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# Catalysis in Solid-State Ionics

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**Abstract.** With the solid oxide-fuel cell, a technology exploiting ionic conductivity in electroceramic materials, small-scale co-generation plants for combined production of heat and electricity can achieve clean high-efficiency operation. However, with thermal activation of the cell chemistry, extremely high operating temperatures, about 1000°, are required, conditions incompatible with long term reliability using conventional structural materials. Lower-temperature operation depends decisively on the application of electrocatalysis at interfaces to the ceramic electrolyte.

## 1. Introduction

Mention of the electrochemical industry is normally taken to refer to the production of hydrogen by electrolysis, to the chloralkali industry, or to chlorate and hypochlorite processing, all of which use aqueous electrolytes. On further reflection, it should also include electrosynthesis and electropolymerization, *e.g.* for the production of conducting polymers, with organic electrolytes. Then there is electrometallurgy: metal finishing by electroplating and Cu refining are also liquid-electrolyte processes at ambient temperature. However, in general even high-temperature electrometallurgy uses liquid electrolytes, such as the molten fluoride, cryolite, in the case of Al smelting. It is a mistake, though, to assume that the term 'electrolyte' necessarily implies a liquid medium. Since the essential characteristic of an

electrolyte is the transport of charge using ionic mobility, even a solid can be an electrolyte. With this awareness, the outline of a significant future industrial development can be perceived. The known solid electrolytes include polymers such as the fluorosulfonates like nafion™, glasses, and even ceramic crystalline solids. The classic example of these ceramics is yttria-stabilized zirconia (YSZ). Zirconia itself, ZrO<sub>2</sub>, is stable in the cubic crystal structure only at elevated temperatures, and after sintering it is subject to phase-change effects during cooling. Additives can suppress this process and stabilize the cubic structure down to room temperature. There is an associated consequence of stabilization with an oxide additive, the metallic component of which exercises a valency lower than that of Zr, *e.g.* Ca<sup>II</sup> or Y<sup>III</sup>. Charge neutrality can then be maintained only by oxygen-lattice defects. For

one Ca or two Y ions on Zr sites in the cation sublattice, a vacant site appears in the oxygen sublattice. Mobility of oxygen ions at high temperature by the thermally activated displacement of lattice oxygen ions into adjacent vacancies then permits passage of oxygen with an associated charge transport through a ceramic membrane impermeable to gas diffusion, under the influence of an oxygen chemical activity gradient or of an applied electric field. Solid yttria-stabilized zirconia, therefore, conforms, at high temperature, of 800° or higher, to the classic definition of an electrolyte, with charge transport associated with ionic mobility only. The way is then open to the technical application of solid-state ionics.

## 2. Solid-State Ionics in Industry

The established application of YSZ is in the field of sensors and diagnostics. As already mentioned, an applied oxygen chemical activity gradient can induce an ionic migration through YSZ, and as a result an electrical potential is generated which is indicative of the oxygen partial-pressure difference across the membrane [1]. A typical application of this type of sensor is the 'lambda probe' which, by analysis of oxygen content in motor vehicle exhaust gas, provides the necessary control input for the electronic fuel injection and ignition system. Similar sensors are used in metallurgy to determine the oxygen content of melts. The real development of solid-state ionics, however, will come with its application to manufacturing industry and the energy economy. Some already established applications should be mentioned. In the area of electrolysis, *e.g.*, oxygen can be removed from steam for production of hydrogen with a higher electrical efficiency than is possible at ambient temperature in a liquid electrolyte, given that a part of the required energy is contributed thermally and that overpotential effects are reduced through thermal activation. A similar but less conventional application of a solid oxygen ionic conducting membrane currently under development is for oxygen supply in aerospace applications: particularly for military aircraft the requirement for compressed or liquid oxygen supplies could be dispensed with. Air enrichment in oxygen for indus-

