. This led to difficulties not only to explain the electrochemical behaviour but also to carry out a systematic study on the effect of certain geometric parameter such as the tpb length on the charge transfer reactions and hence EPOC. Therefore, (i) to systematically study the processes occurring at the tpb such as the backspillover processes which are associated with the origin of EPOC, the utilisation of a model catalyst with a focus on the tpb length is necessary. This can be obtained from the application of electrodes with controlled surface characteristics where the geometric parameters, such as the tpb length, film thickness and surface area, are well defined with a controlled amount of impurities (if there any) present on the catalyst surface.

1.2 Hypotheses

Based on the research background, the following hypotheses are developed.

(i) Commercial catalysts contain impurities and the impurities influence (either by enhancing or hindering) the charge transfer reactions at tpb and hence has significant effect on EPOC.

(ii) The complexity of the geometry characteristics of the patterned electrodes or model catalysts are reduced since the electrodes have a controlled geometry characteristics where the geometric tpb length is known and differs among samples of different width length scale. Therefore, geometry (tpb) dependence of the charge transfer reactions can be studied.

(iii) Patterned electrodes (3rd batch samples) prepared by sputtering should have a controlled amount of impurities in comparison to those prepared manually by
using commercial catalysts. The patterned electrodes were prepared in three batches where the characteristics for each batch are described in Chapter 3 section 3.2. It is therefore assumed that variables associated with impurities (among different samples) are minimised. The question of whether the impurities are necessary for the occurrence of EPOC is not the focus of the present work involving the patterned electrodes.

(iv) Tpb is susceptible to oxidation and the formation of surface oxide can hinder the charge transfer reactions at this interface [17,18]

(v) Oxygen oxidation and reduction processes are occurring at various interfaces in the Pt/YSZ system using the patterned electrodes (such as tpb and binary interface (Pt/YSZ)) where the processes at an interface are dependent on the processes taking place at the other interfaces.

1.3 Objectives of Study

The objectives of the present work are to determine if the patterned electrodes can be utilised as a model catalyst where the focus was on the processes occurring at the tpb involving the backspillover phenomenon and on the factors controlling this process. The study included

(i) the verification of the presence of impurities in commercial catalysts and the influence (which is assumed to interact with the effect of catalyst surface morphology) on the charge transfer reactions in a Pt/YSZ system.

(ii) the utilisation of the patterned electrodes in electrochemical studies in which the focus was on the processes occurring at the tpb which is the most important interface associated with the backspillover phenomena.

(iii) Investigations of the limitations (electrode deactivation and activation phenomena) and advantages of using electrodes with the patterned electrode design in the Pt/YSZ system. This is important in terms of determining the electrodes suitability as (i) the model catalyst and (ii) a catalyst in EPOC.
1.4 Scopes of Study

(i) The study on the influence of impurities on the oxygen charge transfer reactions was carried out using three commercially available Pt catalysts. The experiments or analyses included surface (SEM and ICP) and electrochemical characterisations by cyclic voltammetry (CV) at low temperature and under atmospheric condition and a nonreactive condition in which the samples were exposed to the flow of 200 mlmin\(^{-1}\) 20% O\(_2\)/He at temperatures between 300 °C and 450 °C.

(ii) The study using the model catalyst or patterned electrodes included surface (SEM) and electrochemical characterisations by CV, electrochemical impedance spectroscopy (EIS), current overpotential under nonreactive condition and kinetic and electrochemical promotion (EPOC) experiments under reactive conditions at low temperature and under atmospheric condition. The electrodes were of different width length scale. Under the nonreactive condition, the electrodes were exposed to the flow of approximately 100 mlmin\(^{-1}\) 20% O\(_2\)/He while under the reactive condition, the electrodes were exposed to 5% CO/He, 20% O\(_2\)/He and He. The electrodes were also exposed to 5% H\(_2\)/He during chemical treatment study.

1.5 Research Contributions

The main contribution of the present work is the description of the electrochemical behaviour of the Pt/YSZ system utilising patterned electrodes in which (i) the role of backspillover species under polarisation, (ii) factors controlling the backspillover phenomena, and (iii) limitations (different than those described in section 1.6) during the utilisation of the patterned electrodes are discussed. The findings included

(i) demonstration of the significant influence of impurities on the charge transfer reactions.

(ii) repeatability study, which included chemical treatment, as an approach (i) to describe the tpb dependence of the catalytic rate and charge transfer reactions and (ii) to indicate the presence of impurity oxide or Pt oxide of different oxidation state at the binary interface.

(iii) observations of EPOC at small anodic potential of 0.10 V and 0.20 V during CO oxidation at low temperature.
(iv) the observation and the description of the mechanism of the permanent poisoning effect during CO oxidation.

(v) the finding of a similarity in the role of the stored oxygen at the binary Pt/YSZ interface and Pt bulk with the backspillover species in controlling the surface oxygen activity, stabilising the effective double layer and enhancing the catalytic rate.

(vi) a suggestion of five types of oxygen species which can present on the Pt surface during the experimental works where the coverage of these species on the Pt surface controls or influences the amount of oxygen ionic species which can migrate onto the Pt surface.

