THE USE OF SOFC FOR CHEMICAL COGENERATION AND FOR ELECTROCHEMICAL PROMOTION (NEMCA)

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ABSTRACT

Solid electrolyte galvanic cells offer two unique and potentially attractive possibilities. The first one is chemical cogeneration, i.e., the use of solid oxide fuel cells (SOFCs) with appropriate electrocatalytic anodes to simultaneously generate chemicals and electric power. The ratio of electric power to heat generated, as well as reactant conversion, can be conveniently controlled by varying the external resistive load.

The second potential application of solid electrolyte cells stems from the recently discovered effect of nonfaradaic electrochemical modification of catalytic activity (NEMCA). The NEMCA effect causes dramatic and reversible alterations in the catalytic properties of metal films interfaced with solid electrolytes via polarization of the metal/solid electrolyte interface. Non-faradaic steady state catalytic rate changes can be induced exceeding by up to $3 \times 10^5$ times the corresponding rate of ion transfer through the solid electrolyte, while significant changes in product selectivity have been also observed. SOFC-type reactors can thus be used to carry out catalytic reactions more effectively and under conditions of high selectivity to the desired products.

The cases of several catalytic or electrocatalytic systems under cogeneration and NEMCA conditions in SOFCs and SOFC-type reactors are presented here.
1. INTRODUCTION

Solid oxide fuel cell reactors have attracted the scientific interest for two main reasons. First, because they can be used as energy conversion systems able to convert chemical energy directly to electrical energy without the inherent Carnot type efficiency limitation present in conventional fuel combustion systems. Second, because they can be used to both study and influence catalytic phenomena on metals interfaced with solid electrolytes.

In recent years the above applications have been elaborated into two unique and potentially attractive possibilities which combine the concepts of a fuel cell and of a chemical reactor. The first one is chemical cogeneration (1), i.e. the simultaneous production in SOFCs of electric power and valuable chemicals and the second one, far more promising in our opinion, is the use of SOFC-type chemical reactors to carry out catalytic reactions under conditions of the newly discovered effect of non-faradaic electrochemical modification of catalytic activity (NEMCA effect), i.e., under conditions of electrochemically induced dramatic, reversible and controlled, to a large extent, enhancement of catalytic activity and selectivity to desired products, via polarization of the catalyst -solid electrolyte interface (2,3).

In contrast to conventional fuel cell applications (Figure 1a) where inexpensive chemicals are converted into low-value products while generating electrical power, in chemical cogeneration fuel cells the value of the product chemical itself is comparable to the value of the obtainable electrical energy (Figure 1b). The rather unique ability of SOFCs to coproduce chemicals and electrical power in an efficient manner stems from their high operating temperature which: (i) Decreases drastically the anodic and cathodic activation overpotential, that would very severely reduce the efficiency in a low temperature (e.g. aqueous solution environment) fuel cell (ii) Permits the use of anodes made of catalyst materials known to possess high activity and selectivity for the corresponding catalytic reactions in the same temperature range. In comparison to a conventional chemical reactor a cogenerative SOFC offers the advantages of no-mixing of fuel and oxygen in the gas phase, allowing in principle for significant reduction in reactor size by using higher pressures without flammability or explosion hazards and of simplified reactor control, as the electrical and thermal generation rates are controlled primarily by the external resistive load. However, the inherent complexity and higher capital cost investment of cogenerative SOFCs places stringent demands on their product selectivity and on the expected value of the electrical energy by-product, which must be comparable with the added value of the chemical product itself to make an
exothermic reaction attractive for chemical cogeneration (4). Reactions suitable for chemical cogeneration must be fairly exothermic, must involve inexpensive reactants and products and must be carried out at high temperatures (at least 800°C) in order for the SOFC capital cost to be reasonable (1,4). As a result, despite recent experimental progress, cogeneration is limited to a small number of reactions at least with the existing technology.

