

Electrochemical Promotion of Catalyst Surfaces Deposited on Ionic and Mixed Conductors

A.C. Kaloyannis, C.A. Pliangos, D.T. Tsiplakides, I.V. Yentekakis,
S.G. Neophytides, S. Bebelis and C.G. Vayenas
Department of Chemical Engineering, University of Patras
GR-26500 Patras, Greece

Abstract. The effect of non-Faradaic electrochemical modification of catalytic activity (NEMCA) or electrochemical promotion (EP) was investigated on Pt films deposited on Y₂O₃-stabilized-ZrO₂ (YSZ), an O²⁻ conductor, TiO₂, a mixed conductor, and Nafion 117 solid polymer electrolyte (SPE), a H⁺ conductor and also on Pd films deposited on YSZ and β"-Al₂O₃ a Na⁺ conductor. Four catalytic systems were investigated, i.e. C₂H₆ oxidation on Pt/YSZ, C₂H₄ oxidation on Pd/YSZ and Pd/β"-Al₂O₃, C₂H₄ oxidation on Pt/TiO₂ and H₂ oxidation on Pt/Nafion 117 in contact with 0.1 M aqueous KOH solution.

In all cases pronounced and reversible non-Faradaic electrochemical modification of catalytic rates was observed with catalytic rate enhancement up to 2000% and Faradaic efficiency values up to 5000.

All reactions investigated exhibit a pronounced electrophobic behaviour which is due to the weakening of chemisorptive oxygen bond at high catalyst potentials. Ethane oxidation, however, also exhibits electrophilic behaviour at low potentials due to weakened binding of carbonaceous species on the surface.

The general features of the phenomenon are similar for all four cases presented here showing that the NEMCA effect is a general, electrochemically induced, promoting catalytic phenomenon not depending on the reaction and the type of supporting electrolyte.

1. Introduction

The effect of non-Faradaic electrochemical modification of catalytic activity (NEMCA) [1-18] or electrochemical promotion in catalysis [19, 20] has been described for over twenty-five catalytic reactions on Pt, Pd, Rh, Ag and Ni surfaces using different ion conducting solid electrolytes, such as yttria-stabilized zirconia (YSZ) an O²⁻-conductor [1-9, 14-18], β"-Al₂O₃ a Na⁺-conductor [10,20], CsHSO₄ a H⁺-conductor [21] and CaF₂ a F⁻-conductor [22], as the active catalyst support. Work prior to 1992 has been reviewed [2]. Very recently the effect has been demonstrated in aqueous electrochemistry [23].

One of the important parameters in order to describe the phenomenon is the enhancement factor or Faradaic efficiency, Λ , which is defined by:

$$\Lambda = \Delta r / (I/2F) \quad (1)$$

where Δr is the induced change in catalytic rate expressed in mol of atomic oxygen, I is the applied current, and F is Faraday's constant. A reaction exhibits the NEMCA effect when $|\Lambda| > 1$. When $\Lambda > 1$ the reaction is termed electrophobic, while when $\Lambda < -1$ the reaction is termed electrophilic.

It has been shown both experimentally [1,11] and theoretically [2,5,6,13] that there exists an one-to-one relationship between the change in catalyst potential V_{WR} , with respect to a reference electrode, and the change of the work function of the catalyst surface $e\Phi$:

$$\Delta(e\Phi) = e\Delta V_{WR} \quad (2)$$

As originally proposed [1,2,4] this work function change results from an electrochemically controlled backspillover of ions from (or to) the solid electrolyte to (or from) the