(vii) surface oxides formation at tpb as the limiting factor of the charge transfer reactions and EPOC.

(viii) durability of the patterned electrodes during the applications in the field (possible applications include (i) CO oxidation catalytic rate sensor (ii) EPOC)

1.6 Limitations of Study

Uncertainties of the results are associated with limitations in
(i) the number of patterned electrode samples
(ii) the design of the patterned electrodes where the electrodes are not completely dense and susceptible to oxidation
(iii) the time to carry out the experiments
(iv) the output of the Binos 100 CO₂ analyser where the transient results were digitised
(v) carrying out chemical treatment at high temperature where the counter and reference electrodes are susceptible to damages
(vi) data analyses where the utilisation of certain software may produce better demonstrations of the results
(vii) in situ measurement where this type of investigation can further verify the findings of the current work
1.7 Structure of Thesis

Chapter 1 presents research backgrounds, problem statements, hypothesis, objectives, scopes of study, research contributions and limitations of study. Chapter 2 discusses the literature review while Chapter 3 describes the experimental procedures used in this study. Results are presented and discussed in Chapter 4, 5, and 6. Chapter 4 verifies the presence of impurities in the commercial catalysts and sintered Pt films and these impurities are shown to influence the charge transfer reaction where this effect interacts with the morphology of the Pt film. Chapter 5 presents the study on the tpb length dependence of the charge transfer reaction using the model catalyst where the discussions were on the effect of electrode morphology (microstructure and surface oxides). Chapter 6 present the role of backspillover species and mechanism of the backspillover processes in the Pt/YSZ system utilising the patterned electrodes. Chapter 7 presents the conclusions and recommendations for future works.
Chapter 2. Literature review

2.0 Introduction

Catalysis is the process in which the rate of a chemical reaction is either increased or decreased by means of a chemical substance known as a catalyst. A catalyst is not consumed by the reaction itself and may participate in multiple chemical transformations. The activity of catalysts can be increased by substances known as the promoters and the activity can be decreased by substances known as catalytic poisons. Homogeneous catalysts are those that are present in the same phase as the reactants while heterogeneous catalysts are those that are present in a different phase. In heterogeneous catalysis, promoters play an important role. Promoters can be added to the catalyst ex situ, during catalyst preparation or in situ via electrical potential or current application when the active phase is supported by an ionic or mixed-ionic-electronic conductor which can donate promoting species to the catalyst/gas interface via backspillover [19].

2.1 Electrochemical Promotion of Catalysis (EPOC)

The catalytic activity and selectivity of a porous catalyst film deposited on a solid electrolyte can be modified in situ in a very pronounced and reversible manner via electrical potential application between the catalyst film and a counter electrode also in contact with the electrolyte [20]. This phenomenon has been termed as electrochemical promotion of catalysis (EPOC) or non-faradaic electrochemical modification of catalytic activity (NEMCA) or in situ controlled promotion which has been studied and applied quite successfully for many catalytic systems. Catalytic oxidations of \( \text{C}_2\text{H}_4 \), \( \text{C}_3\text{H}_6 \) and CO were among the catalytic systems being studied. Catalysts used in EPOC studies such as Platinum (Pt), Palladium (Pd) and Rodium (Rh) were normally deposited on either a proton conductor, an ionic conductor or a mixed ionic-electronic conductor. The origin of EPOC has been studied by using analytical methods such as X-ray photoelectron spectroscopy (XPS) [21], work function measurements [22], scanning tunnelling microscopy (STM) [21], temperature programmed desorption (TPD) [23, 24] and scanning photoelectron microscopy [25], scanning electron microscopy (SEM) [7, 26-28], SEM/EDX [4,29,30] and cyclic voltammetry (CV) [7,31, 32].
The EPOC phenomenon is believed to be due to the electrochemically controlled migration of backspillover species from the solid electrolyte onto the gas exposed electrode surface through three phase boundary (tpb). Backspillover species can be $O^\delta-$ in the case of $O^{2-}$ conductors such as $Y_2O_3$-stabilized $ZrO_2$ (YSZ) and mixed ionic-electronic conductors such as $TiO_2$ or $CeO_2$. For the case of $Na^+$ conductors such as $\beta-$ and $\beta''-$ aluminas which are nonstoichiometric compounds corresponding to $Na_{1+x}Al_{11/2}O_{17+x/2}$ ($0.15 \leq x \leq 0.3$) and $Na_{1+x}M_xAl_{11/2}O_{17}$, respectively, where $M$ is a divalent metal such as $Mg^{2+}$, $Ni^{2+}$, $Zn^{2+}$, the backspillover is $Na^{\delta+}$ [33]. $O^\delta-$ can have a charge between $O^-$ and $O^{2-}$ [9], while for $Na^{\delta+}$ the charge is in the order of 0.8–0.5 [33].