The application of SOFCs as chemical reactors under NEMCA effect conditions overcomes the above stringent requirements of cogenerative processes. The goal in this case, instead of power production, is the enhancement of the activity and selectivity of catalyst surfaces (Figure 1c). It is accomplished by interfacing a porous conductive catalyst film with a gas-impervious solid electrolyte in a cell of the type

\[
gaseous \text{ reactants, metal catalyst} \mid \text{solid oxide electrolyte} \mid \text{metal, O}_2
\]

and by applying a certain current or voltage to the cell with concomitant pumping of ions to or from the catalyst surface at a rate \(I/nF\), where \(F\) is Faraday’s constant and \(n\) is the charge of the ion. Under conditions of appearance of severe activation polarization at the gas/metal/solid electrolyte three-phase-boundaries, charged spillover species can be created there and forced to spread (spillover) onto the gas-exposed catalyst surface altering its work function (2,3,5) and concomitantly the strengths of chemisorptive bonds (3,6), thus inducing drastic changes in catalytic activity and selectivity. The induced catalytic rate changes are non-faradaic, i.e. they can exceed by orders of magnitude the corresponding rate on ion transfer through the solid electrolyte. Catalytic rate changes up to \(3 \times 10^5\) times larger than the rate of ion transfer through the solid electrolyte and up to a factor of 200 larger than the regular (open circuit) catalytic rate have been measured so far (3,7-15). Significant changes in product selectivity have been also observed. The NEMCA effect is actually an in situ, reversible and to some extent controllable "electrochemical promotion" (16) which has been studied in over twenty catalytic systems using Pt, Pd, Ag, Rh and Ni films interfaced with \(\text{Y}_2\text{O}_3\) doped \(\text{ZrO}_2\) and \(\beta''\text{-Al}_2\text{O}_3\) solid electrolytes.

The common features of all previous NEMCA studies have been summarized in detail elsewhere (3,9). One of the central findings of the NEMCA effect is that over wide ranges of the ohmic-drop-free catalyst potential \(V_{WR}\) with respect to a reference electrode, catalytic rates depend exponentially on \(V_{WR}\) and on work function of the gas exposed catalyst surface (2,3), while the catalytic relaxation time constants during galvanostatic transients are of the order of \(2FN/I\) where \(I\) denotes the current and \(N\), expressed in g-atoms, the catalytic surface area.
The latter observation shows that NEMCA is not an electrocatalytic phenomenon restricted to the three phase boundaries but a catalytic one taking place over the entire gas-exposed catalyst surface.

Another general observation regarding NEMCA is that the order of magnitude of the rate enhancement factor $\Lambda$ defined from

$$\Lambda = \Delta r(\text{catalytic})/(I/nF) \tag{1}$$

where $\Delta r$ (catalytic) is the change in the rate of the catalytic reaction and $I/nF$ is the rate of ion transport to or from the catalyst, can be estimated from

$$\Lambda = 2Fr_0/I_0 \tag{2}$$

where $I_0$ is the exchange current density of the gas-catalyst-solid electrolyte three-phase-boundary and $r_0$ the open-circuit (regular) catalytic rate. This means that, contrary to conventional fuel cell applications, one needs highly polarizable interfaces (low $I_0$ values) in order to obtain high $\Lambda$ values, i.e. in order to observe the NEMCA effect.

The non-faradaic nature of NEMCA means that small currents are required to induce large changes in catalytic activity which permits SOFC-reactor operation at temperatures as low as 200°C, thus covering the temperature range of most catalytic processes. In addition the cost of energy sacrificed in NEMCA SOFC-reactors is negligible in comparison with the value of the chemicals produced (4).

In conclusion, SOFC-type reactors operating under the conditions of NEMCA effect can be effectively used as chemical reactors for carrying out catalytic reactions at conditions of high activity and selectivity.