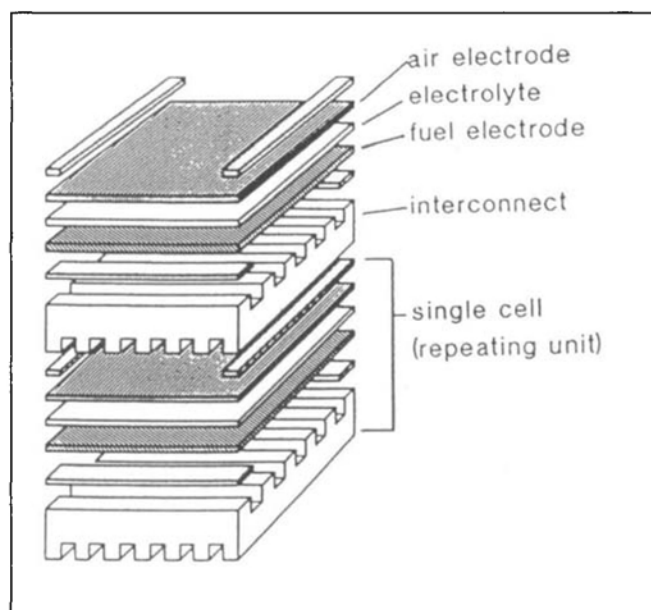


Fig. 1. Schematic of a fuel cell, showing air (cathode) and fuel (anode) electrodes, electrolyte membrane, series interconnector plates, and gas manifolding

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trial or medical applications is also an easy and attractive option with YSZ 'oxygen pump' membranes under forward electrical bias. Similar devices have been reported for the deoxygenation of metal melts with reversed bias, the production of oxygen-free Cu being an example. Also, when considering the industrial prospects for solid-state ionics it should be remembered that electrolytes transporting charge in association with ions other than oxygen are known, and for these also applications are being developed: CaF<sub>2</sub> is a fluoride-ion conductor and β'-Al<sub>2</sub>O<sub>3</sub> is electrolytic for Na and other alkali metals, while the already-mentioned polar polymer nafion™ and BaCeO<sub>3</sub> can be conductors for hydrogen ions. An exotic application for this last material is the separation of the hydrogen isotopes, given their different ionic mobilities in the cerate lattice.

**3. Catalysis Over Solid Electrolyte Surfaces**

In all the examples quoted so far, the action is faradaically electrochemical, with the ionic current passed by the membrane determining the extent of chemical reaction by Faraday's law. The best known catalytic application of solid-state ionic materials, however, has a reaction rate not directly related to the ionic current density. The interface behaviour of the substrate, in this case the ionic conductor, such as YSZ, is modified by the application of an electric field. By inducing a change in the oxygen activity of the substrate, the adsorption and reaction mechanisms on the catalytic layer also modify significantly, with an associated influence on the electrolyte work function. The chemical reactions are essentially between species adsorbed from the gaseous environment contacting the catalyst. This effect of modified kinetics and associated influence on reaction selectivity following modulation by an applied electric field in a solid ionic substrate was observed and reported by Vayenas [2] and termed by him NEMCA (Non-faradaic Electrochemical Modification of Catalytic Activity). As an example, when applied to the activation of CH<sub>4</sub> it can increase the selectivity towards dimerization forming ethylene as a product of significant added value.

**4. Solid Ionics for Energy Conversion and Storage**

Electricity generation and storage is a classical application of conventional am-

Table. Maximum Efficiencies of Fuel Cells at 25° and 1 atm Operating Pressure

Fuel	Reaction product	n	V <sub>OC</sub>	η [%]
H <sub>2</sub>	H <sub>2</sub> O	2	1.229	83
CO	CO <sub>2</sub>	2	1.07	91
CH <sub>4</sub>	CO <sub>2</sub> and H <sub>2</sub> O	8	1.06	92

