

# Electrochemically Promoted Catalysis: The Case of Ethanol Oxidation over Pt

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Ethanol oxidation was investigated over polycrystalline Pt films deposited on 8 mol% Y<sub>2</sub>O<sub>3</sub>-stabilized-ZrO<sub>2</sub> (YSZ) in the temperature range of 300–350°C. It was found that electrochemical supply of oxygen anions (O<sup>2-</sup>) to the Pt catalyst results in significant changes both in the rate of ethanol consumption and in the yield of acetaldehyde. Electrochemical supply of O<sup>2-</sup> anions induces an enhancement of the reaction rate that was found typically 10<sup>3</sup>–10<sup>4</sup> times larger than the Faradaic rate of O<sup>2-</sup> supply and an almost seven-fold increase in the reaction yield to acetaldehyde. In the range of the applied currents, it was found that the catalytic activation energies of ethanol consumption and acetaldehyde formation can be lowered by 70 and 80%, respectively, with respect to the regular (open-circuit) values. The observed behavior is discussed and explained on the basis of the theory of NEMCA. © 2002 Elsevier Science (USA)

**Key Words:** electrochemical promotion; NEMCA; ethanol oxidation; acetaldehyde production; platinum catalyst.

## 1. INTRODUCTION

During the past decades, the terms “electrochemical promotion” and “non-Faradaic electrochemical modification of catalytic activity (NEMCA)” have been considered the most appropriate to describe those cases in which electrochemistry serves as an activator of catalysis. More specifically, it was observed that the catalytic behavior of metals interfaced with solid electrolytes can be altered dramatically and reversibly upon polarizing the metal/solid electrolyte interface. This effect was successfully explained theoretically in terms of modifications induced in the work function of metal catalysts due to changes on the catalyst (electrode) overpotential. Results of numerous studies for various heterogeneous reactions are summarized in recent reviews or as chapters in books of solid-state electrochemistry (1–5).

It has been shown that electrochemical supply or removal of oxygen anions (O<sup>2-</sup>) to or from the catalyst through the solid electrolyte can dramatically enhance the rate of catalytic reactions and tune their selectivity on useful chemicals.

The main features that were found common in all NEMCA studies can be summarized as follows.

1. Over a wide range of experimental conditions catalytic rates of heterogeneous reactions depend exponentially on the Ohmic-drop free catalyst potential,  $V_{WR}$ , with respect to the reference electrode, according to the expression

$$\ln(r/r_o) = \alpha F(V_{WR} - V_{WR}^*)/RT, \quad [1]$$

where  $r_o$  is the regular (i.e., open-circuit) catalytic rate and  $\alpha$  and  $V_{WR}^*$  are catalyst and reaction-specific constants. The parameter  $\alpha$  typically takes values between  $-1$  and  $1$ . Depending on the sign of this parameter, catalytic reactions can be classified as electrophobic ( $\alpha > 0$ ) or electrophilic ( $\alpha < 0$ ).

Moreover, it was shown that the electromotive force (emf) of the solid electrolyte cells with metal electrodes provides a direct measure of the difference in work function of the catalyst and reference-electrode gas-exposed surfaces. Thus, when the catalyst potential is changed by  $\Delta V_{WR}$ , either by changing the composition of the gas in contact with the catalyst or by polarizing the catalyst/solid electrolyte interface, the average catalyst surface work function  $e\Phi$  changes by

$$\Delta e\Phi = e\Delta V_{WR}. \quad [2]$$

Important information about both the thermodynamic considerations leading to this conclusion and the exploitation of Eq. [2] for the prediction of the extent of the modification of the rate of a heterogeneous reaction can be found *inter alia* in recent literature (5–7).

2. The order of magnitude (typically between 1 and 10<sup>5</sup>) of the absolute value  $|\Lambda|$  of the enhancement factor  $\Lambda$ , defined as

$$\Lambda = \frac{\Delta r}{I/2F}, \quad [3]$$

where  $\Delta r$  is the change in catalytic reaction rate and  $I/2F$  is the rate of supply ( $I > 0$ ) or removal ( $I < 0$ ) of O<sup>2-</sup> to or from the catalyst, can be estimated from the following expression:

$$|\Lambda| = \frac{2Fr_o}{I_o}, \quad [4]$$

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where  $I_0$  is the exchange current of the catalyst/solid electrolyte interface. Therefore, to observe a strong non-Faradaic enhancement (i.e.,  $|\Delta| \gg 1$ ), highly polarizable (i.e., low  $I_0$ ) catalyst/solid electrolyte interfaces are required.

3. During galvanostatic transients, the relaxation time constant,  $\tau$ , defined as the time required for the rate change to reach 63% of its steady-state value, are typically of the order

$$\tau = \frac{2FN}{I}, \quad [5]$$

where  $N$ , expressed in g-atom, is the total gas-exposed catalyst film surface area. This shows that electrochemical promotion changes the catalytic properties of the entire catalyst surface and is not restricted to the vicinity of the three-phase boundaries (tpb) gas/catalyst/solid electrolyte. The preceding observations were interpreted semiquantitatively on the basis of the changes induced in the strength of chemisorptive bonds of reactants and intermediates due to an electrochemically induced and controlled ion spillover with consequent change in catalyst work function.

The results presented in this work are concerned with the electrochemical promotion of a Pt catalyst during the reaction of ethanol oxidation using 8 mol%  $Y_2O_3$ -stabilized- $ZrO_2$  (YSZ), an  $O^{2-}$  conductor, as solid electrolyte. Because of the high cost of noble Pt catalysts, the optimization of the design and the amount of Pt used in practice via appropriate promotion is of significant interest. The unexamined case of the reaction of ethanol oxidation was selected because of the possible utilization of ethanol for generation of electricity in fuel cells in addition to the feasibility of generation of useful chemicals of increased value such as acetaldehyde. Acetaldehyde is a highly reactive compound and widely used as an intermediate in industrial organic synthesis. It can be produced by hydration of acetylene, vapor-phase oxidation of butane, and oxidation or dehydrogenation of ethanol (8, 9). Based on these interests, the current study focuses on the existence, the extent, and the results of the *in situ* electrochemical promotion of Pt-catalyzed ethanol oxidation.