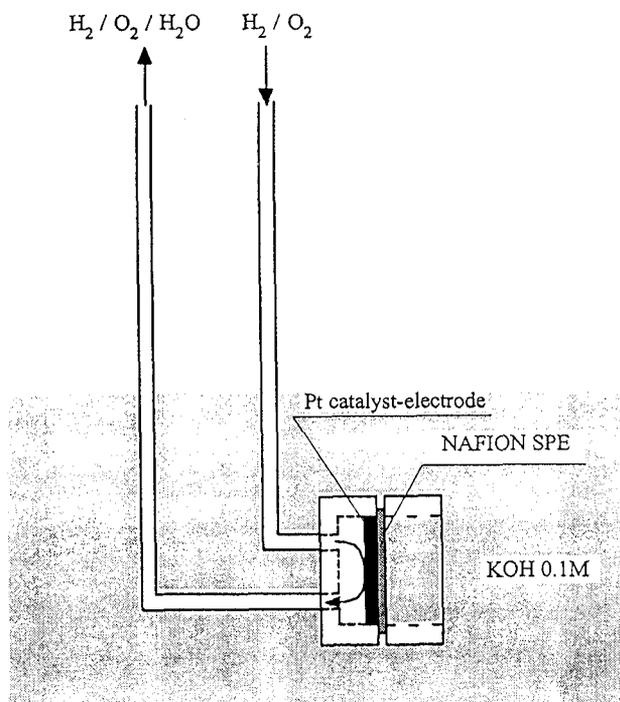


Fig. 1. Catalyst holder assembly for the study of H_2 oxidation on Pt/Nafion 117.

catalyst surface. These backspillover ions, together with their compensating charge in the metal, spread over the catalyst surface, act as promoters and establish an effective electrochemical double layer on the catalyst surface. They thus alter the catalyst surface work function $e\Phi$ and its chemisorptive and catalytic properties. Recent in situ XPS investigation of Ag [24,25] and Pt [26] catalyst films interfaced with YSZ and cyclic voltammetry studies on Pt [27] have confirmed that this is indeed the case when the solid electrolyte is YSZ.

One common conclusion, emerging from all previous studies [1-18], is that over wide ranges of catalyst surface work function $e\Phi$, catalytic rates depend exponentially on $e\Phi$ according to

$$\ln(r/r_0) = \alpha(e\Phi - e\Phi^*)/k_b T \quad (3)$$

where r_0 is the open-circuit catalytic rate and α and $e\Phi^*$ are reaction- and catalyst-specific constants. The value of α is in most cases between -1 and 1 and, depending on its sign, catalytic reactions are termed electrophobic ($\alpha > 0$) or electrophilic ($\alpha < 0$).

In this work we present results of the NEMCA behaviour of C_2H_6 oxidation on Pt/YSZ, C_2H_4 oxidation on Pd/YSZ and Pd/ β'' - Al_2O_3 , C_2H_4 oxidation on Pt/ TiO_2 and H_2 oxidation on Pt/Nafion 117. All these reactions

are found to exhibit a pronounced NEMCA effect with the same general features.

2. Experimental

The NEMCA studies during C_2H_6 oxidation on Pt/YSZ, C_2H_4 oxidation on Pd/YSZ and C_2H_4 oxidation on Pt/ TiO_2 were carried out in a continuous flow CSTR single pellet reactor [2,16]. The solid electrolyte element was an YSZ disk (3/4" O.D., 2 mm thickness) or a TiO_2 pellet (1/2" O.D., 3.5 mm thickness). The Pt or Pd catalyst-working electrode was deposited on the one side of the disk (pellet) and the Au auxiliary electrodes on the opposite side. All electrodes are thus exposed to the reacting gas mixture.

In the case of C_2H_4 oxidation on Pd/ β'' - Al_2O_3 a continuous flow CSTR type reactor was used and the β'' - Al_2O_3 pellet (17 mm O.D., 4 mm thickness) was attached, via a ceramic adhesive, on one side of an open ended α -alumina tube (3/4" O.D.). The Pd catalyst-working electrode was deposited on the one side of the β'' - Al_2O_3 pellet and the Au counter and reference electrodes were deposited on the other side which was exposed to ambient air.

In the case of H_2 oxidation on Pt/Nafion 117 the apparatus shown in Fig. 1 was used. According to the Takenaka-Torikai design [28] the Nafion film was sandwiched between two appropriately carved plexiglass blocks. Two compartments are created which are separated by the Nafion solid polymer electrolyte (SPE). In order to deposit the Pt film one face of the SPE membrane is exposed to 0.01M H_2PtCl_6 and the other side to 0.1 M sodium borohydride alkaline aqueous solution. The Pt film is deposited on one side of the membrane via reduction of H_2PtCl_6 by sodium borohydride which diffuses through the SPE membrane [28]. The deposition was carried out at room temperature. The Pt plating area was circular with 2 cm diameter. Two glass tubes mounted on the electrode compartment serve as the inlet and outlet of the H_2/O_2 reaction mixture which is in direct contact with the Pt catalyst electrode. After Pt deposition, the whole Pt/SPE assembly is immersed in a 0.1 M KOH aqueous solution which is in direct contact with the Pt free side of the membrane as shown in Fig. 1. Electric contact of the Pt electrode with a lead Pt wire was established using a ring of an ultrathin gold gauze inserted between the membrane and the plexiglass block. The Pt counter electrode was immersed in the KOH solution. The Pt electrode potential was measured with