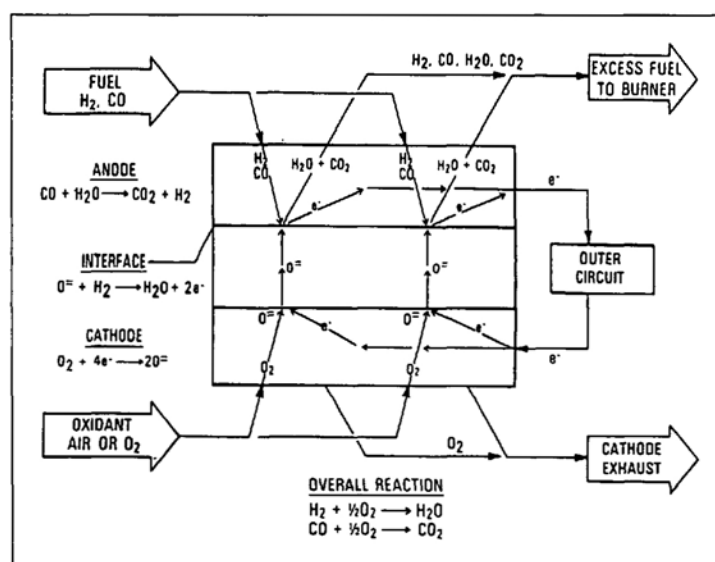


Fig. 2. Schematic of chemical reactions and charge transfer in SOFC [4]

bient-temperature liquid electrolytes, in batteries and accumulators. It is, therefore, to be expected that energy-related devices should provide promising applications for the solid-state analogues. For example, the sodium-sulfur battery with a β'-Al<sub>2</sub>O<sub>3</sub> ionic conductor separating a sodium electrode from a S<sup>2-</sup>/S<sub>n</sub><sup>2-</sup> redox system is a high-efficiency solid electrolyte accumulator, though with the disadvantage of a 300° operating temperature. Of more immediate interest is the solid oxide-fuel cell (SOFC), which is under intensive development in Japan, USA, and Europe. Switzerland has played a leading role in this research, particularly cultivated by the Federal Office of Energy (OFEN/BEW) and now sustained also under the national Priority Programme for Materials (PPM/WF). Both EPFL and ETHZ are engaged, with emphasis in Lausanne on electrochemical and interfacial catalytic aspects of the technology and Zürich giving priority to materials science and fabrication aspects. Swiss industry is far advanced in the development and demonstration of a combined heat and power generation unit in the HEXIS (Heat EX-changer Integrated Stack) concept of Sulzer Innotec, vacuum plasma spray fabrication methods have been verified by Medicoat AG, and EMPA has supported the effort with materials synthesis and analytical techniques. A second fuel cell configuration, using a hydrogen-ion-conducting

polymer as electrolyte (PEFC) and with specific advantages for vehicle applications, is under development at Paul Scherrer Institute (PSI).

The principal characteristic of fuel cells is that an isothermal electrochemical oxidation of the fuel takes place. In consequence the system escapes the Carnot efficiency limitation which applies to all thermomechanical energy-conversion systems. The efficiency (η) of the process is given by:

$$\eta = (\Delta G_T / \Delta H^0) \cdot 100\% \quad (1)$$

where ΔG is the free energy of the fuel oxidation process at the operating temperature of the cell and ΔH<sup>0</sup> is the standard reaction enthalpy. Therefore, the open circuit cell voltage is:

$$V_{OC} = -\Delta G_T / nF \quad (2)$$

where n = number of electrons transferred in oxidizing a fuel molecule and F = Faraday constant. Compared to a modern coal-fired power plant which has a conversion efficiency η of only 34% [3], thermodynamically fuel cells can reach very high efficiencies. The Table illustrates this fact.

For higher-temperature operation, as in the solid oxide-fuel cell, V<sub>OC</sub> and η are calculated by taking into account the heat capacities of reagents and latent heats of