## 2. EXPERIMENTAL

The apparatus used in the course of this study was described in detail in previous works (10). It consisted of the feeding unit, the oven/YSZ reactor system and the system of analysis. The mixture of the reactants was formed by feeding streams of 5.5 (or 21) vol%  $O_2$  diluted in  $N_2$  and pure  $N_2$  (99.999 vol%) in a saturator containing pure ethanol at 25°C and 1 bar. Gas-flow rates before the saturator were continuously monitored by digital mass flow controllers (Brooks series 5800).

The YSZ (8 mol%  $Y_2O_3$  in  $ZrO_2$ ) atmospheric pressure, continuous-flow stirred-tank reactor was a cylindrical tube

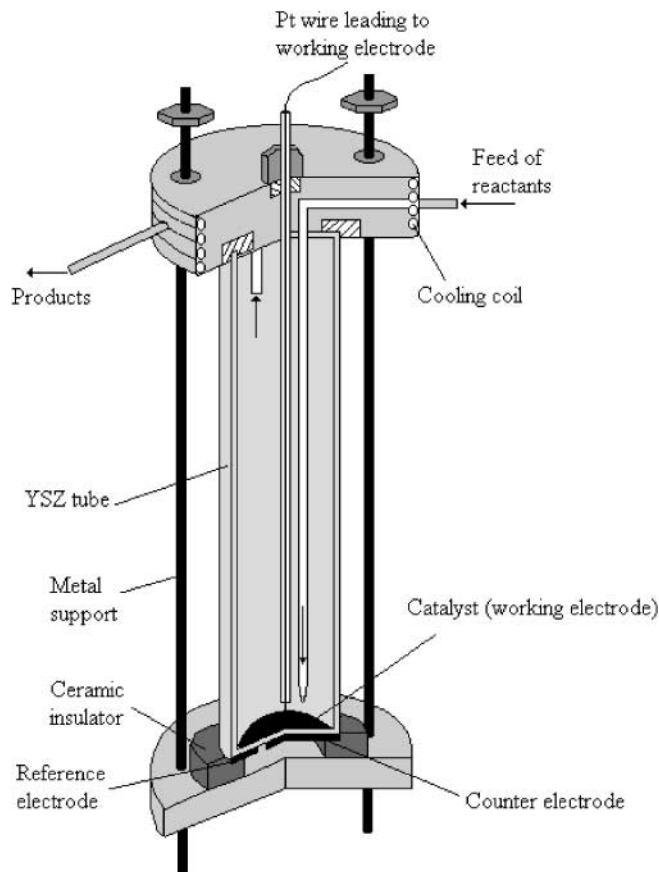


FIG. 1. Schematic illustration of the YSZ reactor.

closed flat at the bottom end with a total volume of 30 cm<sup>3</sup> (Fig. 1). On the inside bottom wall of the tube, the porous Pt-catalyst film was deposited by applying a thin coating of Engelhard A1121 Pt paste. Two similar Pt films were deposited on the outside bottom wall of the YSZ tube which was exposed to ambient air and served as counter- and reference electrodes, respectively. Previously, to remove possible impurities of the YSZ tube, it was slowly heated to 900°C and then cooled, also slowly, to 25°C and bathed in acetone. After the application of the Pt paste, the ceramic reactor was dried at 120°C for 30 min and then heated up to 500°C in a furnace with slow air feeding. The reactor remained at this temperature for 2 h for both the evaporation of the paste solvent and the adhesion of Pt crystallites at the YSZ surface to take place. Then, the temperature was increased at 850°C causing partial sintering of the Pt and formation of coarse Pt crystallites. Coarse Pt structure was desired for the reduction of the extension of the tpb (Pt/YSZ/gas) and therefore for the reduction of the magnitude of the exchange current,  $I_0$ . The reactor remained at 850°C for 30 min. Through all these stages, increase of temperature was done at slow rates of about 200°C/h to avoid both fracture of YSZ and blistering of electrodes. The thickness of the Pt-catalyst film was of the order of

5–10  $\mu\text{m}$ . The superficial area was 2  $\text{cm}^2$  and the true surface area was about 50  $\text{cm}^2$  as measured by a surface titration technique utilizing  $\text{O}_2$  and  $\text{C}_2\text{H}_4$  described previously (11). In this way, the total exposed catalyst-film surface area was estimated at about  $N = 4 \times 10^{-8}$  g-atom of Pt.

In the course of the experiments, a potentiostat/galvanostat (AMEL system 5000) was used to apply currents between the catalyst and the counterelectrode while monitoring the Ohmic-drop free potential,  $V_{\text{WR}}$ , between the catalyst and the reference electrode. The analysis of reactants and products was carried out by utilizing a mass spectrometer (Balzers Omnistar), an FID gas chromatograph (Shimadzu GC 14B), and a series of online gas analyzers (Hartmann & Braun Advance Optima). By making a set of preliminary measurements at different flow rates in the range of 20–160 ml/min STP and using the same reactants composition the apparent reaction rate was found constant, which demonstrates the absence of external mass transfer phenomena. Further, internal diffusion of gaseous reactants in the porous catalyst was considered negligible due to the small thickness of the Pt film.

### 3. RESULTS AND DISCUSSION

#### 3.1. The Electrocatalytic Activity of the Three-Phase Boundary (tpb)

It is well known (2–5) that the estimation of the magnitude of the purely electrochemically promoted catalytic modifications (resulting from the application of current or potential) requires the estimation of the electrocatalytic activity of the tpb formed by the interfaces of the catalyst crystallites, the solid electrolyte, and the gas phase. This magnitude mainly refers to the intensity of the electrocatalytic actions taking place on the tpb that cause transfer of electrical charge. A measure of the electrocatalytic activity of the tpb is the value of the exchange current,  $I_o$ , or the exchange current density  $i_o$ :

$$i_o = \frac{I_o}{A}, \quad [6]$$

where  $A$  represents the superficial catalyst surface area (in  $\text{cm}^2$ ). The calculation of  $I_o$  is accomplished according to the low field approximation of the Butler–Volmer equation, which can be written as

$$I = I_o \left[ \exp\left(\frac{\alpha_a F \eta_{\text{act},j}}{RT}\right) - \exp\left(\frac{\alpha_c F \eta_{\text{act},j}}{RT}\right) \right]. \quad [7]$$

This equation allows for the calculation of the exchange current density,  $I_o$ , and the charge transfer coefficients  $\alpha_a$  and  $\alpha_c$ .