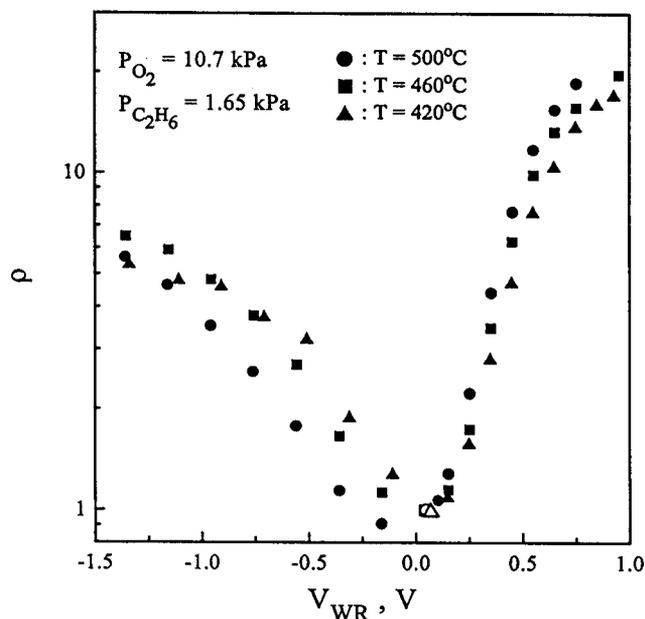


Fig. 2. Effect of catalyst potential on the rate enhancement ratio ρ ($=r/r_o$) of C_2H_6 oxidation on Pt/YSZ; $P_{O_2}=10.7$ kPa, $P_{C_2H_6}=1.65$ kPa; $r_o=6.8\cdot 10^{-9}$, $1.27\cdot 10^{-8}$ and $2.04\cdot 10^{-8}$ mol O/s at 420°, 460° and 500°C, respectively.

respect to a reference H_2 electrode (r.h.e.) via a Luggin capillary.

In all systems investigated the electrodes are connected with a galvanostat/potentiostat which is used to apply constant currents between the catalyst and the counter electrode or constant potentials between the catalyst and reference electrode.

3. Results and Discussion

3.1. NEMCA Studies of C_2H_6 Oxidation on Pt/YSZ.

Figure 2 shows the effect of catalyst potential, with respect to the gold reference electrode, V_{WR} , on the rate enhancement ratio, ρ , defined [1,2] from:

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

where r_o is the open-circuit catalytic rate.

The catalytic rate, expressed in terms of atomic oxygen consumption, increases both with positive and negative potentials, i.e., the reaction exhibits both electrophobic and electrophilic behaviour [2]. It is worth noting the exponential dependence of r on catalyst potential both for positive and negative potential values.

Figures 3 and 4 show the effect of catalyst potential on the reaction kinetics with respect to oxygen (Fig. 3) and to ethane (Fig. 4). As shown again in these Figures

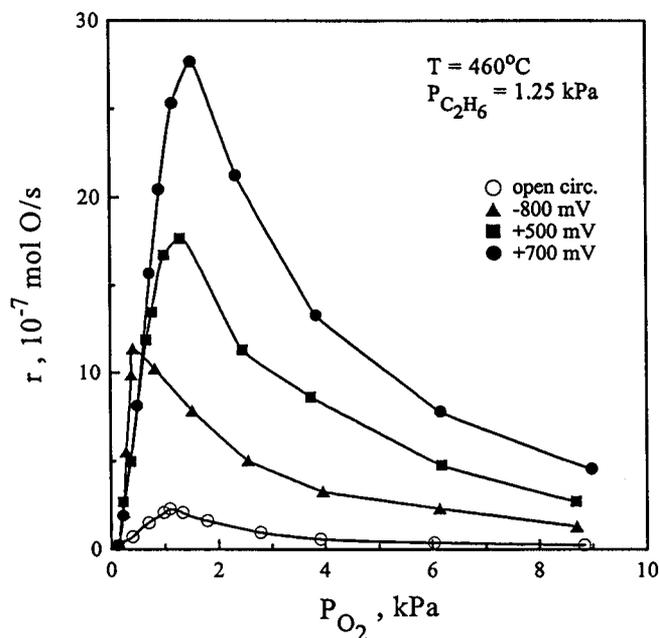


Fig. 3. Effect of P_{O_2} and catalyst potential on the rate of C_2H_6 oxidation on Pt/YSZ.

the reaction exhibits both electrophobic and electrophilic behaviour.

