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REVIEW PAPER

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ELECTROCHEMICAL PROMOTED CATALYSIS: TOWARDS PRACTICAL UTILIZATION

Electrochemical promotion (EP) of catalysis has already been recognized as "a valuable development in catalytic research" (J. Pritchard, 1990) and as "one of the most remarkable advances in electrochemistry since 1950" (J. O'M. Bockris, 1996). Laboratory studies have clearly elucidated the phenomenology of electrochemical promotion and have proven that EP is a general phenomenon at the interface of catalysis and electrochemistry. The major progress toward practical utilization of EP is surveyed in this paper. The focus is given on the electropromotion of industrial ammonia synthesis catalyst, the bipolar EP and the development of a novel monolithic electropromoted reactor (MEPR) in conjunction with the electropromotion of thin sputtered metal films. Future perspectives of electrochemical promotion applications in the field of hydrogen technologies are discussed.

Key words: electrochemical promotion; NEMCA effect; catalysis; bipolar reactor; monolithic electropromoted reactor.

The electrochemical promotion of catalysis (non-Faradaic electrochemical modification of catalytic activity, NEMCA effect) refers to the very pronounced and reversible changes in the catalytic properties of conductive catalysts deposited on solid electrolytes caused by application of small electrical currents or potentials [1]. There are shorter [2-5] as well as more detailed recent reviews [1,6,7] describing the phenomenology, limits and a molecular origin of the phenomenon. Electrochemical promotion (EP) has been studied extensively for more than 15 years almost exclusively in research laboratories but there is also a strong industrial interest and involvement aiming to its commercialization.

"The possibility of application of the NEMCA effect in conventional flow reactors and of its extension to oxide catalysts may be of great importance in the future, though both the nature of the migrating, spillover species and their effect on the molecular-scale mechanism require further studies", B. Grzybowska-Swierkosz and J. Haber, Annual Reports on Chemistry, 1994. More than a decade later after this statement, the ultimate direct utilization of electrochemical promotion in commercial reactors, in the chemical in-

dustry and in automotive exhaust catalysis, depends on several technical and economical factors [8] which are intimately related to the following specific technical considerations and problems:

I. *Material cost minimization.* The main consideration here is the problem of the efficient catalyst material utilization which requires the use of thin (on the order of few nm thick) catalyst electrodes or dispersed catalysts [9].

II. *Ease of electrical connection.* The main problem here is that of the efficient electrical current collection, ideally with only two electrical leads entering the reactor and without an excessive number of interconnects, as in fuel cells. This is because the competitor of an electro-chemically promoted chemical reactor is not a fuel cell but a classical chemical reactor.

III. *Efficient and compact reactor design.* Since the main competitor of an electrochemically promoted chemical reactor is a chemical reactor itself (fixed bed, monolithic, fluidized bed) it follows that the efficient, compact and intelligent reactor designs must be utilized to make an electrochemically promoted reactor commercially attractive.

The present review discusses a series of studies towards direct utilization of EP:

- i) the electrochemical promotion of a commercial NH_3 synthesis catalyst,
- ii) the bipolar electrochemical promotion using a YSZ monolithic reactor,

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iii) the development of a bipolar EP unit for the electropromotion of a particulate matter (soot) combustion and

iv) the development of the novel monolithic electro-promoted reactor (MEPR), in conjunction with the electro-promotion of 40-50 nm thick sputtered metal films.

RESULTS AND DISCUSSION

Electrochemical promotion of an industrial NH_3 synthesis catalyst

One of the first attempts to electro-promote a commercial catalyst was reported by Yiokari *et al.* [10] for the NH_3 synthesis. The catalytic synthesis of ammonia from its elements *via* the Haber-Bosch process is of major industrial importance, and the high pressure synthesis is catalyzed by Fe promoted with K_2O , CaO and Al_2O_3 . In that study, a commercial fully pro-

moted Fe-based catalyst (BASF S6-10RED) was used, deposited on $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\alpha}$, a proton conducting solid electrolyte. The catalyst was milled and deposited *via* slurry. Since the commercial Fe-based catalyst is electronically conducting, as it is not supported on an insulating support (*e.g.* SiO_2 , Al_2O_3), it was found that this catalyst film deposited on the H^+ conductor had sufficient conductivity to also act as an electrode of the solid electrolyte cell.

This electrochemical promotion study was novel in three respects: a) the catalyst electrode was a fully promoted industrial catalyst, b) the study was carried out at high pressure (50 atm) and c) this was the first attempt for the scale-up of an electrochemically promoted reactor since 24 $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\alpha}$ cell-pellets, electrically connected in parallel, were placed in the high pressure reactor (Fig. 1) [10].

