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NOTE

Electrochemical Promotion of Electronically Isolated Pt Catalysts on Stabilized Zirconia

The effect of non-Faradaic electrochemical modification of catalyst activity (NEMCA) or electrochemical promotion in catalysis has been studied for more than 40 different catalytic reactions using a variety of metal catalysts and solid electrolytes (1, 2). Work in this area has been extensively reviewed (1, 2). In brief it has been found that the catalytic and chemisorptive properties of polycrystalline metal films interfaced with solid electrolytes, such as yttria-stabilized-zirconia (YSZ), an O^{2-} conductor, β''-Al_2O_3, a Na^+ conductor, CaF_2, a F^- conductor, or TiO_2, a mixed electronic–ionic conductor, can be affected dramatically and reversibly by electrically polarizing the metal–solid electrolyte interface. This is accomplished by cofeeding the reactants on the working electrode of a solid electrolyte cell:

gaseous reactants | catalyst = working electrode | solid electrolyte | counter electrode | gaseous reactants

and using the working electrode both as an electrode and as a catalyst for the heterogeneous reaction under study.

The results presented in this note are a first step in our ongoing research to extend NEMCA to well-dispersed catalytic systems. This step consists in exploring whether a direct electrical connection between the metal active phase and the counter electrode is necessary to obtain an electrochemical promotion effect.

A continuous conductive platinum film and three gold films were deposited on a YSZ disk as shown in Fig. 1. The platinum film was deposited on the YSZ pellet using a thin coating of A1121 Engelhard platinum paste followed by calcining first at 400°C for 2 h and then at 850°C for 20 min. The YSZ disk was suspended in a quartz well-mixed reactor with all four electrodes exposed to the reactant gas mixture (Fig. 2). Four gold wires were used as electron collectors or suppliers. Only three out of the four films were used at a time as electrodes (working, counter, or reference) and therefore different geometrical configurations could be tested, as shown in Fig. 1. Among these configurations, the "wireless" ones correspond to situations where platinum is not used as an electrode and is thus electronically isolated with current passing between the gold electrodes. In the "conventional" NEMCA configurations, the platinum catalyst film is also used as the working electrode (Fig. 2).

The oxidation of ethylene was chosen as a model reaction since this system has been studied extensively and has been shown to exhibit a pronounced NEMCA behavior on platinum interfaced with YSZ (1–4). Figure 3 shows galvanostatic transients for three different wiring configurations; i.e., it depicts the transient effect of a constant applied current on the rate of ethylene oxidation (expressed in mol O/s). Initially ($t < 0$), the circuit is open ($I = 0$) and the open-circuit catalytic rate, r_0, is 1.65×10^{-7} mol/s. Then at $t = 0$ a galvanostat is used to apply a constant current I between the working and counter electrodes. A 40% enhancement in the rate is measured for the "wireless" system (config. 1) as a current of $I = +20\ \mu A$ is applied between *the gold working and counter electrodes*. The increase of the catalytic rate $r - r_0$ (0.71×10^{-7} mol/s) is 688 times larger than the rate of transport of O^{2-} between the two gold electrodes as calculated from Faraday's law. This implies that the Faradaic efficiency, Λ, defined (1, 2) from $\Lambda = \Delta r/(I/2F)$ equals 688 for this experiment. It must be emphasized that no catalytic activity has been measured under open or closed circuit during blank experiments in the absence of the platinum film. *Thus this experiment demonstrates that a direct electrical connection to the catalyst is not necessary to observe an electrochemical promotion effect.*

A comparison of the galvanostatic transients obtained when platinum is used as the working electrode (configs. 5 and 6) and when it is not (config. 1, "wireless") is shown on the same figure. For the "conventional" NEMCA configurations, rate enhancement ratio $\rho (= r/r_0)$ values ranging between 2 and 2.5 are observed for $I = -20\ \mu A$, while ρ values between 0.7 and 0.9 are obtained for $I = +20\ \mu A$. The rate enhancement ratio ρ is always defined (1, 2) as the ratio of the promoted to the unpromoted catalytic rate. This system therefore exhibits an electrophilic NEMCA behavior (i.e., the rate increases with a decreasing value of the catalyst potential or work function (1, 2)) with relatively small ρ values. This behavior is in apparent contradiction with the literature (1–4), where opposite trends are reported. This difference is related to the kinetic regimes where these experiments where performed. Large ρ values and electrophobic behavior is reported for a kinetic regime where the rate is zero order in oxygen and first order in ethylene (3). In the present system, and possibly due to differences in the