In the present paper we demonstrate some features of cogenerative processes and of NEMCA effect studies in SOFC-type reactors, focusing on recently investigated catalytic systems, i.e. the methanol anodic oxidation on Cu, the CO oxidation on Pt and the oxidative coupling of CH$_4$ on manganese oxide.

2. EXPERIMENTAL

The atmospheric pressure, continuous flow SOFC reactor used in this study and shown in Figure 1d, has been described elsewhere (8-11) along with details of
catalyst preparation and characterization, flow system set-up, and product analysis. The three electrode configuration shown in Figure 1d in conjunction with the current interruption technique permits accurate determination of the catalyst ohmic-drop-free potential $V_{WR}$ and of the overpotential $\eta = V_{WR} - V_0^c$ ($V_0^c$ is the open circuit catalyst potential) (10,11), either in the case of cogeneration (Figure 1b) or in the case of NEMCA studies (Figure 1c). Porous catalyst films used were typically 5 to 10 $\mu$m thick, had superficial surface areas of 1 to 2 cm$^2$ and true surface areas on the order of 50 to 500 cm$^2$ as measured by a surface titration technique (3,13).

3. RESULTS AND DISCUSSION

1. Chemical cogeneration: The oxidation of CH$_3$OH to H$_2$CO on a copper anode

The anodic oxidation of methanol was investigated at temperatures 550 to 650°C in the fuel cell:

$$\text{CH}_3\text{OH}, \text{products, CulZrO}_2(9\%\text{mol Y}_2\text{O}_3)\text{Ag, air}$$

and for CH$_3$OH partial pressures between 1 and 8 kPa. Under open circuit conditions the copper anode catalyzes the dehydrogenation of CH$_3$OH to H$_2$CO and CO with a selectivity to H$_2$CO of about 90%. The dehydrogenation reactions obey simple Langmuir type kinetics and their rates are proportional to the surface coverage of methanol as in the case of methanol dehydrogenation on Ag (17).

Under closed circuit, i.e. chemical cogeneration, conditions copper acts as a selective electrocatalyst for methanol electro-oxidation to H$_2$CO with main by-products CO and CO$_2$. The selectivity $S_{H_2CO}$ to formaldehyde is only slightly affected by current. As shown on Figure 2 the rate of H$_2$CO formation equals, within experimental error, the rate $I/2F$ of O$_2^-$ supplied spontaneously through the solid electrolyte, according to the electrocatalytic reaction:

$$\text{CH}_3\text{OH} + \text{O}_2^- \rightarrow \text{H}_2\text{CO} + \text{H}_2\text{O} + 2\text{e}^- \quad [3]$$

which is the dominant overall electrocatalytic reaction. The same figure shows the current-voltage characteristics of the cell. The cogenerated electric power output of the
fuel cell was typically on the order of 4 mW/cm² of solid electrolyte.

Although this power output is two orders of magnitude lower than maximum power output obtained with state-of-the-art solid oxide fuel cells operating on H₂ as the fuel, due to differences in solid electrolyte thickness, electrode morphology and composition and operating temperature, the system demonstrates the technical feasibility of oxidizing CH₃OH to H₂CO on copper anodes with simultaneous generation of electricity, as in the case of Ag anodes (17) where the results were similar. The use of copper-cermets to increase the exchange current density value and concomitantly decrease activation overpotential losses in conjunction with the use of thin solid electrolyte components to limit ohmic losses could allow for future technical applications.