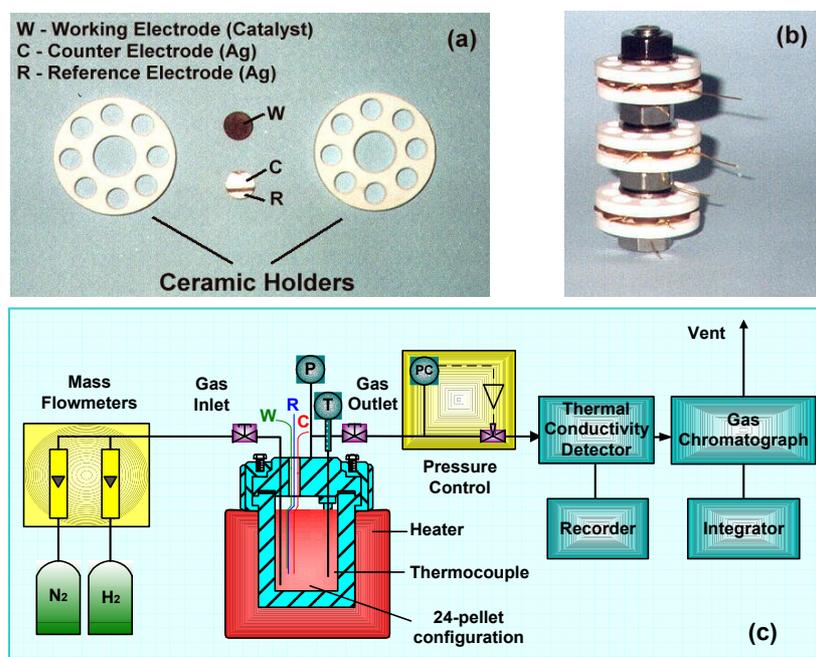


Fig. 1. Experimental set-up. (a) Machinable ceramic holders and two proton conducting pellets showing the location of catalyst, counter and reference electrodes; (b) twenty-four pellet unit; (c) high-pressure reactor, gas feed and analysis unit [10].

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The rate of ammonia production was enhanced by more than 1100 % in the nitrogen rich regime (Figs. 2 and 3), upon a potential application of -1.0 V between the working electrode and the Ag reference electrode. The extent of the NEMCA effect depends strongly on the kinetic regime of the reaction. Very pronounced non-faradaic behavior is observed in the regime $0.33 \leq \text{H}_2/\text{N}_2 \leq 0.67$ where ρ values of 12 or more are obtained.

The enhancement in the catalytic activity is due to the electrochemical supply of H^+ to the catalyst

which decreases the catalyst work function and thus strengthens the chemisorptive bond of the electron acceptor N while at the same time weakening the bonds of the electron donor H and NH_3 .

Electrochemical promotion using a bipolar monolithic reactor

The pioneer work of Marwood and Vayenas has demonstrated that a direct electrical contact, *via* a metal wire, to the catalyst electrode is not necessary to induce the effect of the electrochemical promotion

[11]. It was found that it suffices to apply the potential, or current, between two terminal electrodes which may, or may not, be catalytically active. This experimental set-up comprises the bipolar or "wireless" NEMCA design concept [11-14]. The concept appears to be very similar to that of the "bipolar" design used now routinely in aqueous electrochemistry. The implications of this discovery for electrochemical promotion are quite significant since it shows that, at least in principle, the design of an electrochemically promoted reactor can become much simpler than that of a fuel cell.

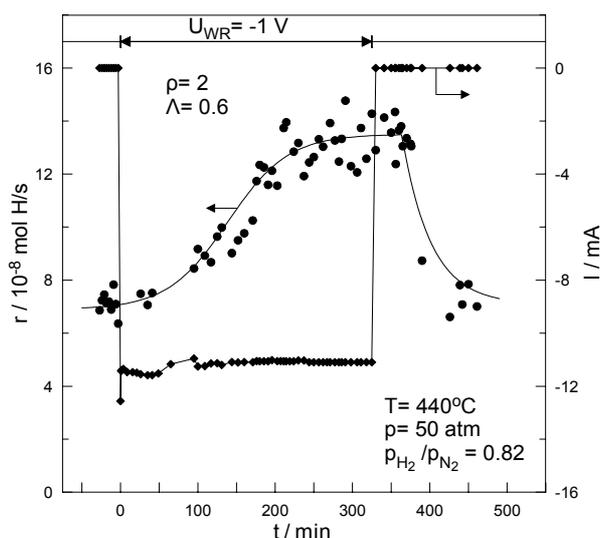


Fig. 2. Ammonia synthesis rate and current response to a step change in the catalyst potential U_{WR} of the promoted $\text{Fe}/\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\delta}$ catalyst [10]. Reprinted with permission from the American Chemical Society.

The first attempt to impose NEMCA in a bipolar configuration was realized by utilizing multi-stripe and multi-dot [13] Pt catalysts placed between two Au terminal electrodes on YSZ for the C_2H_4 oxidation reaction. In this case, large terminal voltages (of the order of 30 V) are applied between the two Au electrodes, so that the potential difference in each individual cell formed between the Pt stripes or dots is of the order of 1 V. The Pt films become "bipolar" electrodes as half of them are polarized anodically, while the other half are polarized cathodically. This can easily explain the smaller ρ values as compared with those obtained in classical electrochemical promotion experiments (Fig. 4).