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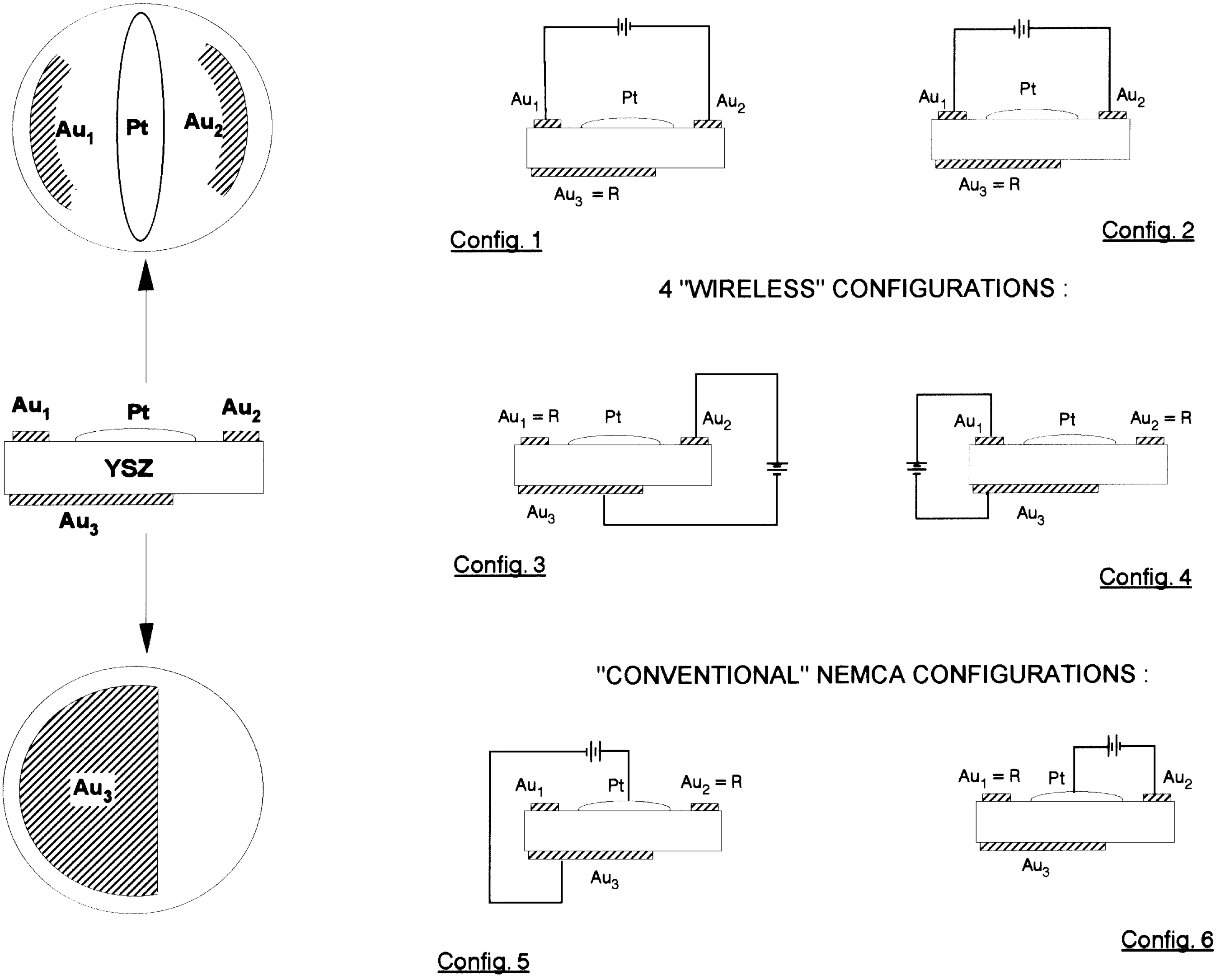

FIG. 1. Pt catalyst and Au electrode geometry (left); corresponding electrical connection in four "wireless" and two conventional configurations (right). Electrical connections to the reference (R) electrode not shown for simplicity.

preparation of the Pt film, such a regime is not attained in the experimental working conditions and the rate is always first order in oxygen. Vayenas *et al.* (1–3) report that the adsorption of oxygen, which seems to be the rate-limiting step in the present system, is insensitive to changes in the potential or work function of the catalyst. The relatively small ρ values obtained are in good agreement with this (3). However, the adsorption of oxygen seems not to be totally insensitive to changes of the work function and the electrophilic behavior can be rationalized by an enhanced adsorption of oxygen as the catalyst work function is decreased, oxygen behaving as an electron-acceptor adsorbate.