The spillover effect can be described as the mobility of adsorbed species from one phase on which they easily adsorb (donor) to another phase where they do not directly adsorb (acceptor) [33]. Backspillover species such as $O^\delta-$ in the case of $O^{2-}$ conductors act as normal promoters once they have migrated onto the metal surface. The species occupies the strongly bonded oxygen chemisorptions state while adsorbed oxygen from the gas phase populates the weakly bonded state. The reaction rate will be at a new steady state value when the backspillover species achieve a steady state coverage on the metal surface.

The electrical promotion operational principle is shown in Figure 2.1 [9]. Under the influence of the applied potential (between the catalyst and a catalytically inert counterelectrode, also deposited on the solid electrolyte), ionic species backspillover onto the catalyst surface accompanied by their compensating charge and establish an overall neutral effective double layer on the gas exposed catalyst surface. The effective double layer created at the metal-gas interface due to potential-controlled migration of backspillover species is shown in Figure 2.2 [34]. The presence of this effective double layer modifies the catalyst’s work function and changes the binding strength of the chemisorbed reactants and reaction intermediates, thus affecting the catalytic rate [33, 34, 35 ].

The work function of a surface is the minimum energy which an electron must have to escape from the surface when the surface is electrically neutral [33]. Catalyst work function can be measured by using Kelvin probe [23, 34, 36-38] in which the correlation
between the applied potential and the change in the work function at the metal gas interface is described as [2, 34, 38]

\[ e\Delta U_{WR} = \Delta \Phi_W \]  

(1)

where \( \Delta U_{WR} \) and \( \Delta \Phi_W \) are the change in the catalyst potential and the work function, respectively.

Figure 2.1: Schematic diagram of electrochemically induced spillover species onto a metal or Pt surface. The oxygen ions are transported through YSZ and discharged at the tpb and the discharged species migrate onto Pt electrode surface [9].

Figure 2.2: Schematic representation of a metal electrode deposited on a (a) \( \text{O}^2^- \) conducting and (b) \( \text{Na}^+ \) conducting solid electrolyte which indicates the location of the metal-electrolyte double layer and of the effective double layer created at the metal-gas interface due to potential-controlled migration of backspilover species [34].

Upon varying the catalyst potential (or work function) of a given catalyst at constant temperature and gas composition, four types of the promoted catalytic rate dependence on the work function (or potential) can be observed which include [19]
(i) an electrophobic reaction when the catalytic rate increases with catalyst work function and potential
(ii) an electrophilic reaction when the catalytic rate decreases with catalyst work function and potential
(iii) an inverted volcano type reaction when the rate passes through a minimum with the catalyst potential and work function
(iv) a volcano type reaction when the rate passes through a maximum with the catalyst potential and work function.

For the electrophobic reaction, the positive potential increases the work function due to the O$_2^-$ or promoter supply onto the catalyst surface. The presence of this promoter weakens the chemisorptive bond of electron acceptor adsorbates and strengthens the chemisorptive bond of electron donor adsorbates [2]. The negative potential, however, should withdraw the promoter from the Pt electrode thus causing a decrease in the reaction rate [9].

2.1.1 Transient Behaviour

The typical catalytic rate versus time behaviour during an electrochemical promotion experiment is shown in Figure 2.3, where the catalytic rates, $r_o$ (I=0) and r, are the rates under open and close circuit conditions, respectively.

![Figure 2.3: Catalytic rate versus time during an EPOC experiment [39]](image_url)

The promoted rate, r, could be up to 200 times larger than the open circuit rate, $r_o$, after the application of an electric current, I, or a potential difference between working and the
reference electrode. The promotion-induced change in catalytic rate (mol O per s) can be expressed as

\[ \Delta r = r - r_0 \]  \hspace{1cm} (2)

The occurrence of the electrochemically controlled migration (backspillover) or promoting species from the solid electrolyte support to the metal gas interface is indicated by the long rate response time constants during constant current imposition [34]. This is equivalent to the time required to form a monolayer of \( O^\delta^- \) on the metal surface or for \( \Delta r \) to reach 63% of its steady state value when atomic oxygen is supplied at the tpb at a rate of \( I/2F \) according to Faraday's law which is defined as the EPOC time constant, \( \tau \) [34]

\[ \tau = 2FN_{op}/I \]  \hspace{1cm} (3)

where \( N_{op} \) is the reactive oxygen uptake of the metal catalyst which is expressed in mol. The formation of these backspillover species at the tpb can be written as [34]

\[ O^2- \rightarrow (O^\delta^- - \delta^+) + 2 \text{e}^- \]  \hspace{1cm} (4)

However, according to the sacrificial promoter mechanism, an \( O^2- \) arriving from the solid electrolyte support to the tpb can also desorb as \( O_2 \) or react with adsorbed CO to form \( CO_2 \) besides migrating (backspillover) at the metal/gas interface as a surface dipole [24]. Besides the EPOC time constant, another important parameter which is often used to describe the EPOC effect is the Faradaic efficiency, \( \Lambda \), defined as [40]

\[ \Lambda = \Delta r/(I/2F) \]  \hspace{1cm} (5)

where \( \Lambda \) can also be approximated by [2]

\[ |\Lambda| \approx 2F r_0/I_0 \]  \hspace{1cm} (6)

where \( I_0 \) is the exchange current of the catalyst-solid electrolyte interface. If \( |\Lambda| > 1 \) then the reaction exhibits the EPOC effect. For oxidation reactions, \( \Lambda \) expresses the ratio of the
reaction rates of normally chemisorbed atomic oxygen on the promoted surface over that of backspillover oxide ions. It also describe the ratio of the average lifetimes \( \tau_p \) and \( \tau_r \) of the promoter and of the gas-supplied reactants, respectively, on the catalyst surface [34]

\[
\Lambda = \frac{\tau_p}{\tau_r}
\]  