As shown in Fig. 3 increasing catalyst potential increases the P_{O_2} value corresponding to maximum rate, indicating a weakening of the Pt=O bond. This is expected, since oxygen is an electron acceptor [2].

Conversely, as shown in Fig. 4, increasing catalyst potential causes significant deviations from linearity in

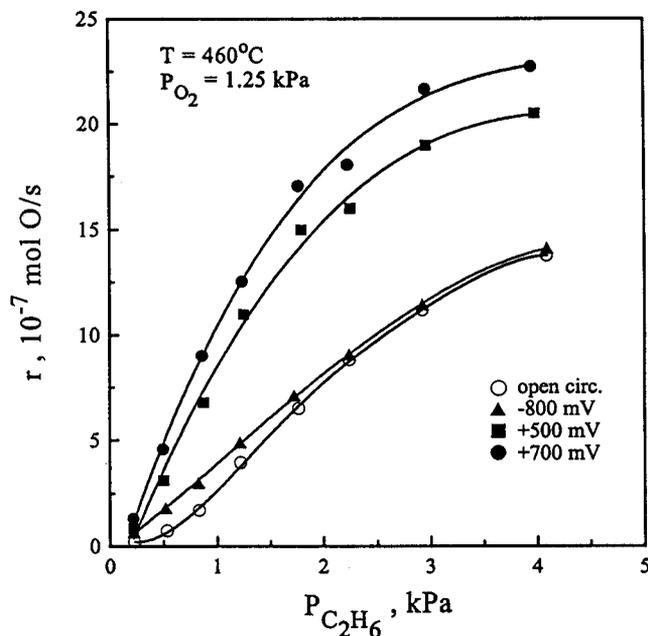


Fig. 4. Effect of $P_{C_2H_6}$ and catalyst potential on the rate of C_2H_6 oxidation on Pt/YSZ.

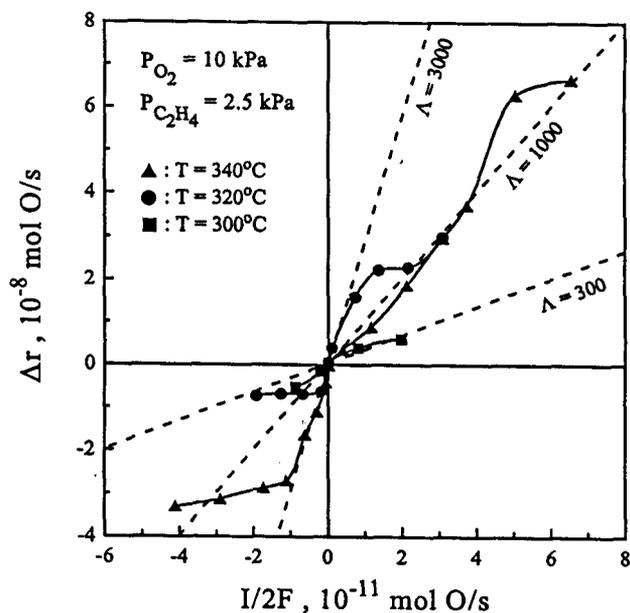


Fig. 5. Effect of applied current on the change in the rate of C₂H₄ oxidation on Pd/YSZ; Dashed lines are constant enhancement factor (Faradaic efficiency) lines.

the r vs $P_{C_2H_6}$ plots, indicating a pronounced strengthening in the chemisorptive bond of C₂H₆. This is again expected, since C₂H₆ is an electron donor [2].

From the two Figs 3 and 4 it is evident that adsorption of oxygen on the platinum surface is stronger than adsorption of ethane and this is the reason for the more pronounced electrophobic behaviour of this reaction (Fig. 2).