The maximum rate enhancement ratio obtained in the "wireless" configuration is a factor 2 smaller than the one observed when platinum is used as the working electrode. Two effects may be responsible for this difference. The first is *current bypass*. Part of the current may pass through the bulk of the YSZ without affecting the platinum film and therefore much larger currents are needed in order to obtain performances similar to the ones obtained in the "conventional" configuration. A thinner YSZ pellet and appropriate geometry of the electrodes should allow to diminish this loss of current. The second effect deals with the mode of polarization of the platinum film. It is proposed that the platinum film behaves as a *bipolar* electrode (e.g., (5)) as schematized in Fig. 4. Part of the platinum film is therefore polarized with a positive charge while the other part is polarized with a negative charge. There is thus not a uniform catalyst work function as in the case when platinum is used as the working electrode (1, 2). The resulting effect is a combination between the activity of negatively and positively polarized catalyst surfaces. Since a decrease in the catalytic

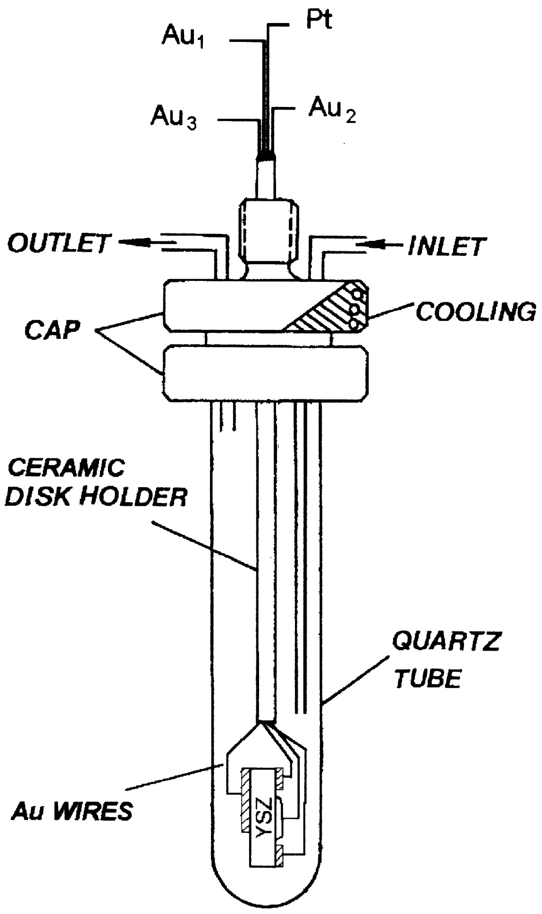

FIG. 2. Single pellet catalytic reactor.