(7)

where this promoter lifetime \( \tau_p \) can be directly obtained from the \( r \) versus time transient upon current interruption since the observed catalytic rate decrease is due to the consumption by the fuel of the promoting backspillover \( O^\bullet \) species. Besides the faradaic efficiency, the rate enhancement ratio, \( \rho \), defined as the ratio of the promoted, \( r \), over open circuit catalytic rate, \( r_0 \), is also often used to determine the magnitude of the EPOC effect [40].

2.1.2 Advantages of EPOC

In EPOC, the promoting species that would normally have a short life-time on the catalyst surface can still be used as a promoter since its coverage on the catalyst surface can be fixed by setting an appropriate potential between the working and counter electrodes. This allows the direct examination of the effect of promoter coverage and of work function on the catalytic reaction kinetics [2]. It has been shown that the EPOC phenomenon is equivalent to the phenomenon of strong metal-support interactions (SMSI) [41] and the difference between EPOC and SMSI is that in the former case it is possible to control in situ the supply of the promoter on the catalyst surface.

2.1.3 Model Reaction (Carbon Monoxide Oxidation)

Electrochemical promotion has been studied for various catalytic reactions that included \( CH_4, C_2H_4, CO, SO_2, C_2H_6 \) oxidations [3, 35, 42-52], NO reductions [20, 53-57] and \( CO_2 \) hydrogenations [58-60]. In the present work, CO oxidation over Pt catalyst was used as the model reaction during the EPOC study. Extensive studies on carbon monoxide (CO) oxidation over noble metal catalyst such as platinum (Pt) and palladium (Pd) have been carried out since these two metals are widely used as automobile catalytic exhaust
converters. The advantages of using CO oxidation over Pt catalyst as model reaction are as the followings [61]

a. No side reactions in a CO oxidation reaction.
b. The Pt-based catalyst was very stable towards the oxidation reaction.
c. Information on CO oxidation is available due to its importance in the catalytic control of automobile emissions.

CO oxidation can be expressed as:

\[ CO + \frac{1}{2} O_2 \rightarrow CO_2 \]  

(8)

A pronounced EPOC effect with a rate enhancement ratio, \( \rho \), of approximately 9 and a faradaic efficiency, \( \Lambda \), of approximately 1500 when \( U_{WR} \) exceeded 0.4 V has been reported during study using CO oxidation as the model reaction [50]. Another study on CO oxidation over nano-dispersed Pt particles catalyst supported on YSZ under high vacuum conditions showed reaction rate enhancement by a factor of 500 at 300 °C [62]. The results of EPOC experiments on CO oxidation from literatures are indicated in Chapte: 6 (Table 6.3).

2.1.4 EPOC by the Thermally Induced Oxygen Ionic Species

It has been established by Vayenas and co-workers that EPOC involves the migration of \( O^2- \) ionic species, from YSZ onto the Pt surface under the influence of polarisation. However, Vernoux et al. [63] has demonstrated that EPOC can be thermally induced without any electrical polarisation for a Pt/YSZ system involving nanoparticles of metallic catalysts supported on ionically conducting ceramics during propane deep oxidation. The occurrence of this thermally induced oxygen ionic species has also been described for a very thin and dense sputtered Pt layer (very low internal diffusion) [64]. This mechanism is similar to the effect of backspillover of \( O^2- \) induced by polarisation. The advantage of this effect is that it does not require electrical connections and complicated specific devices. In contrast to electrical polarisation, it may be difficult to
control in situ the thermal migration to achieve the optimal coverage of ionic promoters and the maximal catalytic rate [63].

As mentioned by Karoum et al. [65] in the literatures, the thermal migration ionic species from YSZ to the Pt surface, which contributed to the initial $O^2^-$ coverage on Pt without any polarisation, has often been neglected and assumed not to influence the catalytic rate measured at the open circuit condition. To observe a real impact of polarisation for a Pt/YSZ system where these thermally induced backspillover species present on the catalyst or Pt surface, a negative potential can be applied [64,65] where the negative polarisation causes the migration of $O^2^-$ ionic species from the Pt surface toward the electrolyte and this step assures the same Pt surface state before each anodic polarisation. Karoum et al. [65] also demonstrated the importance to define a normalised rate enhancement ratio from a reference value of the catalytic rate corresponding to a Pt surface state free of $O^2^-$ ions. The normalised rate enhancement ratio, $\rho_n$, is defined as

$$\rho_n = \frac{r}{r_{\text{ref}}} = \frac{r}{r_{(-2V \text{ during 1 hour})}} \quad (9)$$

where $r_{\text{ref}}$ is not the open circuit catalytic rate which depends on the sample thermal history but the catalytic rate corresponding to a reproducible Pt free surface, i.e. with a negligible $O^2^-$ coverage on Pt.