Figure 2 illustrates the effect of the overpotential,  $\eta$ , on the logarithm of the current,  $I$ , for both positive and negative currents under constant gas composition ( $P_{\text{ethanol}} =$

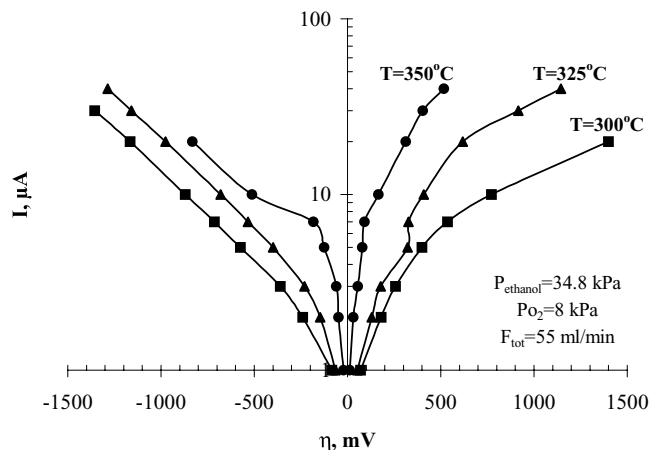


FIG. 2. Effect of overpotential,  $\eta$ , on the current  $I$  (Tafel plots) ( $V_{\text{WR}}^o \approx -440$  mV).

34.8 kPa,  $P_{\text{O}_2} = 8$  kPa at the reactor outlet) at various temperatures. The overpotential,  $\eta$ , is defined as

$$\eta = V_{\text{WR}} - IR - V_{\text{WR}}^o \quad [8]$$

where  $V_{\text{WR}}^o$  is the catalyst potential  $V_{\text{WR}}$  during open-circuit conditions ( $I = 0$ ). Due to the low operating temperatures of 300–350°C, relatively high values of Ohmic-drop  $IR$  were expected. The standard current interruption technique (12) was followed to quantify this parasitic effect and  $IR$ -drop values were measured to be typically about 20–40% of the corresponding overpotential values. The charge-transfer coefficients,  $\alpha_a$  and  $\alpha_c$ , were calculated from the slopes of the linear parts (Tafel region) of the curves of Fig. 2 that correspond to low overpotential values, and are given in Table 1. As shown, both anodic and cathodic transfer coefficients are similar, indicating the same dominant electrocatalytic reactions during both modes of operation. Moreover, Table 1 also presents the values of the anodic and cathodic exchange currents calculated by extrapolating the linear (Tafel) regions of the curves of Fig. 2 at  $\eta = 0$ . In this case it is shown that the Pt/YSZ interface can be considered highly polarizable because it is characterized by very low values of  $I_o$  (about 1–10  $\mu\text{A}$ ).

Figure 3 illustrates the dependence of the exchange current on temperature. The apparent activation energy

TABLE 1

Exchange Currents and Charge-Transfer Coefficients during Anodic ( $I > 0$ ) and Cathodic ( $I < 0$ ) Operation

Temperature ( $^{\circ}\text{C}$ )	$I_{o,\text{anodic}}$ ( $\mu\text{A}$ )	$I_{o,\text{cathodic}}$ ( $\mu\text{A}$ )	$\alpha_{\text{anodic}}$	$\alpha_{\text{cathodic}}$
300	2.5	1	0.1	0.12
325	7	1.7	0.11	0.13
350	12	3	0.14	0.16

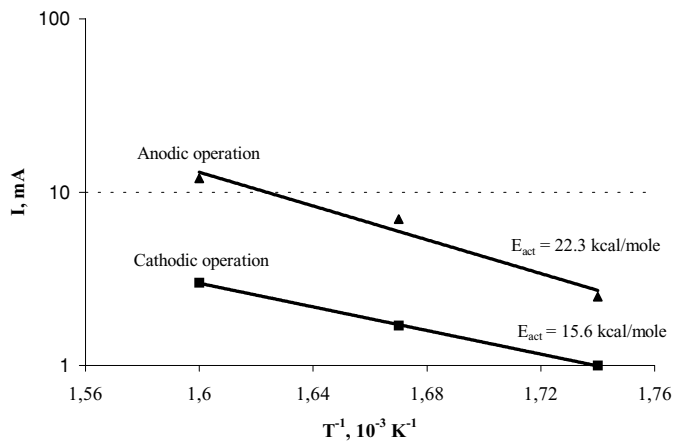
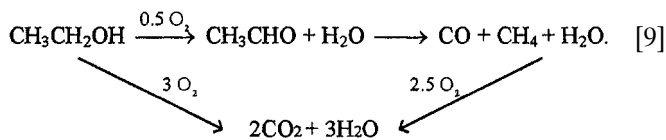


FIG. 3. Effect of temperature on exchange current.

during cathodic operation was calculated equal to about  $E_{act} = 15.6$  kcal/mole, while at anodic operation it was found to be approximately  $E_{act} = 22.3$  kcal/mole. In practice, these values express the energy required for charge transfer to occur through cathode/YSZ and anode/YSZ interfaces, respectively. Given that previous studies on oxygen adsorption on platinum suggest an apparent activation energy of about 45 kcal/mole when oxygen-anion de-electronation is the only electrocatalytic reaction in the tpb (13, 14), it is likely that the lower values measured here must be due to other elementary steps involving ethanol adsorbed on the catalytically active sites of the Pt film. From the viewpoint of electrochemical promotion, the exact determination of this complex mechanism of charge-transfer steps is not crucial, because the only parameter of practical importance is the exchange current,  $I_o$ , which determines the expected magnitude of the dimensionless factor of rate enhancement through Eq. [4].

### 3.2. Galvanostatic Transients

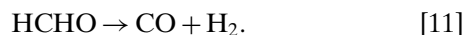
The application of small positive currents between the catalyst and the counterelectrode was found to induce significant changes on the rate of ethanol oxidation in a reversible manner. Experiments were conducted in the temperature range of 300–350°C at atmospheric pressure, at conditions where ethanol dehydrogenation to acetaldehyde was found to be the primary reaction step. Indeed, under the examined conditions, acetaldehyde, carbon dioxide, and steam were the main products, probably due to the following reaction sequence:



Taking into account the trace presence of formaldehyde, one might also consider the following reaction:



and the subsequent reaction of formaldehyde decomposition,



The preceding reaction steps also justify the amounts of HCHO, CO, CH<sub>4</sub>, and H<sub>2</sub> detected by mass spectrometry in very low quantities (less than 0.3 vol%).