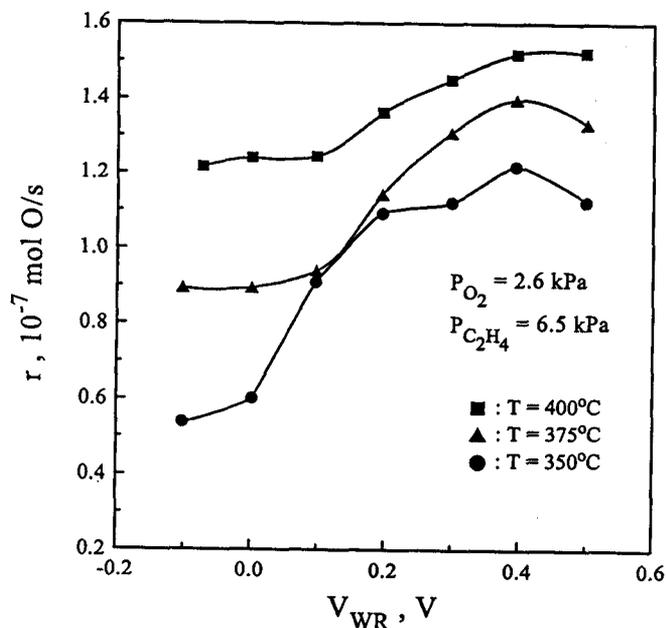


Fig. 6. Effect of catalyst potential on the rate of C₂H₄ oxidation on Pd/β''-Al₂O₃.

2. NEMCA Studies of C₂H₄ Oxidation on Pd/YSZ or Pd/β''-Al₂O₃. Figure 5 shows the steady state effect of current on the change in the rate of ethylene oxidation on Pd/YSZ, expressed in mol O/s. Dashed lines are constant enhancement factor Λ lines. Enhancement factor, or Faradaic efficiency, Λ values up to 3000 were measured, i.e., each O²⁻ supplied to the catalyst can cause on the average up to 3000 chemisorbed oxygen atoms to react with ethylene. As shown in this Figure, ethylene oxidation on Pd/YSZ is an electrophobic reaction, i.e. the catalytic rate decreases with negative current application and increases with positive current application (O²⁻ supply to the catalyst).

Figure 6 depicts the effect of varying catalyst potential or equivalently [1,2,11] catalyst work function on the CO₂ production rate at three different temperatures for the case of ethylene oxidation on Pd/β''-Al₂O₃. The catalytic rate decreases with decreasing catalyst potential, i.e., by supplying sodium ions to the catalyst surface. Thus similarly to the case of C₂H₄ oxidation on Pd/YSZ, the reaction exhibits electrophobic behaviour.

3.3. NEMCA Studies of C₂H₄ Oxidation on Pt/TiO₂.

Figure 7 shows a typical galvanostatic rate transient, i.e., it depicts the effect of constant applied current between the Pt catalyst and the Au counter electrode on the rate of C₂H₄ oxidation on a Pt catalyst film deposited on TiO₂ [35]. The steady-state open-circuit ($I=0$) catalytic rate is $2.4 \cdot 10^{-8}$ mol O/s. Application of a positive current $I=50$

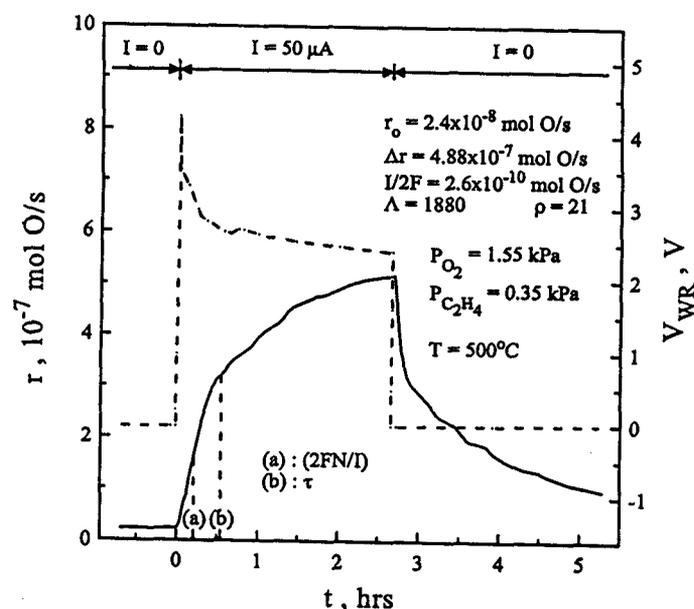


Fig. 7. Transient effect of applied positive current on the rate of C₂H₄ oxidation on Pt/TiO₂ (solid curve) and on catalyst potential (dashed curve).