2.1.5 The Role of Backspillover Species in the Pt/YSZ System

In EPOC, backspillover species (either induced by thermal effect or polarisation) acts as a promoter which can dramatically enhance the catalytic rate. The species however has been discussed in the literatures to also have other roles in the Pt/YSZ system such as

(i) causing and or stopping oscillations in the catalytic rate,
(ii) causing permanent EPOC effect and
(iii) restoring the catalytic activity when the Pt surface is poisoned by oxides during a negative polarisation.

These roles and the mechanisms of the related processes are discussed below.
2.1.5.1 The Oscillatory Phenomenon during EPOC

Between 350 °C and 450 °C, PtO$_2$ and dissociatively chemisorbed oxygen can present on the catalyst surface where for long oxygen exposure time more of the oxygen of the PtO$_2$ (multilayer oxidation of Pt) present on the catalyst surface than that of the chemisorbed oxygen [66]. The oscillatory phenomenon such as during CO and ethylene oxidation at atmospheric pressure for a Pt/YSZ system is commonly associated in the literatures with the formation and decomposition of these surface oxides (PtO$_2$/PtO$_x$). The steady state and the oscillatory behaviour of CO oxidation on Pt depended on the catalyst pretreatment where the rate and emf oscillations of those produced on a peroxidised surface spike up and those produced on a prereduced surface spike down [66].

The application of the appropriate external voltages to the cell can cause either the appearance or disappearance of catalytic rate oscillations during CO [51, 66] and ethylene oxidation [10]. The findings of this oscillatory phenomenon during EPOC studies are listed in Table 2.1. This phenomenon was explained by the role of the electrochemical backspillover species which migrated from the electrolyte to the Pt surface in controlling or altering the oxygen activity on the catalyst surface during the potential application [51, 66]. Positive polarisation during CO oxidation which strengthened the Pt-CO interaction and weakened the Pt-O interaction enhanced the CO coverage on the catalyst surface which led to PtO$_x$ decomposition and hence stopped the catalytic rate oscillations [51]. Oscillations which were induced during polarisation, on the other hand, can be explained by the decomposition of surface oxides via repulsive lateral interaction between the electrochemically controlled backspillover of O$_2^-$ on the catalyst surface and the oxygen of the surface oxide followed by surface reoxidation by gaseous O$_2$ [67].
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ratio to $pO_2$</th>
<th>Effect of Polarisation/ Promoter</th>
<th>Mechanism</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/YSZ, C$_2$H$_4$ oxidation</td>
<td>$pC_2H_4/pO_2$: 0.5/8</td>
<td>Anodic and cathodic polarisations stopped catalytic rate oscillations</td>
<td>Not discussed</td>
<td>[10]</td>
</tr>
<tr>
<td>Porous Pt film, Surface area: 0.88 cm$^2$, Clean sample and 0.11% sodium coverage, T:350 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh/YSZ, C$_2$H$_4$ oxidation,</td>
<td>$pC_2H_4/pO_2$: 0.58/1.8</td>
<td>Anodic polarisation caused oscillations of the catalytic rates</td>
<td>Interaction of the promoter with oxygen of the surface oxides and surface reoxidation by gaseous oxygen</td>
<td>[67]</td>
</tr>
<tr>
<td>Film thickness:10 µm, Surface area: 2 cm$^2$, T: 330 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/YSZ, Sputtered Pt, CO oxidation</td>
<td>$pCO/pO_2$: a.1.2/3 b.2/1</td>
<td>a. Anodic polarisation(15 µA) stopped the rate oscillations. b. Cathodic polarisation (-17 µA) caused a permanent oscillatory behaviour.</td>
<td>a. The enhanced CO coverage on Pt surface led to Pt$<em>{O_x}$ decomposition. b. CO depletion on Pt surface and surface Pt$</em>{O_x}$ formation</td>
<td>[51]</td>
</tr>
<tr>
<td>Film thickness: 60 nm, T: 250 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/YSZ, CO oxidation</td>
<td>$pCO/pO_2$: 1/34</td>
<td>Negative polarisation stopped rate oscillations, positive polarisation led to rate oscillations (at high anodic currents)</td>
<td>Formation and decomposition of surface Pt$_{O_x}$. Oscillatory mechanism is the same both under open circuit conditions and during oxygen pumping</td>
<td>[66]</td>
</tr>
<tr>
<td>Porous, Film thickness: 5 µm, Surface area: 2 cm$^2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.1.5.2 Permanent EPOC

EPOC is in general a fully reversible process and the catalytic rate returns to the initial rate $r_0$ after the current interruption. However, there have been cases where the catalytic rate remained in a highly active steady state even after the current was interrupted and only returned to the initial catalytic rate after the application of a similar current of the opposite polarity [3, 68]. This phenomenon is termed permanent EPOC or persistent enhancement of the catalytic activity [3, 68-70]. Permanent EPOC can be studied or observed from the response of the catalytic rate after current interruption upon application of different anodic potential and polarisation at different time. The magnitude of the permanent EPOC can be quantified by a permanent rate enhancement ratio, $\gamma$, described in equation (8) [3, 68].

$$\gamma = \frac{r_{\text{P-EPOC}}}{r_0} \quad (10)$$

Where $r_{\text{P-EPOC}}$ is the open circuit rate after current interruption and $r_0$ is the open circuit rate before polarisation. The permanent rate enhancement ratio from previous studies on EPOC is summarised in Table 2.2.