Constant current ( $I > 0$ ) application (galvanostatic operation) between the catalyst and the counterelectrode results in steady-state supply of O<sup>2-</sup> to the catalyst through the YSZ electrolyte with Faradaic rate equal to  $I/2F$  (in g-atom O/s where  $F$  is Faraday's constant). Electrochemical pumping of O<sup>2-</sup> anions was found to alter significantly the rate of ethanol oxidation. Figure 4 (plots a and b) illustrates transient responses of the consumption rates of ethanol and oxygen upon the sequential application of positive currents  $I = 20 \mu\text{A}$  and  $40 \mu\text{A}$ , respectively.

As shown in Fig. 4, at time  $t = 0$  the circuit is closed by applying a constant current  $I = 20 \mu\text{A}$ . Electrochemical supply of O<sup>2-</sup> anions to the catalyst results in gradual increases in the consumption rates of both reactants (Fig. 4, plots a and b). More specifically, the consumption rate of ethanol increases from the initial (open-circuit) value of  $r_o = 2.6 \times 10^{-7}$  g-atom O/s to a new value,  $r = 7.1 \times 10^{-7}$  g-atom O/s at the steady state closed-circuit condition. Similarly, the consumption rate of oxygen also increases from  $r_o = 4.5 \times 10^{-8}$  g-atom O/s up to about  $12.7 \times 10^{-8}$  g-atom O/s. Note that electrochemical O<sup>2-</sup> supply to the catalyst causes a decrease in the oxygen concentration at the exit of the reactor. Figure 4 (plot b), shows the essence of the appearance of the effect of NEMCA, which is the activation of previously (under open-circuit conditions) more inert chemisorbed oxygen atoms due to supply of partially charged O<sup>δ-</sup> anions (15). After the establishment of the new (closed-circuit) steady-state condition, the circuit is opened again at time  $t = 9$  min and all rates are restored to their regular,  $r_o$ , (open-circuit) values, indicating the reversibility of the observed phenomenon.

The aforementioned behavior for the reactants is naturally compensated by increases in the formation rates of the products. Thus, Fig. 4 (plots c and d) shows the galvanostatic transient responses of the major reaction products (i.e., acetaldehyde and carbon dioxide) upon sequential application of currents ( $I = 20 \mu\text{A}$  and  $I = 40 \mu\text{A}$ ), at the same conditions ( $P_{\text{ethanol}} = 34.8$  kPa,  $P_{\text{O}_2} = 2$  kPa, and  $T = 325^\circ\text{C}$ ). For  $I = 20 \mu\text{A}$ , the formation rate of acetaldehyde changes from  $r_o = 2.18 \times 10^{-7}$  g-atom O/s up to about  $7.98 \times 10^{-7}$  g-atom O/s and the formation rate of carbon dioxides

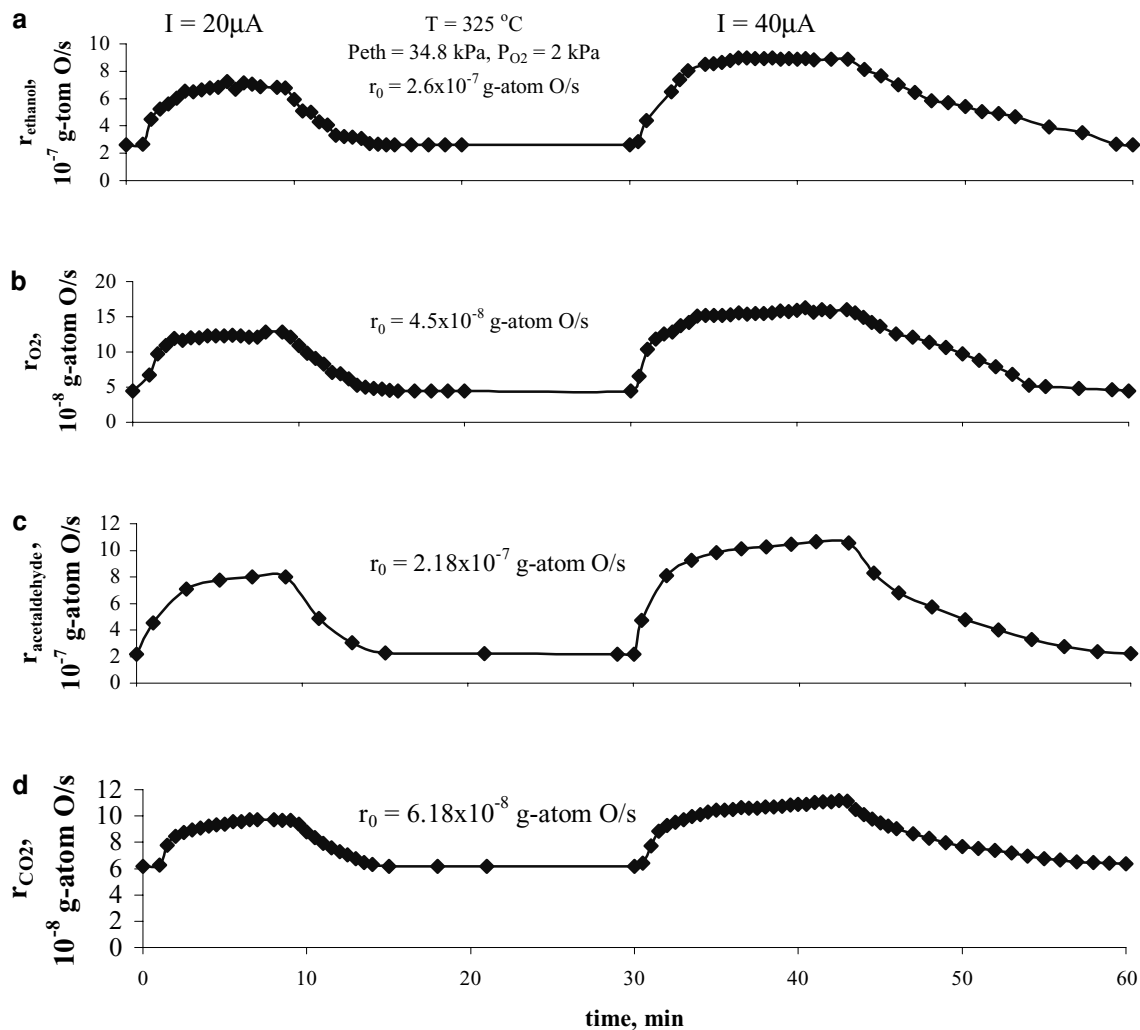


FIG. 4. Transient behavior of the rates of (a) ethanol consumption, (b) oxygen consumption, (c) acetaldehyde formation, and (d) carbon dioxide formation after the sequential application of currents equal to  $I = 20 \mu\text{A}$  and  $I = 40 \mu\text{A}$  ( $P_{\text{ethanol}} = 34.8 \text{ kPa}$ ,  $P_{\text{O}_2} = 2 \text{ kPa}$ ,  $T = 325^\circ\text{C}$ ).