A brilliant demonstration of the bipolar design concept came from the group of Comninellis at EPFL (Fig. 5) [12]. A monolith was made from YSZ and the surface of the monolith channels was covered with a RuO_2 catalyst (Fig. 5, inset). Two terminal Au electrodes were deposited on the outside surface of the

monolith. The potential application between the two terminal Au electrodes was found to induce NEMCA on the RuO_2 catalyst which is not in electrical contact with any metal wire [12]. The faradaic efficiency, Λ , values for C_2H_4 oxidation are on the order of 103, while C_2H_4 conversion could be enhanced from 35 to 50 % (Fig. 5) [12].

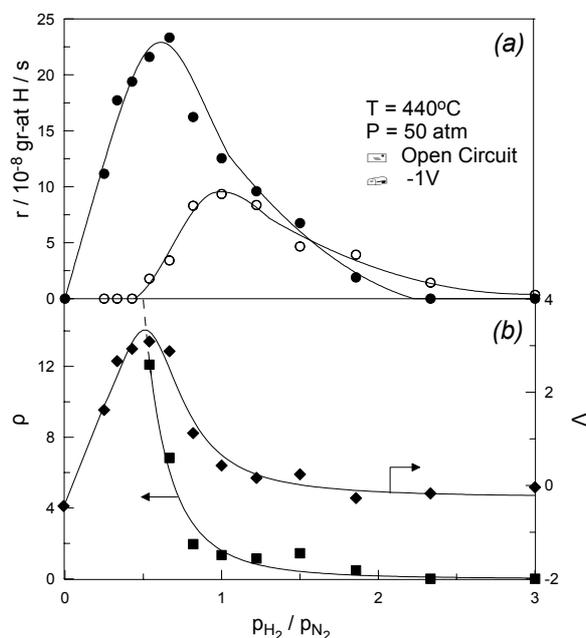


Fig. 3. (a) Effect of inlet H_2/N_2 ratio on the rate of NH_3 synthesis over promoted $\text{Fe}/\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\delta}$ under open-circuit (O) and for $U_{WR} = -1.0$ V (●); (b) corresponding ρ (r/r_0) (■) and Λ ($= \Delta r_H / (-I/F)$) (◆) values [10]. Reprinted with permission from the American Chemical Society.

Recently, a novel configuration using a mixed ionic-electronic conducting (MIEC) support has been developed by Poulidi *et al.* for use in electrochemical promotion experiments [15-17]. The mixed conductivity of the support eliminates the need for an external circuit. In this system, the polarization is achieved by the use of an appropriate sweep gas that creates a chemical potential difference across the membrane. In analogy with a classic EPOC experiment where the promoter is driven by the application of an over-potential across the membrane-support, the principle of the operation of this wireless configuration lies in the use of the oxygen sweep on one side of the reactor which creates the necessary oxygen chemical potential difference that drives the oxygen ion promoters across the membrane and ensure the supply of these promoters to the catalyst. The initial results on mixed oxide-ion-electronic and protonic-electronic conductors showed the feasibility of the wireless configuration of EPOC experiments, while the significant rate changes were obtained [15-17].