μA causes a reversible 2000% increase in the catalytic rate over a period of approximately 3h, i.e., the reaction exhibits electrophobic behaviour as in previous studies of C_2H_4 oxidation on Pt deposited on YSZ [2,5] or $\beta''\text{-Al}_2\text{O}_3$ [5,10]. Upon current interruption the catalytic rate returns to its initial value over a period of 3-4 h. The rate increase $\Delta r = 4.88 \cdot 10^{-7}$ mol O/s is 20 times larger than the open-circuit (unpromoted) rate and 1880 times larger than $I/2F$, which expresses the rate of O^{2-} transport to the Pt catalyst from the TiO_2 support, if all the current were ionic. Consequently the rate enhancement ratio ρ and the enhancement factor Λ are 21 and 1880 respectively. Because TiO_2 is a mixed conductor only a small fraction f of the applied current is ionic and the remaining fraction $(1-f)$ is electronic. This means that the rate of O^{2-} supply to the catalyst is only $f(I/2F)$ and thus the promoting action of the oxide ions is even more pronounced than the measured Λ value implies. Also the catalytic rate relaxation time constant τ (defined as the time required for the rate increase to reach 63% of its steady-state value) is a factor of 3 larger than $2FN/I$ (N is the Pt catalyst surface area in mol O) which expresses the time required to form a monolayer of backspillover oxidic oxygen on the Pt surface if all the current were ionic. Previous NEMCA studies with YSZ have shown that τ is of the same order of magnitude but typically a factor of 2 shorter than $2FN/I$. The observation that the opposite trend is observed here, is consistent with the fact that

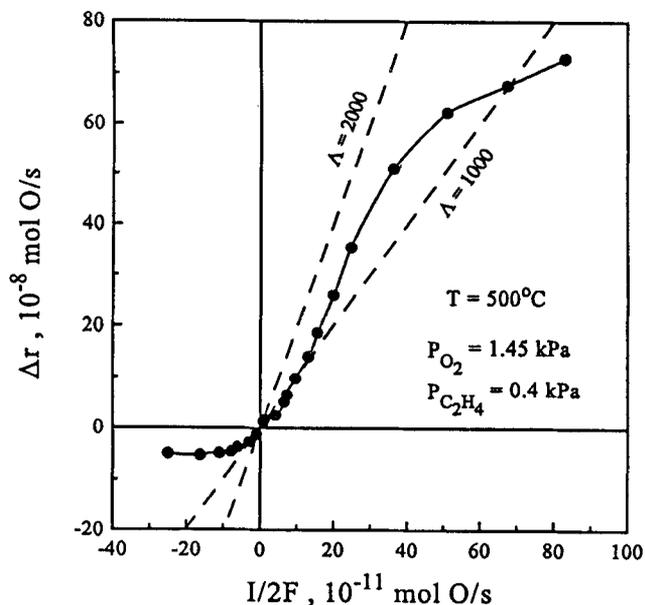


Fig. 8. Effect of applied current on the change in the rate of C_2H_4 oxidation on Pt/ TiO_2 .

only a fraction of the current is ionic.

Figure 8 shows the steady-state effect of current on the rate of ethylene oxidation. It can be seen that the rate increases monotonically with current ($\Lambda > 0$, electrophobic behaviour). Measured Λ values are between 1000 and 2000.

3.4. NEMCA Studies of H_2 Oxidation on Pt/Nafion 117.

Figure 9 depicts the effect of current on the rate of H_2 and O_2 consumption in terms of atomic oxygen consumption, r_o . For low current densities the Faradaic efficiency takes values up to 40 which is in good agreement with the value of 67 predicted from the approximate equation [2,5]:

$$\Lambda \approx \frac{2Fr_o}{I_0} \quad (5)$$

where r_o is the open-circuit catalytic rate and I_0 is the exchange current of electrode-electrolyte interface [2,30]. It should be noted that the difference of the two steady-state rates, i.e., the rate of atomic oxygen and molecular hydrogen consumption, r_{O} and r_{H_2} respectively, is equal to $I/2F$ as shown previously [23].