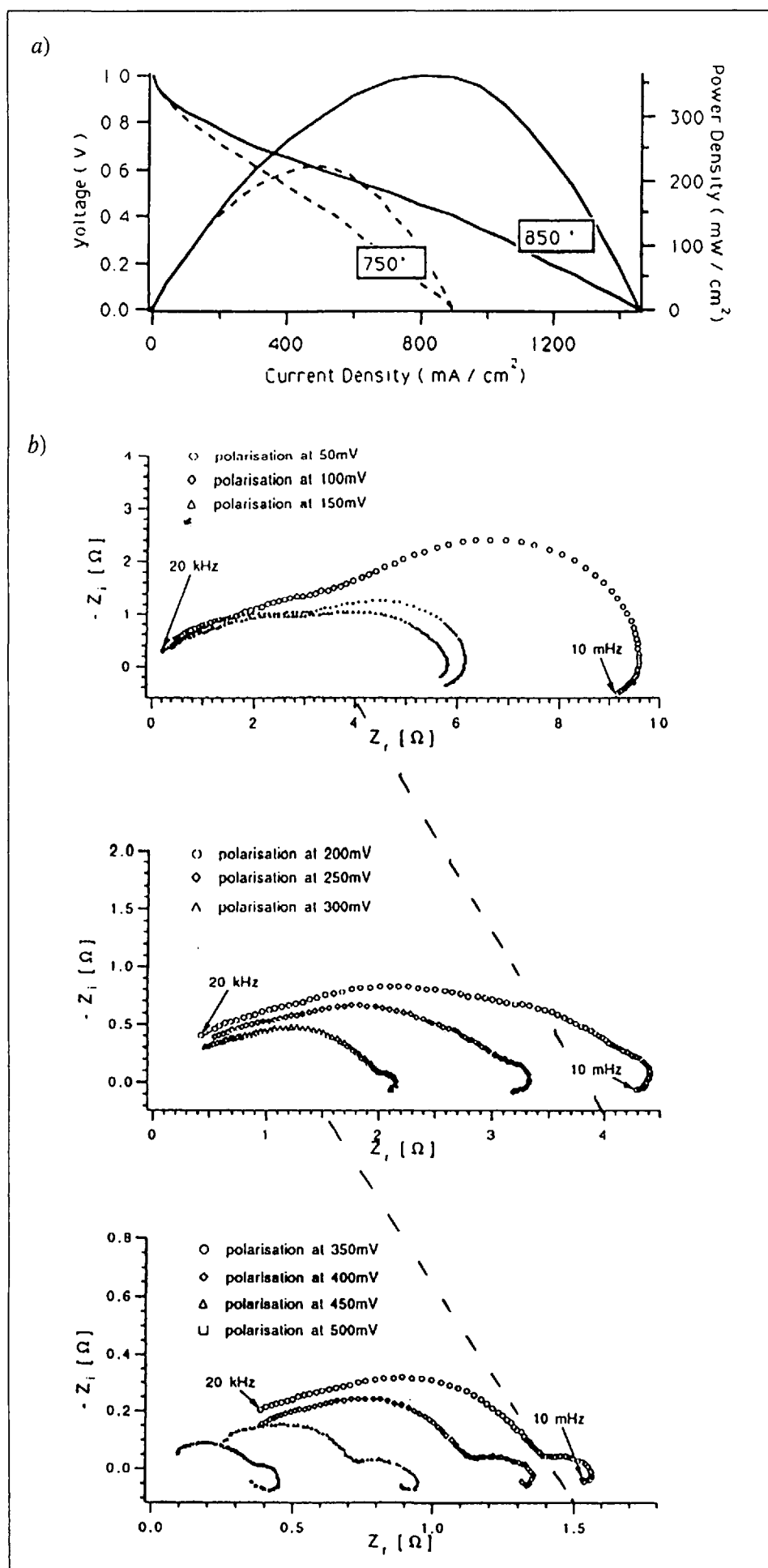


Fig. 3. Electrochemical evidence for catalysis: a) power and voltage characteristic of SOFC test unit; b) reduction of resistive component and incidence of inductive loop in impedance spectroscopy of a cathode-side interface with increasing overpotential

phase changes. Consequently at 1000°, a hydrogen-fuelled cell gives a  $V_{OC}$  of 0.98 V and the correspondingly lower efficiency. In reality, it is possible to achieve an electricity-conversion efficiency of 55% at an acceptable operating temperature, ca. 850°. A further increase by 5–10% in efficiency is attainable, if a co-generation system is installed, where the by-product high temperature heat is used to drive a turbine. Besides conversion efficiency, the other advantages offered by fuel cells are significant. Fuel cells are clean, noise-free, and compact, adaptable to modular design. Furthermore, they produce little or no  $NO_x$  or particulate emissions and produce less  $CO_2$  per kW electricity. Fuel cells in general can be operated using a variety of fuels such as natural gas,  $H_2$ , methanol, higher hydrocarbons, etc. The most interesting fuel is obviously natural gas. The major disadvantages of fuel cells are high cost, materials constraints, and long term stability.