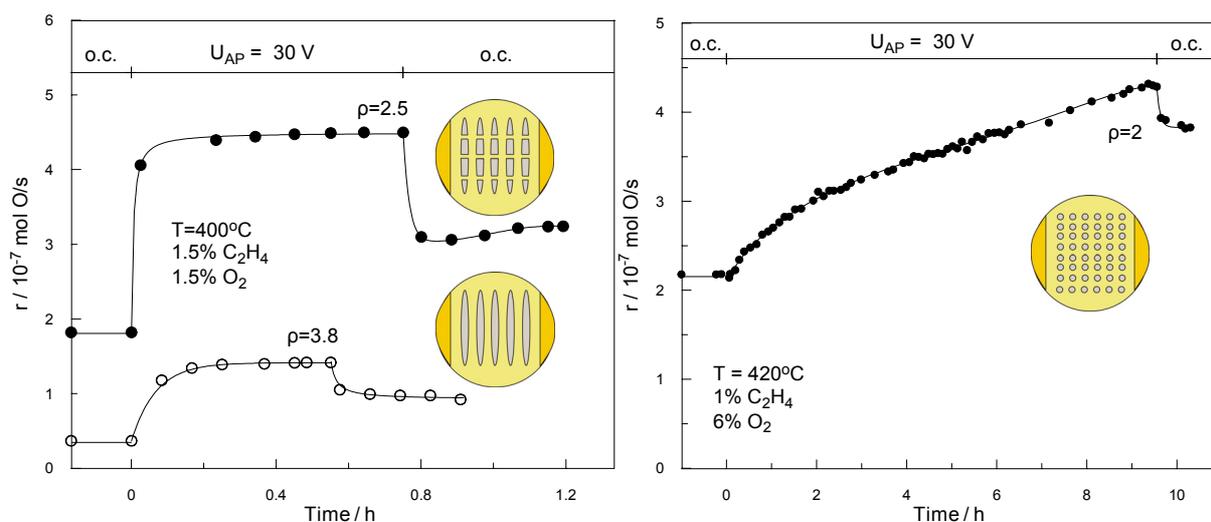


Fig. 4. Transient effect of an applied potential, U_{AP} , between the two terminal gold electrodes (30 V) on the catalytic rate of ethylene oxidation (expressed in mol O/s) for dotted (filled circles) and multi-stripped (open circles) platinum configuration (a) and for a multi-dotted platinum configuration (b) [13]. Reprinted with permission from Elsevier Science.

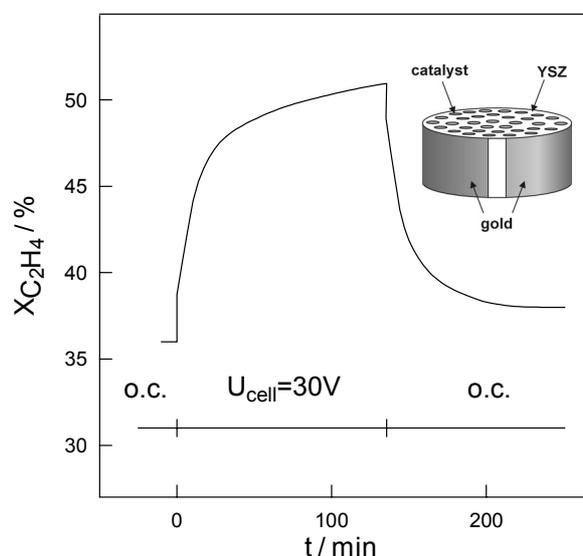


Fig. 5. Temporal evolution of the ethylene conversion in the multiple-channel RuO_2/YSZ cell during a potentiostatic step of $U_{cell} = 30$ V. OC: open-circuit. Feed composition: $C_2H_4:O_2/0.2:12$, $F_v = 175$ cm³ STP/min, $t = 360$ °C; inset: channel electrochemical cell termed bipolar configuration of second generation [12]. Reprinted with permission from The Electrochemical Society.

Electrochemical promotion of particulate matter (soot) combustion using a ceria-gadolinia solid electrolyte and a dispersed perovskite catalyst

A significant step for the commercialization of bipolar electrochemically promoted units has been made by Christensen, Larsen and coworkers at Dinex Filter Technology A/S in Denmark [18,19]. The goal was the development of an efficient catalyst system for the after-

-treatment of Diesel exhausts. This is one of the most challenging problems of the current catalytic research. The main pollutants in Diesel exhausts are NO_x and a particulate matter (PM), mostly soot, with lesser amounts of CO and light hydrocarbons (CH). Table 1 shows the needed conversion efficiency of an electrochemically promoted unit in order to meet the corresponding EURO4 2005 emission standards.

Table 1. Needed conversion efficiency of the electrochemically promoted unit in order to meet the EURO4 2005 standards

Given:	EURO2 Engine
Wanted:	EURO4 Engine
Necessary conversion rates	
CH:	Not critical
CO:	Not critical
PM:	> 87 %
NO_x :	> 50 %

The laboratory prototype of the Dinex electrochemically promoted catalyst unit is shown in Fig. 6a and the assembled unit schematically in Fig. 6b. It consists (Fig. 6c) of a tubular bundle porous (ceramic foam) structure made of $CeO_2-Gd_2O_3$ (CGO) which is an O^{2-} conductor with the ionic conductivity significantly higher than YSZ at temperatures below 500 °C. The active catalyst-electrocatalyst deposited on the CGO structure is based on $LaSrMnO_3$ (LSM), the mixed conducting material used for SOFC cathodes. Electrical potential (~30 V) is applied between two terminal Ag electrodes deposited on the CGO solid electrolyte. The unit was tested on a commercial Diesel engine, while the test parameters and results are

shown in Tables 2 and 3, respectively. The reactor performance is excellent regarding soot (particulate matter) combustion but not yet satisfactory regarding NO_x reduction. From the published data of Tables 2 and 3, and assuming that 80 % of the particulate matter mass consists of C atoms, one calculates a Faradaic efficiency, Λ , of 66. This is the first demonstration of electrochemical promotion on a pre-commercial unit tested on a real Diesel engine.

The results are very encouraging, and show that, as expected, the power consumption of the electrochemically promoted unit, which is promotional to Λ^{-1} , is negligible in comparison to the Diesel engine power output (Table 2). This work demonstrates the great potential of electrochemical promotion for practical applications. The first fifty Dinex units were sold in 2001.