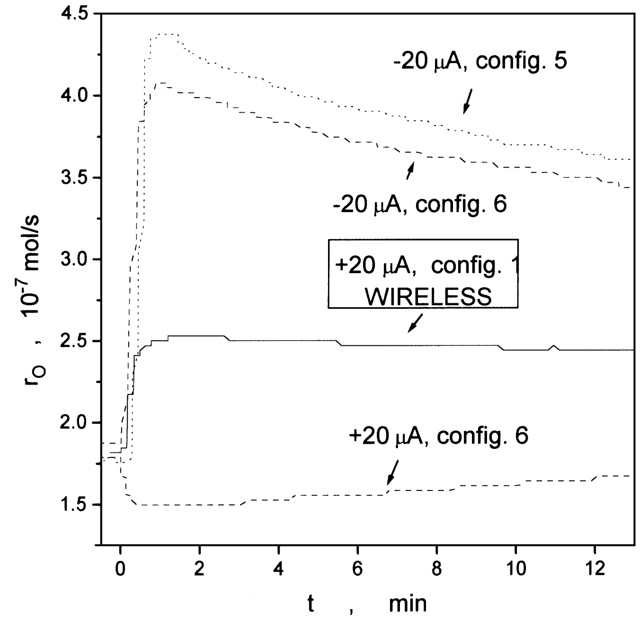

FIG. 3. Transient effect of the applied current on the rate of ethylene oxidation (expressed in mol O/s) for three different electrode configurations: config. 1, I = +20 μA (solid curve); config. 5, I = −20 μA (dotted curve); and configs. 6, I = +20 and −20 μA (dashed curves). Conditions: $T = 353°$C, $P_{C_2H_4} = 0.65$ kPa, $P_{O_2} = 17.5$ kPa, flow = 200 ml/min.

rate is observed for positive currents in the present system, the enhancement obtained in the "wireless" configuration for any fixed applied current can only be smaller than that of the "conventional" configuration. This limitation may be overcome for reactions which exhibit both electrophobic and electrophilic behaviors, such as C_2H_6 (6), CH_4 (7), and CO (8) oxidation on platinum.

The rate enhancement ratios obtained for the four "wireless" configurations during the application of I = +15 μA and I = −15 μA are listed in Table 1. The effect of the current is not symmetric, since a ρ value of 1.38 is obtained for configuration 1 during the application of I = +15 μA while $\rho = 1.21$ is observed for I = −15 μA. This can be explained by a nonsymmetric distribution of the platinum mass and surface area with respect to the two gold electrodes Au_1 and Au_2, with more platinum towards Au_2. Therefore a larger fraction of the platinum surface is polarized negatively during the application of a positive current as compared to the application of a negative current. This is confirmed with the observation of a reversed trend for configuration 2, where the working and counter gold electrodes have been switched.

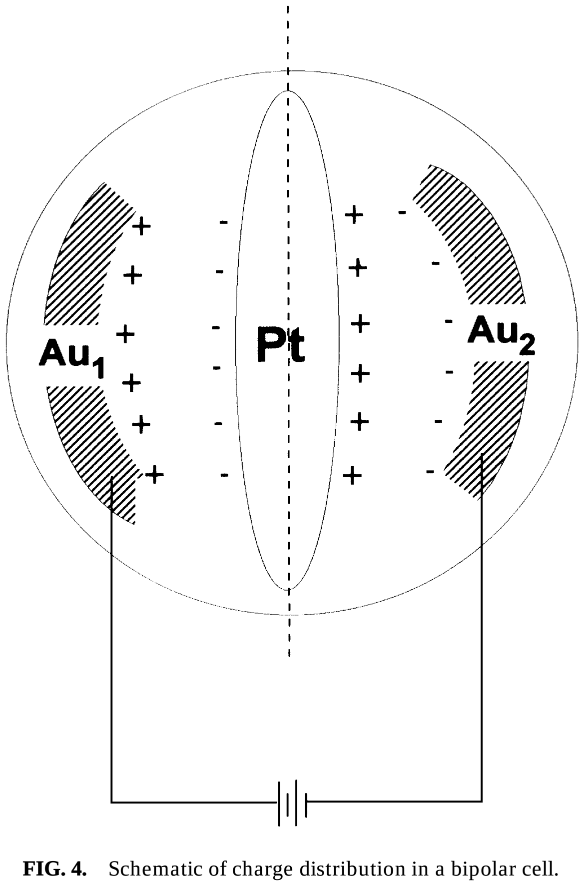

FIG. 4. Schematic of charge distribution in a bipolar cell.

TABLE 1

Measured $\rho(=r/r_0)$ and Corresponding Pt Catalyst Potential Values with Respect to the Reference Electrode for the Four Wireless Configurations of Fig. 1

	I = +15 μA		I = −15 μA	
Configuration	ρ	V_{Pt-R} [V]	ρ	V_{Pt-R} [V]
1	1.38	−0.973	1.21	+0.699
2	1.21	+0.692	1.30	−0.891
3	1.10	+0.031	1.15	−0.891
4	0.92	−0.368	1.00	−0.345

The catalyst potential V_{Pt-R} given in Table 1 is only indicative because the reference is not perfect and also acts as a bipolar electrode. These values, however, show that, as expected, the potential of the platinum film is modified in the "wireless" configurations.