from  $r_0 = 6.18 \times 10^{-8} \text{ g-atom O/s}$  up to about  $9.64 \times 10^{-8} \text{ g-atom O/s}$ . As shown, an increase of the intensity of the applied current further increases the formation rates of the products. Similarly, these increases are also higher when the oxygen partial pressure is higher, as shown in Fig. 5 for  $P_{\text{O}_2} = 8 \text{ kPa}$ .

As mentioned, the relaxation time constant of the catalytic rate of ethanol oxidation was expected to be of the same order of magnitude as the values given by Eq. [5]. In fact, the calculated values obtained by Eq. [5] represent the time period required for the formation of a monolayer of  $\text{O}^{2-}$  ions in a catalytic surface of  $N$  active centers. In the cases of the transient changes described previously, the experimental values of the relaxation time constants were found to be in close qualitative agreement with those expected theoretically, as shown in Table 2.

### 3.3 The Extent of Electrochemical Promotion (NEMCA)

On the basis of previous NEMCA studies and their conclusions, which lay the foundation of the relevant theory today, the quantification of the extent of the promotion can be made using the dimensionless rate-enhancement factor,

TABLE 2  
Comparison between Calculated and Experimental Relaxation-Time Constants

Applied current, $I$ ( $\mu\text{A}$ )	Oxygen partial pressure (kPa)	Experimental time constant (min)	Theoretical time constant (min)
20	2	2.8	6.4
20	8	1.3	6.4
40	2	2	3.2
40	8	1.3	3.2

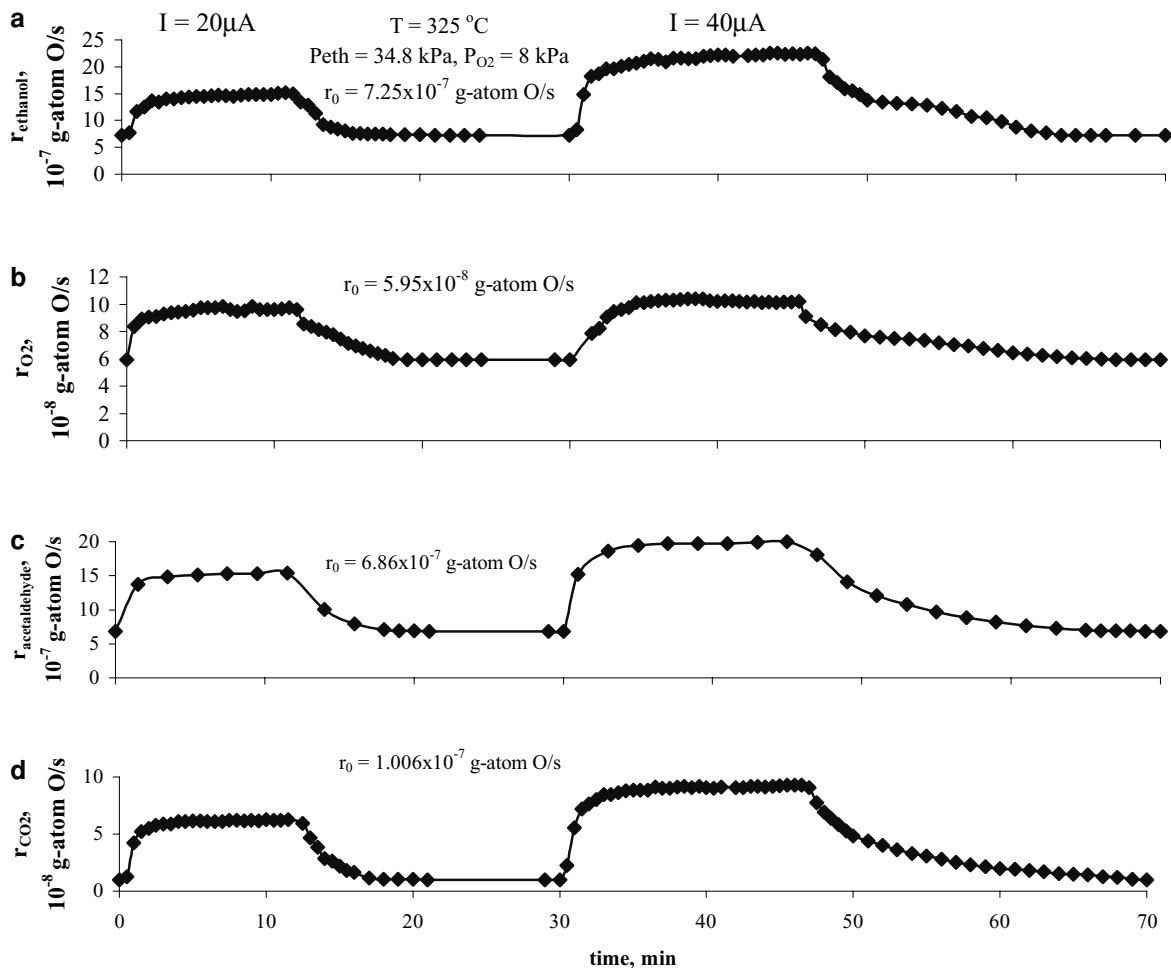


FIG. 5. Transient behavior of the rates of (a) ethanol consumption, (b) oxygen consumption, (c) acetaldehyde formation, and (d) carbon dioxide formation after the sequential application of currents equal to  $I = 20 \mu\text{A}$  and  $I = 40 \mu\text{A}$  ( $P_{\text{ethanol}} = 34.8 \text{ kPa}$ ,  $P_{\text{O}_2} = 8 \text{ kPa}$ ,  $T = 325^\circ\text{C}$ ).