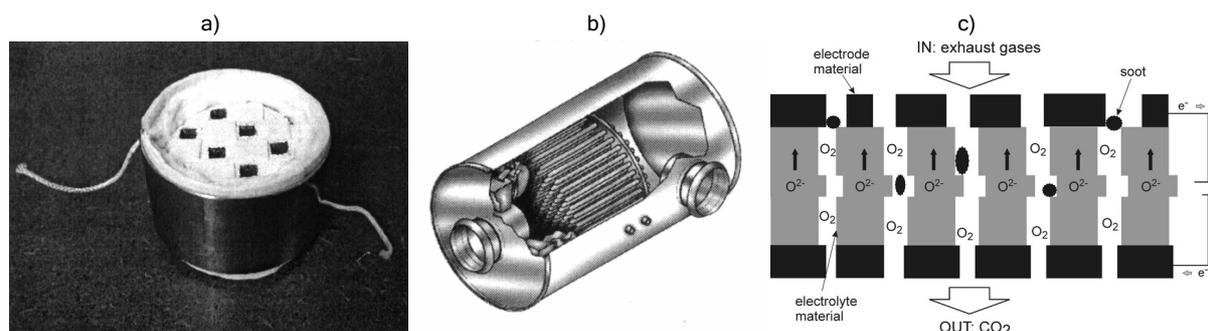


Fig. 6. (a) Near full scale monolithic Dinex reactor for electrochemically promoted soot combustion; (b) sketch of Dinex electrochemically promoted reactor constructed from single tubes; (c) principle of the electrochemically promoted Dinex reactor [18, 19]. Reprinted with permission from the Society of Automotive Engineers.

Table 2. Parameters for part stream test of reactor on bench engine

Parameter	Magnitude
Engine power	18 kW
Reactor flow	200-250 l/min (20 % of total exhaust flow)
Back pressure	8 mbar
Reactor volume	1.2l
Reactor voltage	30 V
Reactor current	250 mA
Reactor power	7.5 W
Reactor power consumption (% of engine power)	0.2 % (compensated for part flow)

Table 3. Conversion rates for near full scale reactor measured on 1.8 l test engine. Conversion rates in % of raw material

PM	90
CO	50
CH	50
NO_x	10

Electropromotion of thin sputtered metal catalysts and development of the novel monolithic electrochemically promoted reactor (MEPR)

A major thrust towards practical utilization of electrochemical promotion was realized through: a) the confirmation of the feasibility of electropromotion of thin sputtered metal films [20,21] and b) the development of the monolithic electrochemically promoted reactor (MEPR) [2,21,22]. Sputtered metal films on untreated YSZ surfaces, with a thickness of 40-50 nm,

were reported to have a metal dispersion higher than 10-20 % [21], which is comparable to that of state-of-the-art conventional supported catalysts. The performance of these films is remarkable not only in terms of electrochemical promotion efficiency but also in reference to long term stability and endurance. On the other hand, the recently developed MEP reactor [21] provides a practical, structured, electrochemically promoted reactor which, in principle, allows the transition from laboratory studies to practical applications. The MEP reactor can be considered as a hybrid between a classical monolithic honeycomb reactor and a planar solid oxide fuel cell [23]. The core of the MEPR is a ceramic casing, made of machinable glass ceramic (Macor[®]TM). The internal faces of the two opposing reactor walls have appropriately machined parallel grooves where a number of solid electrolyte plates are inserted. These surfaces are also used to create the two necessary current collectors, one establishing an electrical contact with all catalyst films deposited on the top side of the plates, while the other current collector establishes an electrical contact with all catalyst films deposited on the bottom side of the plates. In this way, a significant practical simplification is realized as both the top and bottom catalyst films can be electrochemically promoted (with reverse polarity) *via* only two external connecting wires.

The reactor is enclosed in a suitable metal casing of stainless steel with a baffling system at the gas entrance aiming to achieve as uniform a gas flow distribution as possible at the gas entrance. A schematic of the assembled MEPR is shown in Fig. 7.

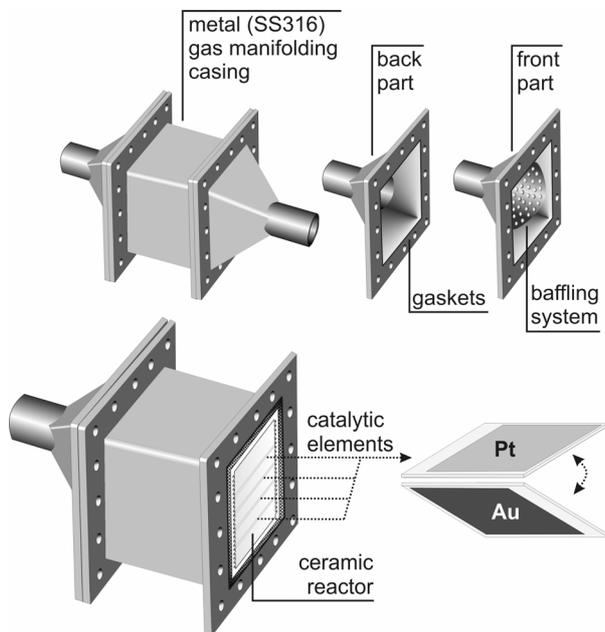


Fig. 7. Schematic of the assembled monolithic electropromoted reactor (MEPR) [25]. Reprinted with permission from Springer.