The practical realization of these advantages presumes the minimization of loss mechanisms, not only the ohmic resistance effects in the cell materials but even more significantly the polarization effects at interfaces. Electrode materials selection must also take account of the working environment of a SOFC, chemical compatibility with YSZ so that interfacial solid-state reactions giving rise to undesirable third phases or volume changes are minimized, and matching of thermomechanical effects such as differential thermal expansion. For these reasons the standard cathode material, exposed to air and at which molecular oxygen is reduced to oxygen ions, is an electronically-conductive perovskite ceramic such as a mixed lanthanum-strontium manganite ( $La_xSr_{1-x}MnO_3$ , LSM). Because each cation is already in a fully-oxidized state these compounds are stable in air at high temperature and so do not suffer the oxidative degradation expected on metallic components. On the anode side where the fuel is oxidized, a Ni-YSZ cermet composite is acceptable. Given these materials, and with a thin electrolyte, ohmic losses tend to be small compared with polarization effects. These were initially dealt with by microstructural optimization, taking into account for example the electrode porosity to maintain a high gas-solid interface area for interaction of reagent gases with the electrodes while minimizing the diffusion limitations [4]. Then followed nanostructural considerations: learning from electronic engineering where junctions are charge-transfer sites between materials of differing conduction mechanisms, it was recog-

nized that electrode-electrolyte interfaces must be atomically well-defined and intimate [5].

### 5. Interfacial Electrocatalysis in SOFC Devices

Only when these materials and structural issues are dealt with does catalysis as normally understood become a further optimization tool, where limitations to device performance are related to the kinetics of chemical processes such as the incorporation of oxygen from the gas phase into a solid lattice as an ion, or indeed the transport of oxygen ions from one lattice to another, *e.g.* from LSM to YSZ. The initial oxygen reduction step is a catalyzable process. Oxygen-isotope exchange experiments had been taken to indicate that the ionic component of conductivity of LSM is low, and exchange between the gas and solid phase slow. The alternative perovskite, replacing Mn by Co, shows a faster oxygen exchange, but at the same time cobaltite is much more reactive with YSZ and the interface is, therefore, unstable. Recent theses in EPFL have shown the advantages of graded-structure LSM, while work at ETHZ has gone in the direction of compositionally-graded electrodes, with a cobaltite phase exposed to the air. It should also be remembered, concerning exchange rates on YSZ-supported electrodes that under oxygen-transport conditions the kinetics can be significantly modified [6], as in the NEMCA case already discussed. For the next step on the reaction pathway, the transport of ions across the interface into the electrolyte, already over twenty years ago during the earliest efforts in Switzerland to realize a SOFC structure, *Tannenberger* and *Van den Berghe* [7] at the *Battelle* Institute (Genève) inserted interlayers, which incorporated transition-metal ions such as U in the stabilized zirconia lattice. They reported a significant enhancement of power density in comparison with abrupt junctions formed with the materials and the techniques of the time. Current practice also recognizes the catalytic effectiveness of a presence of selected transition-metal ions at the interface. On the cathode side, it is suggested that a redox behaviour on the part of these cations is involved: change in their oxidation state requires a modification of electronic distribution only without disturbing the cation lattice, the charge neutrality being maintained by insertion or loss of an oxygen ion from the anion lattice. Since the oxygen defect density at the interface is no longer determined by the concentra-

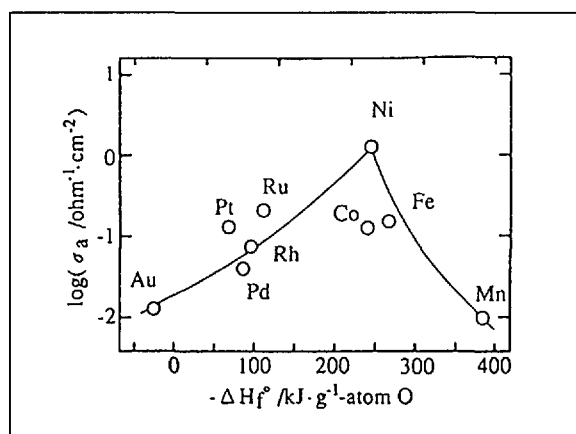


Fig. 4. Volcano curve for anode-side cermet materials [10]

tion of a dopant element, Y, but varies through electronic effects only, charge and mass exchange between cathode and electrolyte are significantly facilitated, as is migration of ionized oxygen species along the interface.