The catalytic rate transient response after current interruption was dependent on the (i) total anodic charge where $\gamma$ increases via increase of the applied potential value [3], (ii) duration of polarisation [69, 71] and (iii) $O_2$ pressure [71]. In contrast to the catalytic rate after the current interruption, the steady state electrochemical promoted rate was independent on the duration of prolonged anodic polarisation under a reactive condition [71]. This suggests that the polarisation at a longer time (which causes an increase in the magnitude of the permanent EPOC) influenced a part of the system which was not exposed to the catalytic reaction [70, 71]. Permanent EPOC is therefore explained by the release of hidden or stored oxygen in non-gas exposed places (or in the subsurface region where it was not in contact with the reaction mixture) in the Pt/YSZ and Pt bulk upon anodic polarisation [3]. The application of a similar negative current, for example in a case of an electrophobic behaviour, serves as a fast and efficient way for the decomposition of the oxide species and the concomitant release of the stored charge species [3, 68].

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The mechanism of the permanent EPOC is described as the following. Upon current interruption, the stored O species were migrated or released to the Pt/gas interface from the electrolyte support through tpb keeping the catalytic rate at the promoted state [3,71]. As discussed by Souentie et al. [3], the migration was caused by the O$^{2-}$ electrochemical gradient between the Pt/gas and the Pt/YSZ interface. This subsequent migration of the backspillover species took place until electrochemical potential equilibrium was reached. The catalytic rate which was at the promoted state although under the open circuit condition is explained by the similarity of the role of this species with those induced during the polarisation where the presence of this previously stored (backspillover) species on Pt surface caused an increase in the Pt work function which resulted in the weakening of the Pt–O$_{ads}$ strength and thus caused an increase in the catalytic rate. Besides oxygen storage at the binary interface and Pt bulk, the enhance coverage of the O$^{2-}$ at Pt surface can also be caused by the local enrichment of the O$^{2-}$ content of the YSZ.

The consumption of the hidden oxygen in the case of the C$_2$H$_4$ oxidation probe reaction after the current interruption can be expressed as:

$$6 \text{Pt-O + C}_2\text{H}_4 \rightarrow 2 \text{CO}_2 + 2 \text{H}_2\text{O} + 6 \text{Pt} \quad (11)$$

The main reason for the quasi permanent effect was the large amount of stored oxygen and their slow diffusion towards the Pt/gas interface [68]. For cases where the PtO$_x$ was near its instability area such as under a less oxidising condition, permanent EPOC was not observed. This instability could attribute to the immediate migration of the oxygen species to the Pt/gas interface after the current interruption and thus the permanent EPOC disappears and reversible EPOC was observed [3].

Besides the migration of the stored oxygen species, the irreversible morphology changes such as bubble formation and the role of dopants or additives such as Fe/FeO$_x$ can also cause the permanent EPOC effect [4]. Morphology changes can alter the catalytic properties of the catalyst due to the appearance of atomic steps, differently oriented surfaces or the generation of structural defects. The iron oxide might either influence the microstructure or act as a reservoir for the promoting oxygen species where this oxide
might be more stable in comparison to the quickly consumed spillover oxygen after the current interruption.

2.1.5.3 Permanent Poisoning Effect

Besides the permanent EPOC effect, there are also cases where the catalytic rate remains at a value lower than the initial open circuit rate after the negative current interruption. This effect was defined as a permanent poisoning which is similar to the permanent EPOC effect. This effect is demonstrated in the work of Nakos et al. [5], who studied EPOC for methane oxidation reaction over Rh catalytic films interfaced with YSZ at temperatures from 350 °C to 550 °C in which after negative current interruption the catalytic rate was found to slowly increase but remained lower than the initial value. The rate poisoning index demonstrating this effect is

\[ \beta = (r_0 - r_{\text{poisoning}})/r_0 \]  

(12)

where \( r_{\text{poisoning}} \) is the catalytic rate in the poisoned permanent EPOC steady state after negative current interruption and the values from previous EPOC studies are summarised in Table 2.3. Nakos et al. [5] associated this poisoning effect with the formation of a catalyst surface oxide by the strongly adsorbed species from the gas phase upon the negative polarisation. This effect has been described due to the slower thermal diffusion of \( \text{O}^2^- \) backspillover to the catalyst surface and hence caused a lower \( \text{O}^2^- \) coverage of the catalyst surface as a result to the difference in the chemical potential gradient between the electrolyte support and the catalyst surface in the presence of the surface oxides. A similar positive potential application however can restore the catalytic activity to the initial open circuit condition.