The MEP reactor is a simple device that permits the easy practical utilization of electrochemical promotion. It accomplishes an efficient and compact reactor design, which can be assembled and dismantled at will, has only two external connecting wires and its catalytic plates can be replaced whenever necessary. It exhibits excellent mechanical and thermal stability enabling its use under harsh environments, such as in a car engine exhaust. Furthermore, it is possible to use one of the plates as a gas sensor element and utilize the potential signal generated by this element to dynamically control the current or the potential applied to the electro-promoted catalytic plates.

The electro-promoted reactor has already been evaluated successfully for hydrocarbon oxidation and NO reduction by C_2H_4 in the presence of O_2 using both conventional thick films and thin sputtered noble metal electrodes [2,21,22,24-26]. Specifically, the MEPR with twenty-two Rh/YSZ/Pt parallel plate elements was found to promote a selective catalytic reduction (SCR) of NO by 450 % with near 100 % selectivity to N_2 , even in high excess of O_2 (10 %) at temperatures 200-300 °C (Fig. 8) [26]. The corresponding Λ_{NO} and Λ_{CO_2} values were up to 2.4 and 350, respectively, and the rate enhancement ratio of the complete C_2H_4 oxidation was up to 900 % (Fig. 9) [26].

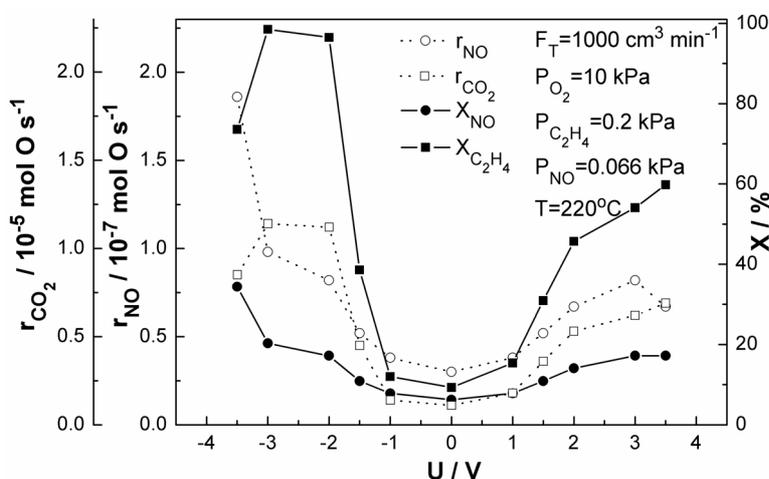


Fig. 8. Steady state effect of the applied potential on the NO conversion rate (r_{NO}), on the CO_2 formation rate (r_{CO_2}) and on the conversion of NO and C_2H_4 (X_{NO} , $X_{C_2H_4}$) at $t = 220$ °C and highly oxidizing conditions [26]. Reprinted with permission from Springer.

The monolithic electro-promoted reactor was also tested under real conditions for the treatment of an automotive exhaust gas of a diesel engine [27] demonstrating excellent mechanical and thermal stability after a prolonged operation at flow rates as high as $56 \text{ dm}^3 \text{ min}^{-1}$ (mean gas residence times of 0.34 s and reactor space velocities up to $2.7 \times 10^4 \text{ h}^{-1}$). The MEP reactor can, conceptually, be scaled-up (or scaled-down) following a stack design and, in principle,

can be used for many practical applications in exhaust treatment units and in the chemical destruction or synthesis processes.

PERSPECTIVES IN HYDROGEN PRODUCTION AND UTILIZATION

While electrochemical promotion has mostly applied to oxidation reactions, there is a plethora of

studies on hydrogenation and hydrogenation reactions [1,28-31]. Among these studies, CO_2 and CO hydrogenation for the production of alcohols and other oxygenated products appear to be of a considerable technological interest. Due to the constantly increasing atmospheric levels of CO_2 , resulting from the combustion of fossil fuels, and the concomitant alarming environmental effects, the one-step hydrogenation of CO_2 to clean transportation fuels is currently one of the major technological challenges of the heterogeneous catalysis. However, so far no catalytic systems have been identified for the efficient one-step conversion of CO_2 to hydrocarbons. Preliminary results [1,31] indicate that there is a significant promise in the selective electropromotion of CO_2 hydrogenation. The successful implementation of electrochemical promotion and EPOC-based catalytic units for the CO_2 hydrogenation are expected to be highly active, selective and durable and hopefully will thus improve the prospects of recycling CO_2 as a C-source for chemicals and fuels using renewable sources of energy.