$\Lambda$ , given by Eq. [3]. For the case of this study, the total change of the reaction rate of ethanol oxidation,  $\Delta r$ , can be expressed either as the steady-state increase of the consumption rates of ethanol and oxygen or as the sum of the steady-state increases of the formation rates of the products ( $\text{CO}_2$ ,  $\text{CH}_3\text{CHO}$ ). Figures 6 and 7 illustrate the dependence of the change of the rates of acetaldehyde and carbon dioxide formation on the rate of electrochemical supply of  $\text{O}^{2-}$  anions through the YSZ at three temperatures and constant oxygen partial pressure  $P_{\text{O}_2} = 8 \text{ kPa}$ . Dashed lines represent  $\Lambda = \text{const.}$  curves derived by Eq. [3]. As shown in Fig. 6, electrochemical promotion of Pt enhances the rate of ethanol dehydrogenation into acetaldehyde by a factor  $\Lambda$  of the order between  $10^3$  and  $10^4$  depending on the operation temperature. Values for  $\Lambda$  are of the order of  $10^4$  at low temperatures when high polarization of the Pt/YSZ interface is achieved by application of low positive currents (10–30  $\mu\text{A}$ ). At higher temperatures (325–350 $^\circ\text{C}$ ) the extent of the promotion decreases with  $\Lambda$  values between  $3 \times 10^3$  and  $7 \times 10^3$ . The same temperature dependence is also evident

in Fig. 7 for the case of carbon dioxide, but  $\Lambda$  values in this case are lower than  $10^3$ . The fact that  $I_0$  increases exponentially with temperature in conjunction with the fact that  $\Lambda$  is proportional to  $I_0^{-1}$  (Eq. [4]) explains why most NEMCA

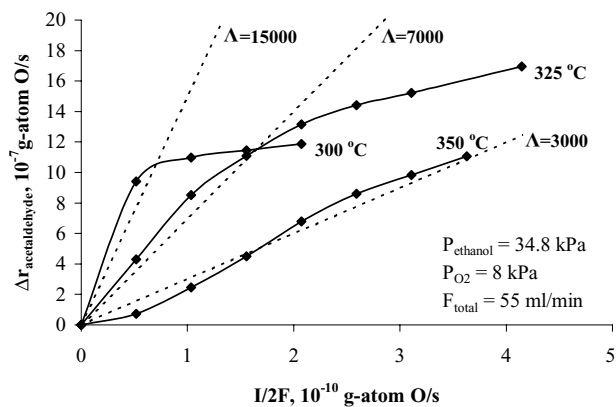


FIG. 6. Steady-state effect of current on the enhancement of the formation rate of acetaldehyde at different temperatures.

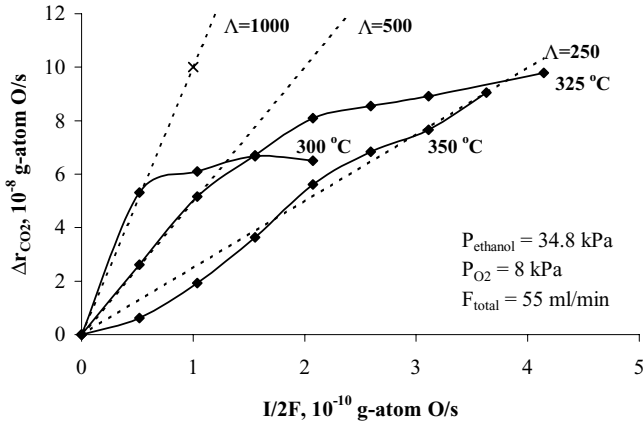


FIG. 7. Steady-state effect of current on the enhancement of the formation rate of carbon dioxide at different temperatures.

studies are restricted to low temperatures (typically lower than 600°C) (3).

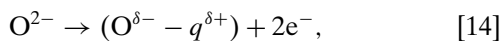
The dependence of the enhancement factor on the oxygen partial pressure is shown in Figs. 8 and 9 for acetaldehyde and carbon dioxide, respectively, at constant temperature  $T = 325^\circ\text{C}$ . For both products the extent of the NEMCA effect is higher at higher oxygen partial pressures and this observation is more profound at high rates of electrochemical oxygen pumping where the intensity of the activation of the chemisorbed oxygen atoms is higher. A comparison between Figs. 8 and 9 shows that current application affects predominantly the formation rate of acetaldehyde. More precisely, the ratios  $\rho = r/r_0$ , taken after the establishment of the steady-state closed-circuit operation, were calculated at all cases for acetaldehyde in the range

$$1 < \rho_{\text{acetaldehyde}} < 5.5, \quad [12]$$

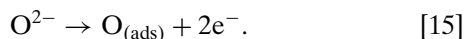
and for carbon dioxide in the range

$$1 < \rho_{\text{carbon dioxide}} < 2. \quad [13]$$

These observations show that electrochemical  $\text{O}^{2-}$  supply to the catalyst surface enhances the oxidative dehydrogenation of acetaldehyde more strongly than the consecutive oxidation of acetaldehyde, CO, and  $\text{CH}_4$  to  $\text{CO}_2$ . An interpretation of this preferential rate enhancement in terms of the NEMCA theory (2–5) is as follows. Oxide ions  $\text{O}^{2-}$  arriving at the tpb form backspillover oxygen ions,



which are less reactive (in fact,  $\Lambda$  times less reactive) than adsorbed oxygen produced by gaseous oxygen adsorption:



Reaction [15] produces adsorbed atomic oxygen,  $\text{O}_{(\text{ads})}$ , which reacts rapidly with other adsorbed species. On the other hand, spillover oxide ions which are formed accord-

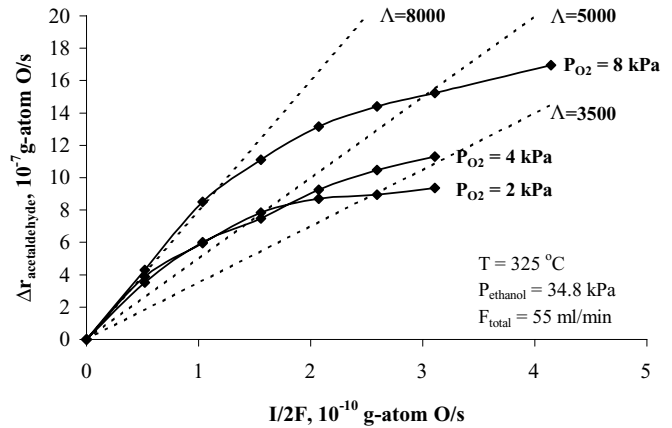


FIG. 8. Steady-state effect of current on the enhancement of the formation rate of acetaldehyde at different oxygen partial pressures.