On the anode side, charge exchange between the intimately associated metallic-electronic and ceramic-ionic conducting components of the cermet is attributed to separate percolation of each charge carrier through the interpenetrating matrix, the chemical reaction taking place at three-phase boundaries where gaseous reagents associate with each of the solid phases. A reducible dopant in the zirconia phase can introduce a degree of electron mobility in the ionic conductor under these circumstances, delocalizing the charge-transfer reaction and removing a significant restriction on the reaction kinetics. In fact it has been demonstrated with a Pt anode on a ceria electrolyte with hydrogen fuel that anodic polarization effects can be completely suppressed, giving rise to a purely ohmic contact [8]: it remains to be verified that this desirable result is also attainable with more practical engineering materials!

The validation of the electrocatalytic model for the enhancement of ionic transfer interface performance is secured by electrochemical impedance spectroscopy (EIS). Dissipative (resistive) and space-charge (capacitive) effects can be distinguished at all interfaces. It is evident that the resistive component decreases significantly with increasing overpotential and current density. Additionally, transition-metal-catalyzed interfaces when investigated by this technique under charge-transfer conditions display a low-frequency inductive component, typical of other electrochemical autocatalytic processes such as corrosion. The disappearance of this feature from the impedance spectrum under open-circuit conditions associates it with a charge-transfer-induced species, in the cathode case the excess anion-lattice

defects consequent on redox activity of the transition-metal sites. A variety of processes to bring about the necessary transition-metal presence have been developed, without resorting to the original concept of a separate layer on the scale of several microns which requires two interfaces in place of one. The selected material, for example Mn or Ce, can be applied to the electrolyte surface as a solution of one of its salts, then pyrolyzed to oxide and diffused thermally into the substrate before application of the electrode. Physical methods have also been used such as sputtering and ion implantation. Currently interfaces enhanced in Mn are fabricated by the simple expedient of using a La deficient LSM, the missing cation charge being compensated in these materials either by oxygen deficiency or by higher oxidation state of a part of the Mn [9]. On sintering, sufficient Mn is released to diffuse into the electrolyte and induce the electrocatalytic interface. This sophisticated solid-state chemistry approach has additional advantages, that the oxygen mobility in and on the LSM grain is enhanced, and that the La defect inhibits topotactic action with the YSZ and any formation of deleterious lanthanum zirconate interphases.

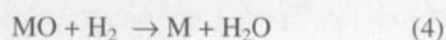
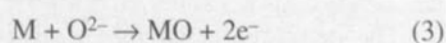
### 6. Fuel-Gas Chemistry and Catalysis for SOFC

While the Ni-YSZ cermet is widely adopted as anode and operates excellently with hydrogen as fuel, it is not nearly so attractive for CH<sub>4</sub> and other commercial hydrocarbon fuels, being liable to coke formation, or deposition of inactivating vitreous carbon layers. Also, the possibility of Ni migration and agglomeration is serious. Technical and economic acceptance depend on surmounting this problem. The various processes for CH<sub>4</sub> fueling in SOFC systems are outlined as follows:

- i) *External reforming with steam* – partial or complete. This strategy complicates the SOFC system with extra volume of the pre-reformer, thermal transport management, and the necessity to maintain a steam generator.
- ii) *Internal reforming* – an interesting area for catalysis researchers. Here several catalyst metals such as Co-, Fe-, and Pd-containing alloys are available. However, reactions between steam and a metal like Fe even in a reducing atmosphere can cause problems in the long term.
- iii) *Direct oxidation* – in the case that coke formation can be suppressed, for example by reducing the oxidation kinetics for the hydrogen component of the fuel to that for carbon, by an alkaline earth oxide coating on the anode, for example.
- iv) *Internal CO<sub>2</sub> reforming* – the most interesting approach where a partial internal reforming is carried out *in situ* on the anode, using CO<sub>2</sub>. In practice, both steam and CO<sub>2</sub> can be used to reform CH<sub>4</sub> on the electrode. This is advantageous since CO<sub>2</sub> (as well as steam) is already present in the exhaust gas of a natural-gas-fuelled SOFC system and can be recycled from the exhaust to the inlet manifold.