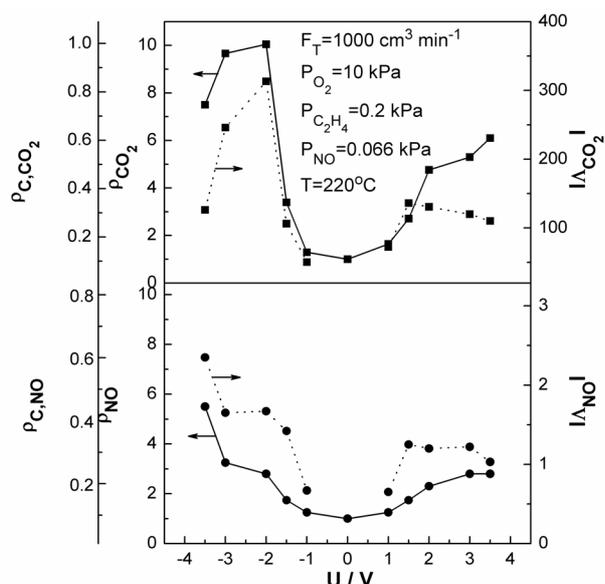


Fig. 9. Steady state effect of the applied potential on the rate enhancement ratio (ρ), on the effective enhancement ratio (ρ_e) and on the apparent Faradaic efficiency (Λ) for CO_2 formation and NO conversion at $t = 220^\circ\text{C}$ and highly oxidizing conditions [26]. Reprinted with permission from Springer.

Hydrogen-fueled PEM fuel cells are considered as one of the most promising means of producing energy in the future. One of the major issues in PEM fuel cell market penetration is related to a hydrogen production. For the short and medium term, the hydrogen production from hydrocarbons or alcohol seems to be the most feasible alternative. However,

during the hydrogen production from these sources, carbon monoxide is formed as well. Even after a thorough treatment of thus produced hydrogen, small traces of CO (in ppm levels) remain in the hydrogen stream which adsorb on the anode and lead to CO -poisoning, thus impairing significantly the cell performance. Electrochemical promotion may offer an alternative tool for the purification of H_2 streams for use in PEM fuel cells through the electropromotion of the water-gas-shift reaction or through EP enhancement of the selectivity of preferential oxidation of CO . Recent studies have proven that this possibility is viable [32].

Fuel cell applications extend beyond power generation, and the introduction of electrochemically promoted organic isomerization reactions at PEFC cathodes by Smotkin and co-workers, extended NEMCA to non-redox reactions [33-35]. More recently, the same group [36] presented the concept of "chemical transistors" based on spillover protons delivered as a base current to the effective double layer of Nafion encased Pd catalysts, creating a new prospect for the development of an area of synthetic chemistry that uses Nafion "wired" spillover protons for catalyzed organic transformations.

CONCLUSIONS

Electrochemical promotion has been proven to be a general phenomenon not limited to any particular electrolyte, conductive catalysts or a type of the reaction. Recent findings on the use of bipolar configurations, the electropromotion of commercial catalysts or highly dispersed metal films, and the development of monolithic electropromoted reactors open new perspectives towards practical utilization of EP. Several aspects related to durability, useful lifetime, electrolyte and stack cost minimization, scale-up and scale-down have not yet been addressed in any detail, but there is already a strong industrial interest and involvement, and the the years to come are likely to lead to commercialization of some electropromoted reactors and processes. Hydrogen production and utilization may be one of the niche market where EP can find an open field for industrialization.

REFERENCES

- [1] C. G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda and D. Tsiplakides, in *Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion and Metal-Support Interactions*, Kluwer Academic/Plenum Publishers, New York, 2001