ing to reaction [14] spread over the catalyst surface and substantially increase the catalyst work function, thus weakening the  $\text{O}_{(\text{ads})}$  chemisorptive bond (2–5). This, in turn, results in significant lowering of the activation energy of the oxidation reactions [9], which determine the overall rate of ethanol consumption. Indeed, a significant decrease was observed in both the catalytic activation energies of ethanol consumption and acetaldehyde formation, which are given in Table 3. As shown, under NEMCA conditions the activation energy of acetaldehyde production becomes negligible ( $\sim 2$  kcal/mole) indicating that the weakening in the chemisorptive bond of  $\text{O}_{(\text{ads})}$  preferentially enhances the ethanol oxidative dehydrogenation step rather than the complete oxidation step to  $\text{CO}_2$ . A similar enhancement in the selectivity to partial oxidation products has been found during  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$  oxidation on Ag (2–5).

The spillover mechanism of reactions [14] and [15] are illustrated by Fig. 10, which indicates the enhancement of the consumption rate of surface oxygen due to the electrochemical supply of  $\text{O}^{2-}$  anions through the YSZ electrolyte. It

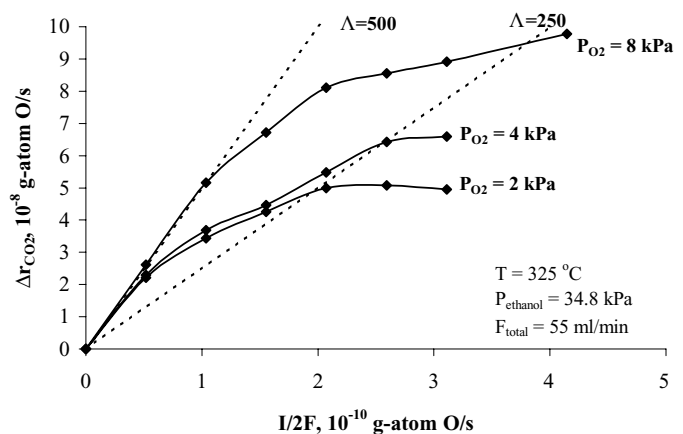


FIG. 9. Steady-state effect of current on the enhancement of the formation rate of carbon dioxide at different oxygen partial pressures.

TABLE 3  
Changes in the Catalytic Activation Energy due to Electrochemical Promotion

Current, $I$ ( $\mu\text{A}$ )	Measured overpotential, $\eta$ (V)	Apparent activation energy (kcal/mole)	
		Acetaldehyde formation	Ethanol consumption
0	0	14.3	27.7
10	0.2	2.3	10.1
20	0.3	2.3	8.3
30	0.35	2.3	7.9

is shown that the number of previously (under open-circuit conditions) inert activated oxygen atoms is typically two to three orders of magnitude higher than the number of the electrochemically supplied  $\text{O}^{2-}$  ions. Figure 11 shows the steady-state effect of current  $I$  (expressed as the rate of  $\text{O}^{2-}$  supply,  $I/2F$ ) on the conversion of ethanol at three temperatures for  $P_{\text{O}_2} = 8$  kPa. As expected, conversion of ethanol is higher at higher temperatures but as shown in Fig. 11 the application of current produces higher changes of ethanol conversion at low temperatures due to the higher polarization of the Pt/YSZ interface. Indeed, current application was found to induce a 500% increase of ethanol conversion at  $300^\circ\text{C}$ , 400% increase at  $325^\circ\text{C}$ , and 150% increase at  $350^\circ\text{C}$ .

### 3.4 Effect of Electrochemical Promotion on the Yield of Acetaldehyde

Ethanol oxidation presents significant interest as a route for the production of acetaldehyde. Considering that acetaldehyde is a product of increased value compared with ethanol, it is obvious that the optimization of this production process is of great practical importance. The determination of the optimal conditions ( $T$ ,  $I$ ) of electrochemical promotion for the maximization of the amount of acetalde-

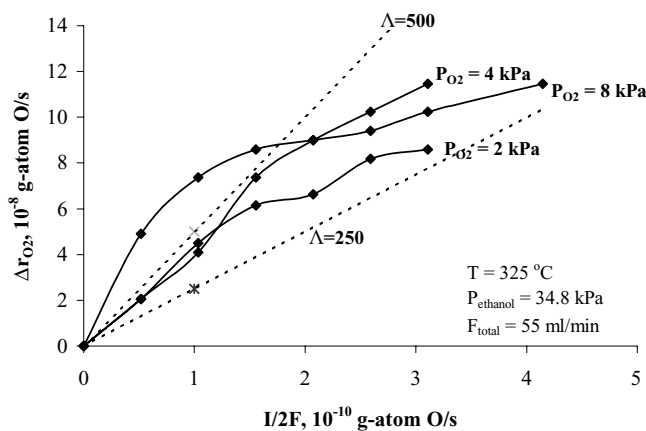


FIG. 10. Steady-state effect of current on the enhancement of the consumption rate of oxygen at different oxygen partial pressures.