2. NEMCA studies in SOFC-reactors

2a. CO oxidation on Pt/[β”-Al₂O₃] : The reaction was studied at temperatures 330 to 450°C and P₂O₅/P CO ratios from 0.1 to 100. The open-circuit kinetic behaviour was found to be similar to the case of CO oxidation on Pt/ZrO₂ (9mol% Y₂O₃) (18), i.e., Langmuir-Hinshelwood type behaviour (Figure 3). Changing catalyst potential VWR and thus, as shown in earlier studies (2,3,5), catalyst work function eΦ causes non-faradaic rate changes, which are quite pronounced for positive overpotentials (sodium ion removal from the catalyst). The observed rate increases could exceed the rate of ion transfer through the solid electrolyte by up to 10⁴. As shown in Figure 3 the location of the rate maximum, which corresponds to roughly equal coverages of CO and oxygen, is affected with changing catalyst potential or equivalently catalyst work function eΦ, indicating changes in the strength of the CO and oxygen chemisorptive bonds. Such bond strength changes have been also observed in the case of stabilized zirconia as solid electrolyte causing the volcano type behaviour shown in Figure 4 (3). This behaviour can be interpreted in the usual way, i.e., increasing eΦ decreases the binding strengths of chemisorbed reactants which both behave as electron-acceptors, thus enhancing their reaction rate, until the point is reached where the coverages of chemisorbed reactants become very low and the rate starts to decrease. Induction and modification of oscillatory states has been also observed (Fig. 5).

2b. CH₄ oxidative coupling on MnOₓ/ZrO₂ (9% mol Y₂O₃) : The oxidative coupling of methane is a reaction particularly attractive for NEMCA application in SOFC chemical reactors, because of the enormous interest for the production of C₂-hydrocarbons from natural gas. It has been the focal point of numerous studies in
recent years, in some of which solid electrolyte cells have been used as well (19-21).

The effect of NEMCA on catalyst activity and selectivity to C2-hydrocarbons has been studied for this reaction using manganese oxide as catalyst-working electrode in a solid electrolyte cell reactor of the type:

\[ \text{CH}_4, \text{O}_2, \text{MnO}_x | \text{ZrO}_2(9\text{mol}\% \text{Y}_2\text{O}_3) | \text{Pt, air} \]

This is the first time an oxide catalyst is used in NEMCA studies and manganese oxide has been selected as it exhibits significant activity for this reaction (22) and adheres well on stabilized zirconia substrates.

The main products of the reaction were CO2, C2H4 and C2H6 both under open and closed circuit conditions. The open-circuit selectivity to C2 hydrocarbons is near 97% at low CH4 conversions (Fig. 6b).

Application of positive overpotentials, i.e. pumping of O2- to the catalyst surface, causes an enhancement of all the catalytic rates, which for the case of CO2 can exceed the open circuit (regular) catalytic rate by up to a factor of 20,000% (Figure 6a). These rate increases were accompanied by a decrease in the selectivity to C2-hydrocarbons, specifically in selectivity to C2H6 (Figure 6b). Nevertheless the C2- yield increased with increasing catalyst potential or equivalently catalyst work function by up to 250%.

Negative current application, i.e. O2- removal from the catalyst, had practically no effect on rates and selectivity.

The experimental observations of the above NEMCA studies, as well as all of previous ones, can be adequately explained by a semiquantitative model based on a macroscopically uniform change of the catalyst work function caused by an electrochemically induced spillover of ions onto the catalyst surface and on the concomitant change in the strength of chemisorptive bonds of covalently bonded reactants and reaction intermediates (2,3,5-15). The creation of such spillover ions, which are accompanied by their compensating charge in the metal, thus forming spillover dipoles, depends solely on the presence of significant activation overpotential, and is not restricted to any particular catalyst-solid electrolyte system. It has been explained theoretically (3,10,11) and confirmed experimentally (2,5) by means of a Kelvin probe that the induced work function change is equal to e\(\eta\), where \(\eta\) is the activation overpotential. The change of catalyst work function causes the strengths of chemisorptive bonds to change significantly. Thus, the early semiempirical relation of Boudart (6) predicts a linear variation in heats of adsorption with changing e\(\Phi\). Similar trends can be extracted from the more modern theoretical considerations of
Shustorovich (23). If the rate limiting step of a catalytic reaction involves cleavage of a metal/adsorbate bond, it is expected, provided that the nature of the activated complex is not changing, that the rate of the reaction will change exponentially with changing heat of adsorption of the adsorbate (-ΔH_{ad}) and consequently with eΔΦ.