Figure 10 depicts the effect of catalyst potential on the rate enhancement ratios of hydrogen (ρ_{H_2}) and oxygen (ρ_{O}). As shown in the Fig. H_2 oxidation on Pt/Nafion exhibits predominantly electrophobic NEMCA behaviour ($\partial r/\partial V_{\text{WR}} > 0$) with ρ values up to five, as in the case of H_2 oxidation on Pt electrodes immersed in alkaline solu-

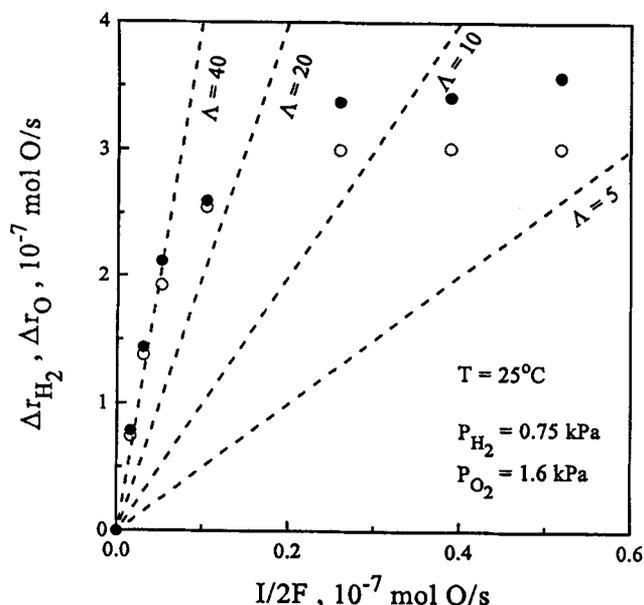


Fig. 9. Effect of applied current on the change in the rate of hydrogen (closed symbols) and oxygen (open symbols) consumption during H_2 oxidation on Pt/Nafion 117.

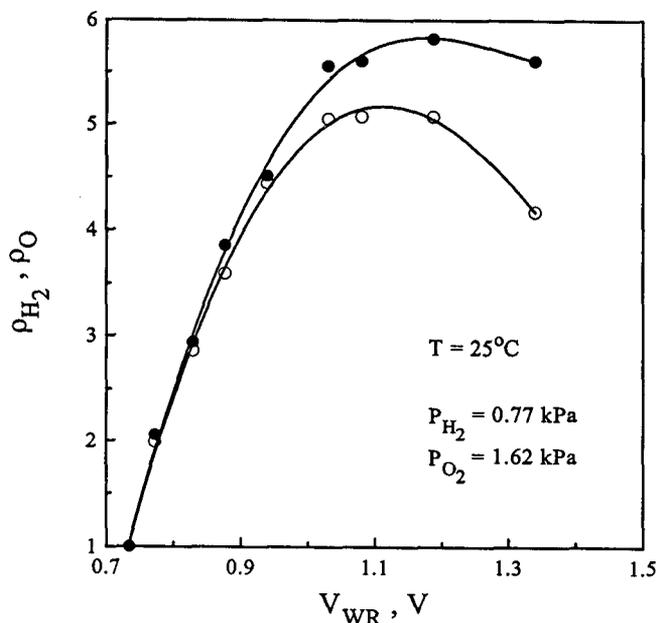


Fig. 10. Effect of catalyst potential on the rate enhancement ratios of hydrogen, ρ_{H_2} (closed symbols), and oxygen, ρ_{O_2} (open symbols), during H_2 oxidation on Pt/Nafion 117; $P_{H_2} = 0.77$ kPa, $P_{O_2} = 1.62$ kPa; $r_{H_2,o} = r_{O_2,o} = 1.4 \cdot 10^{-7}$ mol O/s at 25°C .

tions [23].

4. Conclusions

The present results show that the effect of Electrochemical Promotion (EP) or Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA) is a general catalytic effect, not restricted to any particular type of metal, solid electrolyte or catalytic reaction.

With the exception of ethane oxidation on Pt/YSZ at negative potentials, and ethylene oxidation on Pt/TiO₂ under reducing conditions [35], all the other catalytic oxidation systems of the present work show a pronounced electrophobic NEMCA behaviour, i.e. the catalytic rate increases substantially with increasing catalyst potential and work function [1,2]. This is due to the weakening of the metal-oxygen chemisorptive bond with increasing catalyst work function, since oxygen is an electron acceptor [2]. Electrophilic behaviour, i.e. increasing catalytic rate with decreasing catalyst potential and work function, is obtained only under conditions where the rate is accelerated by a weakening in the metal-hydrocarbon chemisorptive bond. Electrochemical promotion of catalyst surfaces is a new emerging application of solid electrolytes and, as the present results with TiO₂ show, mixed conductors. Aside from potential practical applications, the new effect allows for a systematic study of the role of promoters in

heterogeneous catalysis.

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