Besides the Rh catalyst, the poisoning of the Pt catalyst by Pt oxides which were formed on the catalyst surface during the sintering step performed in air explained the low reaction rates observed in the work of Poulidi et al. [72]. The catalytic activity however increased after hydrogen reduction at 800 °C which was explained either by the reduction of the oxides formed on the Pt catalyst surface or by the synergistic effect between the Pt and the surface of LSCF perovskite membrane that catalyses the reduction of the
perovskite surface. Reoxidation of either the Pt or the perovskite surface caused the subsequent deactivation.

2.1.6 The Role of Impurities on EPOC

Impurities (either by hindering or promoting properties) may significantly cause the observed rate modification in EPOC, via some interaction with the spillover species [10]. The work of Mutoro et al. [4] demonstrated the significant influence of iron (considered as impurity) on EPOC where the presence of iron on Pt (iron doped covering Pt film) appeared to cause the system to exhibit a permanent EPOC effect in comparison to the iron free covering Pt film [4]. This effect has been discussed in terms of the influence of iron on the catalyst microstructure or the role of iron as an oxygen reservoir.

In the work of Ibrahim et al. [10], however, a clear evidence that impurity (sodium) are necessary for the observation of EPOC in a Pt/YSZ system was not found although the presence of this species was found to significantly affect the Pt catalyst catalytic and electocatalytic properties. The effect of sodium at low coverage became less pronounced at high oxygen partial pressure where no significant rate modification was observed. However, the two promoters (sodium and oxygen) were shown not to completely independent of each other especially at high sodium coverage (where the interaction with oxygen became more significant). This requires a complex model to fully predict and explain the behaviour of such a system.

Impurities may affect a catalytic reaction in a number of ways such as [10]
(i) causing a change in the work function of the catalyst (long range effect) or by
(ii) modifying the activity of catalyst sites in the vicinity of the impurity (sodium) species (short range effect) and
(iii) creating different reaction intermediates and pathways through interactions with the gas phase reactants.
Table 2.2: Summary of Permanent EPOC and Permanent Poisoning from EPOC Studies

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>pC&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;/pO&lt;sub&gt;2&lt;/sub&gt;:</th>
<th>γ</th>
<th>β</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtered Pt, Pt/YSZ, C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt; oxidation</td>
<td>350</td>
<td>0.2/4.5</td>
<td>1.2, 1.3</td>
<td></td>
<td>[3]</td>
</tr>
<tr>
<td>Film thickness: 150 nm, Surface area: 1.25 cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sputtered Pt, Pt/YSZ, C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt; oxidation</td>
<td>375</td>
<td>0.2/8.2</td>
<td>1.7</td>
<td></td>
<td>[68]</td>
</tr>
<tr>
<td>Film thickness: 1 μm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh/YSZ, CH&lt;sub&gt;4&lt;/sub&gt; oxidation</td>
<td>430</td>
<td>pCH&lt;sub&gt;4&lt;/sub&gt;/pO&lt;sub&gt;2&lt;/sub&gt;:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film thickness: 10 μm</td>
<td></td>
<td>(a) 1.8/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b) 1.7/3.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(a) 0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(b) 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sputtered Pd, Pd/YSZ, CH&lt;sub&gt;4&lt;/sub&gt; oxidation</td>
<td>350</td>
<td>pCH&lt;sub&gt;4&lt;/sub&gt;/pO&lt;sub&gt;2&lt;/sub&gt;:</td>
<td></td>
<td></td>
<td>[6]</td>
</tr>
<tr>
<td>Film thickness: 380 nm, Surface area: 2cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td></td>
<td>(a) 2.6/1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b) 1.4/2.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(c) 1.3/4.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(a) 0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(b) 0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(c) 0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/YSZ, Iron doped Pt sample, C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt; oxidation</td>
<td>425</td>
<td>pC&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;/pO&lt;sub&gt;2&lt;/sub&gt;:</td>
<td></td>
<td></td>
<td>[4]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.19/8.2</td>
<td>1.7 to 10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.1.7 Three Phase Boundary (tpb)

Electrochemical reactions in the O<sub>2</sub>(g)/Pt/YSZ system may occur at various interfaces or sites including Pt/YSZ, YSZ/O<sub>2</sub>(g) and Pt/O<sub>2</sub>(g) and the three phase boundary (tpb). As indicated in Figure 2.4, the three phase boundary is the region where all the interfaces met (metal/gas/electrolyte). The site of an electrochemical reaction, however, depends on factors such as the temperature of operation, oxygen partial pressure and applied polarisation, electrode preparation method, electrode type, electrode microstructure, and the choice of electrode material [39]. For a O<sub>2</sub>(g)/Pt/YSZ system where Pt is assumed
impermeable for oxygen, the electrochemical reaction which consists of electron exchange between gaseous $O_2$ and $O^{2-}$ of the solid electrolyte can only take place at the tpb since the reaction involves reactants from the three phases. In the charge transfer reaction, oxygen dissociatively chemisorbed on Pt at the tpb (O(tpb)) and $O^{2-}$ are supplied to or from the solid ion conductor. The number of tpb sites is strongly influenced by the electrode morphology and electrodes with a high number of tpb sites are expected to provide faster sensing responses and better resistance to ageing [73].