Smaller ρ values are obtained for configuration 3 while no enhancement of the rate is observed for configuration 4. This is easily understandable in terms of an increase of the current bypass due to the less favorable relative positions of the different electrodes (see Fig. 1), with the limit in configuration 4, where the O^{2-} ions almost do not encounter the platinum film. V_{Pt-R} in this latter case is equal to the open-circuit value. These results confirm the bipolar scheme and show that among the different geometrical configurations, those denoted by 1 and 2 in Fig. 2 are optimal in limiting the losses of current by bypass.

Interesting results are also obtained with the "wireless" NEMCA configuration 1 in the oscillatory region of the oxidation of CO on Pt. Under the experimental conditions of Fig. 5, large oscillations of the CO_2 production rate are observed under open-circuit (Fig. 5, I = 0). The frequency of these oscillations can be significantly increased by imposing a negative current between Au_1 and Au_2, while both the frequency and the amplitude are modified during the application of positive currents. The effect of electrochemical promotion on the oscillatory behavior of the Pt-catalyzed oxidation of CO has been reported for a "conventional" NEMCA configuration (2, 8) and it has been shown that the frequency of the oscillations can be "tuned" by varying the imposed current value. These observations are in good agreement with PtO_2-based models (9–11) proposed to describe the oscillatory behavior of CO oxidation on platinum at atmospheric pressure (8). The present observation that the limit-cycle frequency can be modified by imposing a current in the "wireless" configuration gives a supplementary proof that the modifications of the rate *are taking place on the platinum surface.*

An interesting feature of the effect of the current in the "wireless" mode on the CO oxidation oscillations is shown in Fig. 6. It can be seen that similarly to the results reported for the "conventional" NEMCA configuration (2, 8) the