In the case of CO oxidation on Pt interfaced with β'-Al₂O₃, positive current application, i.e., removal of sodium ions from the catalyst surface, causes an increase in work function eΦ and a weakening in the Pt-O and Pt-CO bonds, since both adsorbates behave as electron acceptors. The behaviour presented on Figure 3 seems to indicate that the effect of changing eΦ on strength of the Pt-CO bond is even more pronounced than in the case of the Pt-O bond (24).

The results of the NEMCA study of CH₄ oxidative coupling on Pt/ZrO₂ (9mol% Y₂O₃) can be also qualitatively explained according to the basic principles of the NEMCA effect. Nevertheless due to the slow kinetics of CH₄ activation and the concomitantly high operating temperature and exchange current I₀, direct electrocatalysis and gas-phase homogeneous reactions play, in addition to NEMCA, an important role in the observed closed-circuit kinetic behaviour (25).

4. CONCLUSIONS

SOFCs can be effectively used to cogenerate electric power and valuable chemical products as well as to carry out catalytic reactions at conditions of high catalyst activity and selectivity via NEMCA effect application.

The NEMCA effect allows for control at will of the work function of catalyst films interfaced with solid electrolytes and this causes dramatic, reversible and to a large extent controllable enhancements of catalytic activity and selectivity, i.e. it permits an in situ electrochemical promotion of catalyst surfaces.

The feasibility of the above processes has been demonstrated for various catalyst systems.

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Figure 1: Operating principle of (a) a solid oxide fuel cell, (b) a chemical cogenerator (c) a NEMCA catalytic reactor, for an oxygen ion conducting solid electrolyte e.g. ZrO$_2$ (9mol% Y$_2$O$_3$) (d) Solid electrolyte catalytic reactor for cogeneration and NEMCA studies.
Figure 2: Oxidation of CH$_3$OH on a Cu anode in a ZrO$_2$ (9mol% Y$_2$O$_3$) fuel cell: Effect of cell current on the rate $r$ of H$_2$CO production and current-cell voltage plot. P$_{CH_3OH}=7$ kPa.

Figure 4: NEMCA generated volcano plots by increasing the catalyst work function $\phi$ or equivalently catalyst potential $V_{WR}$ above its open-circuit value during CO oxidation on Pt/ZrO$_2$(9mol% Y$_2$O$_3$); P$_{CO}=0.2$ kPa, P$_{O_2}=11$ kPa. Open circuit rates: $T=560^\circ$C, $r_0=1.5\times10^{-9}$ g-atom O/s; $T=538^\circ$C, $r_0=0.9\times10^{-9}$ g-atom O/s.

Figure 3: NEMCA study of CO oxidation on Pt in a $\beta$'-Al$_2$O$_3$ cell reactor: Effect of P$_{CO}$ and catalyst potential $V_{WR}$ on the rate $r$ of CO$_2$ production.

Figure 5: NEMCA study of CO oxidation on Pt/$\beta$'-Al$_2$O$_3$: Effect of catalyst potential $V_{WR}$ on catalytic rate oscillations.
Figure 6: NEMCA study of CH₄ oxidative coupling on MnOₓ in a ZrO₂ (9mol%Y₂O₃) cell reactor: Effect of catalyst potential $V_{WR}$ on rate enhancement ratio $r/r_0$ (a) and on selectivity to C₂-hydrocarbons and CH₄-conversion (b). $P_{CH₄}=90$ kPa, $P_{O₂}=0.15$ kPa. Open circuit rates: $T=750°C$, $r_0=1.8x10^{-9}$ g-atom O/s, $T=800°C$, $r_0=4.5x10^{-9}$ g-atom O/s, $T=830°C$, $r_0=6.6x10^{-9}$ g-atom O/s. Open symbols correspond to open circuit conditions.