- [2] D. Tsiplakides, S. Balomenou, A. Katsaounis, D. Archonta, C. Koutsodontis and C. G. Vayenas, *Catalysis Today* **100** (2005) 133
- [3] A. Wieckowski, E. Savinova and C. G. Vayenas, in *Catalysis and Electrocatalysis at Nanoparticles*, Marcel Dekker, New York, 2003.
- [4] C. G. Vayenas, S. Bebelis, S. Neophytides and I. V. Yentekakis, *Appl. Phys. A* **49** (1989) 95
- [5] H.-G. Lintz and C. G. Vayenas, *Angew. Chem. Int. Ed.* **28** (1989) 708
- [6] C. G. Vayenas, M. M. Jaksic, S. Bebelis and S. G. Neophytides, in *Modern Aspects of Electrochemistry*, J. O'M. Bockris, B. E. Conway and R. E. White, Eds., Kluwer Academic/Plenum Publishers, New York, 1996
- [7] C. G. Vayenas, S. Bebelis, I. V. Yentekakis and H.-G. Lintz, *Catalysis Today* **11** (1992) 303
- [8] C. G. Vayenas, S. Bebelis and C. Kyriazis, *CHEMTECH* **21** (1991) 500
- [9] M. Marwood, C. G. Vayenas, *J. Catalysis* **178** (1998) 429
- [10] C. G. Yiokari, G. E. Pitselis, D. G. Polydoros, A. D. Katsaounis, C. G. Vayenas, *J. Phys. Chem.* **104** (2000) 10600
- [11] M. Marwood and C. G. Vayenas, *J. Catalysis* **168** (1997) 538
- [12] S. Wodiunig, F. Bokeloh, J. Nicole, C. Comninellis, *Electrochem. Solid State Lett.* **2** (1999) 281
- [13] S. Balomenou, G. Pitselis, D. Polydoros, A. Giannikos, A. Vradis, A. Frenzel, C. Pliangos, H. Putter, C. G. Vayenas, *Solid State Ionics* **136-137** (2000) 857
- [14] S. Wodiunig, F. Bokeloh, Ch. Comninellis, *Electrochim. Acta* **46** (2000) 357
- [15] D. Poulidi, A. Thursfield, I. S. Metcalfe, *Topics Catalysis* **44** (2007) 435
- [16] D. Poulidi, G. C. Mather, I. S. Metcalfe, *Solid State Ionics* **178** (2007) 675
- [17] D. Poulidi, C. Anderson, I. S. Metcalfe, *Proceedings of the 1st International Conference on the Origin of EPOC (OREPOC)*, Thessaloniki, Greece, 2008
- [18] H. Christensen, J. Dinesen, H. H. Engell, K. K. Hansen, *SAE Paper 1999-01-0472*, 1999
- [19] H. Christensen, J. Dinesen, H. H. Engell, L. C. Larsen, K. K. Hansen, E.M. Skou, *SAE Paper 2000-01-478*, 2000
- [20] E. A. Baranova, A. Thursfield, S. Brosda, G. Foti, Ch. Comninellis, C. G. Vayenas, *J. Electrochem. Soc.* **152** (2005) E40
- [21] S. Balomenou, D. Tsiplakides, A. Katsaounis, S. Thiemann-Handler, B. Cramer, G. Foti, Ch. Comninellis, C. G. Vayenas, *Appl. Catalysis B* **52** (2004) 181
- [22] S. P. Balomenou, D. Tsiplakides, A. Katsaounis, S. Brosda, A. Hammad, G. Foti, Ch. Comninellis, S. Thiemann-Handler, B. Cramer, C. G. Vayenas, *Solid State Ionics* **177** (2006) 2201
- [23] J. N. Michaels, C. G. Vayenas, L. L. Hegedus, *J. Electrochem. Soc.* **133** (1986) 522
- [24] S. P. Balomenou, D. Tsiplakides, C. G. Vayenas, S. Poulston, V. Houel, P. Collier, A. G. Konstandopoulos, C. Agrafiotis, *Topics Catalysis* **44** (2006) 481
- [25] A. Hammad, S. Souentie, S. Balomenou, D. Tsiplakides, J. C. Figueroa, C. Cavalca, C. J. Pereira, C. G. Vayenas, *J. of Appl. Electrochem.*, 2008, in press
- [26] S. Souentie, A. Hammad, S. Brosda, G. Foti, C. G. Vayenas, *J. Appl. Electrochem.*, 2008, in press
- [27] S. P. Balomenou, D. Tsiplakides, C.G. Vayenas, S. Poulston, V. Houel, P. Collier, A. G. Konstandopoulos, C. Agrafiotis, *Topics Catalysis* **44** (2007) 481
- [28] C. A. Cavalca, G. L. Haller, *J. Catalysis* **177** (1998) 389
- [29] A. Giannikos, P. Petrolekas, C. Pliangos, A. Frenzel, C. G. Vayenas, H. Putter, *Ionics* **4** (1998) 161
- [30] S. Tracey, A. Palermo, J. P. H. Vazquez, R. M. Lambert, *J. Catalysis* **179** (1998) 231
- [31] H. Karasali, PhD Thesis, University of Patras, 1994
- [32] F. M. Sapountzi, M. N. Tsampas, C. G. Vayenas, *Catalysis Today* **127** (2007) 295
- [33] L. Ploense, M. Salazar, B. Gurau, E. Smotkin, *Solid State Ionics* **136-137** (2000) 713
- [34] L. Ploense, M. Salazar, B. Gurau, E. S. Smotkin, *J. Am. Chem. Soc.* **119** (1997) 11550
- [35] M. Salazar, E.S. Smotkin, *J. Appl. Electrochem.* **36** (2006) 1237
- [36] E. S. Smotkin, *Proceedings of the 1st International Conference on the Origin of EPOC (OREPOC)*, Thessaloniki, Greece, 2008.

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**DR STELLA BALOMENOU**

She got a Chemical Engineering Degree from the University of Patras in 1999 and a PhD from the University of Patras in 2005. Her PhD Thesis supervised by Professor C. G. Vayenas involved the study of fundamental aspects of electrochemical promotion in conjunction with metal-support interactions, the development of monolithic electropromoted reactors and the introduction of triode fuel cell concept. Her latest scientific efforts focus on the practical utilization of the electrochemical promotion of catalysis and on its use for the enhancement of fuel cell efficiency. She has 11 refereed publications and holds 2 international patents.