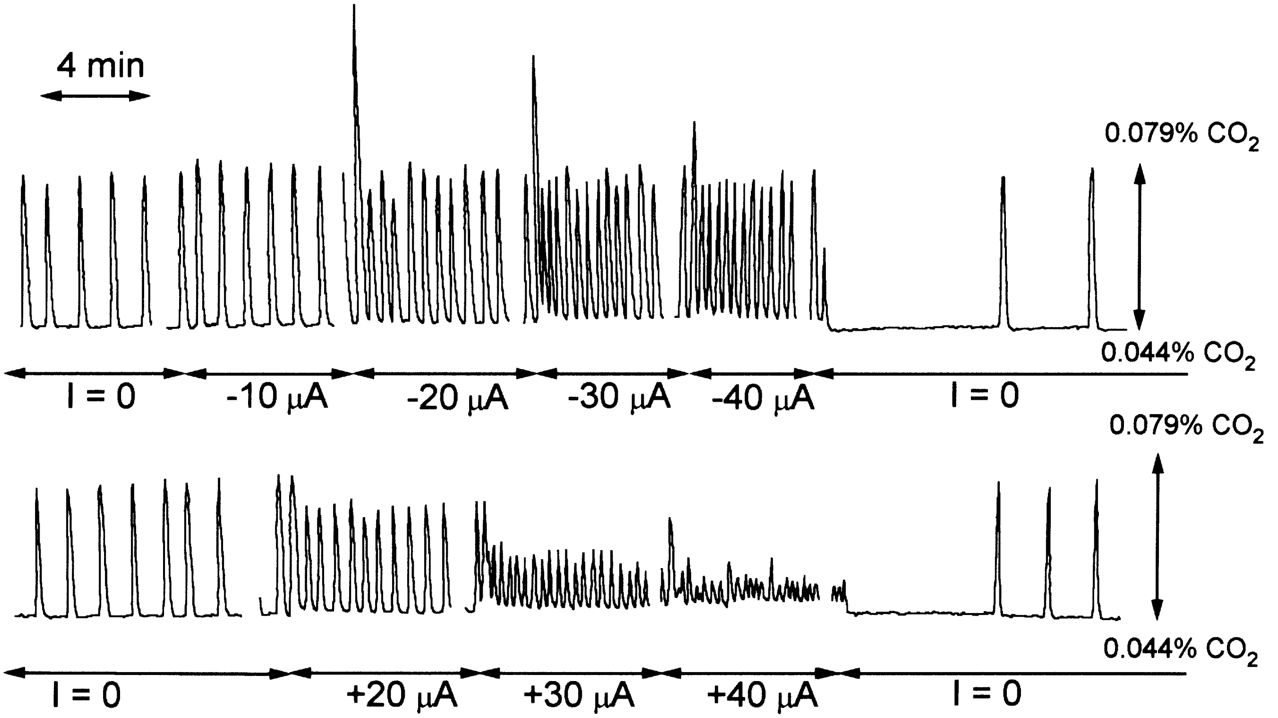

FIG. 5. "Wireless" configuration: effect of applied constant current on the frequency of the self sustained rate oscillations during the CO oxidation on Pt. Conditions: config. 1, $T = 377°C$, $P_{CO} = 0.65$ kPa, $P_{O_2} = 13.0$ kPa, flow = 430 ml/min.

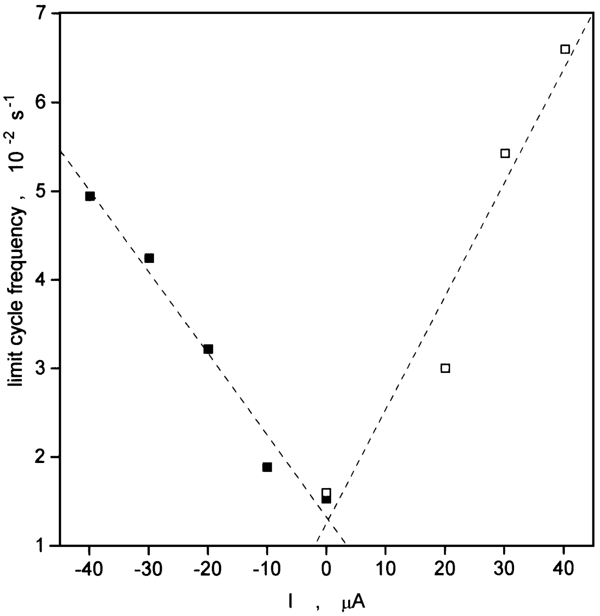

FIG. 6. "Wireless" configuration: effect of applied constant current on the limit cycle frequency of the self-sustained rate oscillations during the CO oxidation on Pt. Conditions as in Fig. 5.

limit-cycle frequency of the oscillations is a linear function of the applied current. This observation is not straightforward to explain, due to the bipolar characteristics of the present configuration.

The present study demonstrates that electrochemical promotion can be induced in systems, where the catalyst is not electronically connected to a galvanostat or potentiostat, and behaves in this case as a bipolar electrode. These results create new possibilities for the practical utilization of electrochemical promotion.

In summary the present study demonstrates that the electrochemical promotion (NEMCA) effect can be induced on electronically isolated metal catalysts deposited on solid electrolytes, i.e., on metal catalyst films without any electronic conductor (wire) attached to them. This "wireless" NEMCA appears to be due to the "bipolar" electrode function of the electronically isolated catalyst located between two other electrodes which are electrically biased via a galvanostat or poteniostat. In this way one part of the catalyst electrode acts as an anode, the other as a cathode.

This observation may be of crucial importance for the ultimate practical usefulness of electrochemical promotion (NEMCA). It shows that, in principle, it may be possible to induce NEMCA on finely dispersed metal catalysts supported on highly porous ionic conductors, such as YSZ, or mixed electronic–ionic conductors, such as TiO_2, where the NEMCA effect has also been recently studied (12). Such electrochemically promoted catalysts could have active surface areas comparable to those of many commercial catalysts supported on more conventional Al_2O_3 or SiO_2 supports. This idea is supported by the successful industrial operation of aqueous electrochemical bipolar cells consisting of many (tens or hundreds) of electronically isolated parallel plates placed between two electrically biased electrodes and each acting as a bipolar electrode (5). Current bypass may be the main problem to be encountered in the design and operation of such "wireless" NEMCA catalysts, consisting of two electrically biased electrodes with a large number of thin catalyst stripes or individual microscopic catalyst particles supported on the solid electrolyte between the two end electrodes. This problem is already manifest, to some minor extent, in the present study and has been addressed and solved in aqueous electrochemistry via appropriate cell design (5). If this problem can also be overcome when using solid electrolytes, via appropriate choice of the conductivity of the solid electrolyte and of the loading and geometric location of the solid electrolyte supported catalyst, then it may be feasible to use electrochemical promotion with finely dispersed catalyst systems.

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