![Diagram of Pt/YSZ system]

a: Three phase boundary (tpb)  
b: Binary Interface (Pt/YSZ)  
c: Electrode surface (Pt/O$_2$)  
d: Electrolyte surface (YSZ/O$_2$)

Figure 2.4: Schematic diagram indicating the interfaces in a Pt/YSZ system

### 2.1.7.1 Tpb Length of a Porous Electrode

The length of the three phase boundary (tpb) of a porous electrode which is prepared by using commercially available catalysts can be estimated from the measured $N_o$ value which corresponds to the reduction of oxygen chemisorbed at the tpb. $N_o$ can be determined by integrating the cathodic peak of the cyclic voltammogram of the $O_2(g)$/Pt/YSZ system. In calculating the tpb length, the effect of surface diffusion cannot be neglected and the surface diffusion coefficient of O(a) on Pt(111) and Pt(100) has been expressed by Lewis and Gomer [74] as

$$D_o = \alpha^2 \exp(\Delta S/R) \exp(-E/RT)$$

(13)

where $\alpha$ is the mean diffusion jump length, $v$ is the (effective) attempt frequency, $\Delta S$ is the entropy of activation, $E$ is the activation energy, $R$ is the gas constant and $T$ is the temperature ($\alpha = 3\AA$, $\Delta S = 17$ cal mole$^{-1}$K$^{-1}$, $v = 10^{12}$ s$^{-1}$). For $T = 673$ K, $D_o = 4 \times 10^{-11}$
cm$^2$s$^{-1}$). By using the surface diffusivity value, the thickness, $\delta$, of the spreading zone can be estimated from

$$\delta = (D_0 \tau_o)^{1/2}$$

where $\tau_o$ is the operational or electrochemical attack time constant. By using an average $\tau_o = 3s$, $\delta = 10^3 \AA$. By assuming a 1:1 of O:Pt stoichiometry and by using the atomic radius of Pt ($r_{\text{Pt}} = 1.4 \AA$), the average $N \approx \delta/2r_{\text{Pt}} \approx O(a)$ atoms diffuse and get reduced per tpb electrocatalytic site during the appearance of the cathodic peak could be estimated. The tpb length ($l$), then, could be estimated from

$$l = N_{\text{tpb}} \cdot N_{\text{AV}} \cdot (2r_{\text{Pt}})(2r_{\text{Pt}}/\delta)$$ \hspace{1cm} (14)

where $N_{\text{AV}}$ is Avogadro’s number. The calculated tpb length, $l$, by using the above formula could be compared with the length calculated based on the information extracted from SEM images. From SEM images, the average diameter of Pt crystallites constituting the Pt catalyst films could be estimated. By assuming that the Pt film consists of Pt crystallites of uniform diameter $d$ which were packed in a tetragonal arrangement and that those crystallites in contact with the flat YSZ electrolyte were half-spheres, each with a circular $\pi d$ tpb contact with the electrolyte, tpb length, $l$, then can be estimated as [32]

$$l = \pi A/d$$ \hspace{1cm} (15)

where $A$ and $d$ are the geometrical area of the Pt film and diameter of Pt crystallites, respectively. Besides the cyclic voltammogram and the SEM images, the number of tpb sites can also be quantified by using the impedance spectrum of the porous electrodes [73].

2.1.7.2 Tpb Length of a Patterned or Dense Electrode

In contrast to the porous electrodes prepared by using the commercial catalysts, the cathodic peaks in the cyclic voltammograms of dense electrodes may correspond to the charge transfer reactions at the binary interface and not at the tpb and therefore the
(v) the electrode design and the coverage of oxygen ionic species at the tpb and on the Pt surface control the backspillover processes.

(vi) Pt/YSZ system using the patterned electrodes exhibited permanent EPOC and permanent poisoning EPOC effect.

(vii) there is a similarity in the role of the stored oxygen at the binary Pt/YSZ interface and Pt bulk with the electrochemical backspillover species in controlling the surface oxygen activity, stabilising the effective double layer and enhancing the catalytic rate.

(viii) the patterned electrodes are durable and can be applied in the field where the possible applications are in (i) sensor technology (CO oxidation catalytic rate sensor) and in (ii) EPOC.

7.2 **Recommendations**

Due to the limitations described in Chapter 1, the findings of the current work can be further explained by carrying out

a. EPOC experiments by using the commercial catalysts under similar experimental conditions of the EPOC experiments carried out on the patterned electrodes. This is to further verify the influence of impurities on EPOC.

b. EPOC experiments at a higher anodic potential (for the case of the patterned electrodes).

c. kinetic study under open circuit conditions. This is to further verify the applications of the patterned electrodes in sensor technology.

d. in situ analyses or measurement for better description or verifications of the mechanisms of the charge transfer and EPOC.

e. sample pretreatment (in order to obtain approximately similar electrode morphology or microstructure) prior to the catalytic and electrochemical experiments.

f. data analyses through the application of software such as those used in demonstrating the data obtained from EIS.
References