Whatever be the fuel-reaction strategy, it should be noted that the anode reaction on Ni is strongly affected by the partial pressure of O<sub>2</sub> (P<sub>O<sub>2</sub></sub>) due to the possibility of metal-oxide formation. Since the kinetics of reforming and shift reactions are fast at the SOFC-operating temperatures, these reactions can easily approach their thermodynamic equilibrium limits. Since reforming is endothermic, a fast kinetics of this reaction can cause local electrode cooling, resulting in mechanical and thermal balance problems for the entire SOFC system.

Placing all these facts in proper perspective, the objectives for new anodes can be stated as follows: a) Identification of new catalyst materials and recipes to solve the above mentioned problems; b) Structural optimization to secure the required high power density. As for the catalyst evaluation, the heat of formation of the metal oxide can be a predictor of its effectiveness for oxidation of a fuel on a SOFC anode. Ni has a favorable heat of formation and is found at the apex of the relevant volcano curve. The approach is based on the equations:



Where the heat of oxide formation is low, the first step is rate determining, and when high, the second. The position of Ni at the peak of the 'volcano curve' [10] indicates an optimal compromise. However, it is too simplistic to consider only this factor and other parameters such as structure and morphology of the anode as a whole must be taken into account. Materials such as Sm-doped ceria and PrO<sub>x</sub>, in the form of a cermet with Ni also show promise. Items to be studied include the effect of the reduction conditions of NiO in the cermet formulation once exposed to fuel, on the effective surface area of Ni, given the different effects of wet and of dry H<sub>2</sub>. It must be determined if such a difference is maintained under electrochemical conditions. In this context, it is particularly interesting to note that a Ni-cermet anode coated by vacuum plasma spray is already electronically conducting without the need for a pre-reduction.

Thermodynamically there is no escape from coking, so to minimize its consequences control of kinetics is necessary. The morphology of the carbon deposited is critical, in that, *e.g.*, dendritic carbon is reactive while graphite is very passive and once formed is very difficult to remove. The direct use of natural gas as a fuel in SOFCs is also hampered by its relatively slow activation, and by the difficulty in controlling the nature of reaction products, notably CO and C. Furthermore, gas-phase reactions on hot parts of the cell stack can create difficulties. By proper engineering this problem can be solved, but for attaining direct oxidation of CH<sub>4</sub> a suitable catalyst with sufficient electronic conductivity (10 S cm<sup>-1</sup>) has to be designed. This can be a simple or a mixed oxide, with sufficiently large oxygen-ion vacancies. These vacancies will then act as active sites where the electrochemically generated O<sup>2-</sup> and adsorbed CH<sub>4</sub> can react. A large number of perovskite compounds with electronic and ionic conductivities (due to oxygen vacancies) have been reported in solid-state chemistry literature. Some of these compounds are even stable under relatively strong reducing atmospheres, for example Ca- or Sr-doped lanthanum chromite over a wide range of temperature. Their catalytic activities for direct CH<sub>4</sub> oxidation still require study.

## 7. Conclusion

The foundations of the future solid-state ionics industry are now being laid. In addition to applications in sensors, in syn-

thetic electrochemistry, and in storage batteries, energy conversion in fuel cells will be a prominent component of this industry. Switzerland is prominent in solid oxide-fuel cell research and development, not least because of close interaction of industry and the research institutes, guided by the Federal Office of Energy. Already prototype electricity-generating stacks of the *Sulzer* HEXIS configuration are under test. However, efficient models with long term reliability, economically competitive with thermomechanical motor-generator sets when functioning on natural gas or other low-cost fuels, presume a mastery of the electrocatalytic effects on the reaction kinetics in the system. An understanding of these processes has already been acquired and their exploitation is in hand.

Recognition is due to our colleagues in ETHZ, in *Sulzer Innotec* our industrial partners, and in *Medicoat AG* where SOFC components are fabricated by plasma technology. The work is supported by the *Federal Office of Energy* under the supervision of Dr. L. Dubal, and by the *National Priority Programme for Materials* in so far as nonconventional materials and structures are concerned.

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