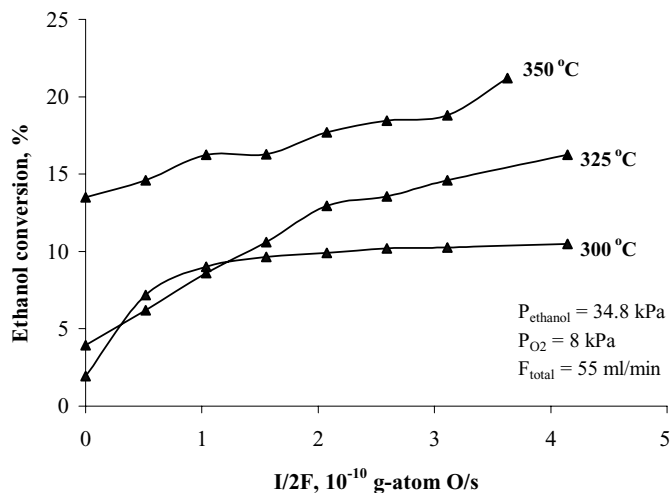


FIG. 11. Steady-state effect of current on ethanol conversion.

hyde cannot be based on selectivity values because these do not represent quantitative measures of the amounts produced. For this reason, the selection of the optimum conditions can be based on the reaction yield (=selectivity of acetaldehyde  $\times$  ethanol conversion) to acetaldehyde as summarized in Fig. 12, which illustrates the distribution of the acetaldehyde yield in the range of currents and temperatures used in the current study. The acetaldehyde yield increases as both temperature and applied current increase. At  $300^\circ\text{C}$ , the open-circuit value of acetaldehyde yield is about 1.2% and may be increased to 8.3–9.1% by applying currents above  $40 \mu\text{A}$ . This is an almost 700% increase in the acetaldehyde yield due to the electrochemical promotion. The same change can be estimated on the order of 540 and 170% at  $325$  and  $350^\circ\text{C}$ , respectively. Finally, the maximum acetaldehyde yield was about 17.6% at  $350^\circ\text{C}$  for  $I = 80 \mu\text{A}$  (16, 17).

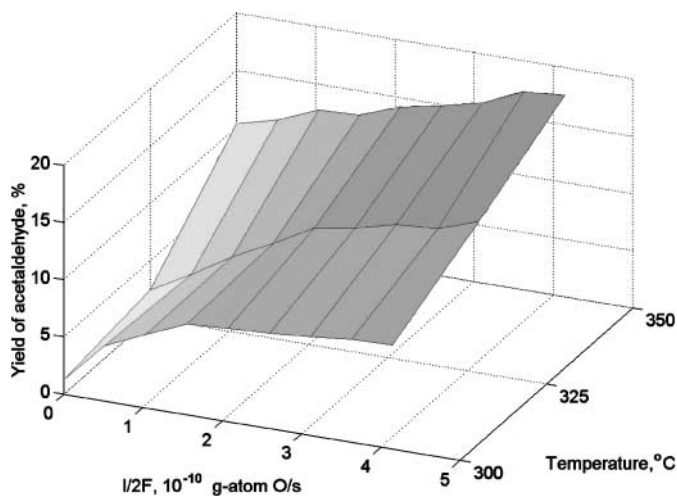


FIG. 12. Effect of electrochemical promotion on the yield to acetaldehyde ( $P_{\text{ethanol,in}} = 36.3$  kPa,  $P_{\text{O}_2} = 8$  kPa).



## 4. SUMMARY

The current study was undertaken to examine the existence, the extent, and the results of the effect of electrochemical promotion (NEMCA) during the reaction of ethanol oxidation over polycrystalline Pt. It was found that polarization of the Pt/YSZ interface is able to dramatically and reversibly enhance the rate of ethanol dehydrogenation into acetaldehyde. The extent of the electrochemical promotion, i.e., the Faradaic efficiency  $\Lambda$ , was found to be on the order of  $10^4$  at relatively low temperatures (300–325°C) and high oxygen partial pressures (8 kPa). The study focused on the optimization of the effect of the electrochemical promotion to maximize the reaction yield to acetaldehyde. As a result, it was found that the acetaldehyde yield can increase up to 700% at 300°C and up to 170% at 350°C due to electrochemical promotion attaining values between 8.3 and 17.6% at high oxygen partial pressures (8 kPa) with application of currents of 80  $\mu$ A. The overall effect was interpreted in terms of the observed decrease in the catalytic activation energy of ethanol dehydrogenation which was found to be 70–85% lower than the corresponding regular (open-circuit) value.

## REFERENCES

1. Stoukides, M., *Catal. Rev.—Sci. Eng.* **42**(1–2), 1 (2000).
2. Vayenas, C. G., Jaksic, M. M., Bebelis, S. I., and Neophytides, S. G., in “Modern Aspects of Electrochemistry” (J. O. M. Bockris, B. E. Conway, and R. E. White, Eds.), Vol. 29, p. 57 (and references therein). Plenum, New York, 1996.
3. Vayenas, C. G., and Neophytides, S. G., in “Catalysis,” Vol. 12, p. 199. Royal Chem. Soc., London, 1996.
4. Vayenas, C. G., Bebelis, S. I., Yentekakis, I. V., and Neophytides, S. G., in “The CRC Handbook of Solid State Electrochemistry” (P. J. Gellings and H. J. M. Bouwmeester, Eds.), p. 445. CRC Press, Boca Raton, FL, 1997.
5. Vayenas, C. G., Bebelis, S., Pliangos, S., Brosda, S., and Tsiplakides, D., “Electrochemical Activation of Catalysis,” Kluwer Academic/Plenum, New York, 2001.
6. Metcalfe, I. S., *J. Catal.* **199**, 247 (2001).
7. Metcalfe, I. S., *J. Catal.* **199**, 259 (2001).
8. Gomez, M. F., Arrua, L. A., and Abello, M. C., *Ind. Eng. Chem. Res.* **36**, 3468 (1997).
9. McKetta, J. J., in “Encyclopedia of Chemical Processing and Design,” Vol. 1, p. 114. New York, Dekker, 1988.
10. Douvartzides, S., and Tsiakaras, P., *Solid State Ionics* **136–137**, 849 (2000).
11. Vayenas, C. G., Bebelis, S., Yentekakis, I. V., and Lintz, H.-G., *Catal. Today* **11**(3), 303 (1992).
12. Wang, D. Y., and Nowick, A. S., *J. Electrochem. Soc.* **126**(7), 1155 (1979).
13. Brennan, D., Hayward, D. O., and Trapnell, B. M. W., *Proc. R. Soc. London* **A256**, 81 (1960).
14. Okamoto, H., Kawamura, G., and Kudo, T., *Electrochim. Acta* **28**(3), 379 (1983).
15. Cavalca, C., Larsen, G., Vayenas, C. G., and Haller, G., *J. Phys. Chem.* **97**, 6115 (1993).
16. Tsiakaras, P. E., Douvartzides, S. L., Sobyenin, V. A., and Demin, A. K., *Solid State Ionics* (2002), in press.
17. Douvartzides, S. L., Ph.D. thesis, Dept. of Mechanical and Industrial Engineering, University of Thessalia, Volos, Greece, 2002.