

In the search for new, improved energy systems for the 21st century, the emphasis is on environmentally friendly, efficient means of energy conversion and storage. High temperature fuel cells offer energy conversion efficiencies as high as 70% although there are still problems to overcome before the optimum fuel – natural gas – can be used without difficulty. Future applications of high temperature fuel cells in addition to power generation, is an area of considerable excitement. There is growing interest in transport applications and the use of alter-

## Optimisation of Solid State Electrochemical Processes for Hydrocarbon Oxidation (OSSEP)

An ESF scientific programme



native fuels. High temperature fuel cells offer considerable promise for working with more complex fuels, such as biogas or reformed higher alkanes, as their high temperature of operation facilitates reforming engineering. Closely allied to these applications in fuel cell technology is the use of electrochemical reactors for the industrially important electrocatalytic oxidation of hydrocarbons. In the long term solid oxide fuel cell (SOFC) technology is foreseen as a candidate for a much more efficient electrolysis of steam and carbon dioxide. The OSSEP Programme focuses on both fundamental and applied aspects.

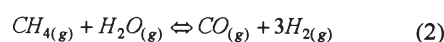
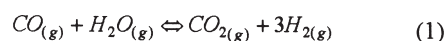
The high temperature electrochemical oxidation of hydrocarbons is an area of considerable strategic, environmental and economical importance. The purpose of this ESF Programme is to promote investigations into the processes involved in the solid state electrochemical oxidation of hydrocarbons and hence to develop new fuel cell materials and systems to meet the challenges of the new millennium. The Programme will facilitate the exchange of ideas and develop common programmes of activity. This will be achieved by organising workshop meetings each year, by regular exchange of personnel on short-term visits, short Fellowships and by shared Fellowships involving periods of research at two or more host laboratories.



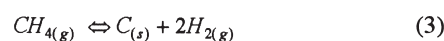
The European Science Foundation acts as a catalyst for the development of science by bringing together leading scientists and funding agencies to debate, plan and implement pan-European initiatives.

## Background

Probably the most important materials problem to be addressed in the development of the first and succeeding generations of SOFCs is the fuel electrode. A major objective is the development of SOFC anodes capable of operating in natural gas, without suffering from carbon build up due to catalytic cracking; this objective is still far from being achieved. At present Ni/ZrO<sub>2</sub> cermet anodes, which are inexpensive and exhibit high catalytic activity for hydrogen oxidation have been widely used in SOFCs with hydrogen fuel. The Nickel loading is generally chosen to be slightly in excess of the limit for percolation electronic conduction. At higher Ni loadings there are problems with thermal expansivity mismatch between the Ni and the zirconia electrolyte substrate. The major disadvantage of the Ni cermet electrode arises from the promotion of competitive catalytic cracking of hydrocarbon reactions. The rapid deposition of carbon at Ni cermets means that direct oxidation of methane is not technically viable in Ni-containing solid oxide fuel cells. In order to use methane as fuel in this type of SOFC the fuel needs to be externally or internally reformed with steam<sup>†</sup>. The reforming reaction (1) is generally associated with a following water gas shift equilibrium reaction (2).



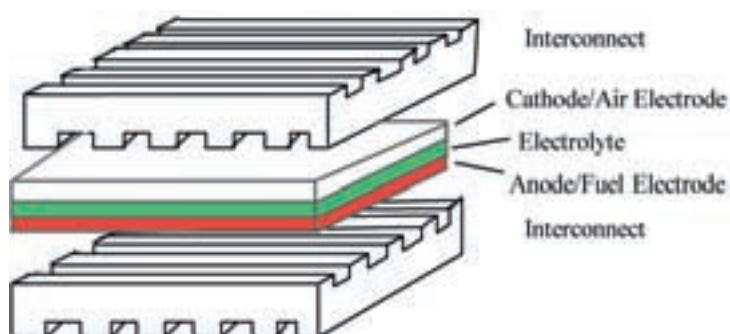
Both these reactions are favoured by low pressures and high temperatures and by large steam partial pressures. If insufficient steam is present, carbon may be deposited according to reaction 3.



## Introduction

At the forefront of developing energy technologies is the Solid Oxide Fuel Cell (SOFC) which should find widespread application in the conversion of chemical to electrical energy. The Solid Oxide Fuel Cell (SOFC) is an all-ceramic device that operates at temperatures in the range 850-1000°C. This design holds particular promise for power generation, particularly for combined heat and power operation. Most current development centres on designs based on the yttria-stabilised zirconia (YSZ) electrolyte, with (La,Sr)MnO<sub>3</sub> as the preferred cathode, Ni/ZrO<sub>2</sub> cermets as the preferred anode, and lanthanum chromite or special alloys as interconnects.

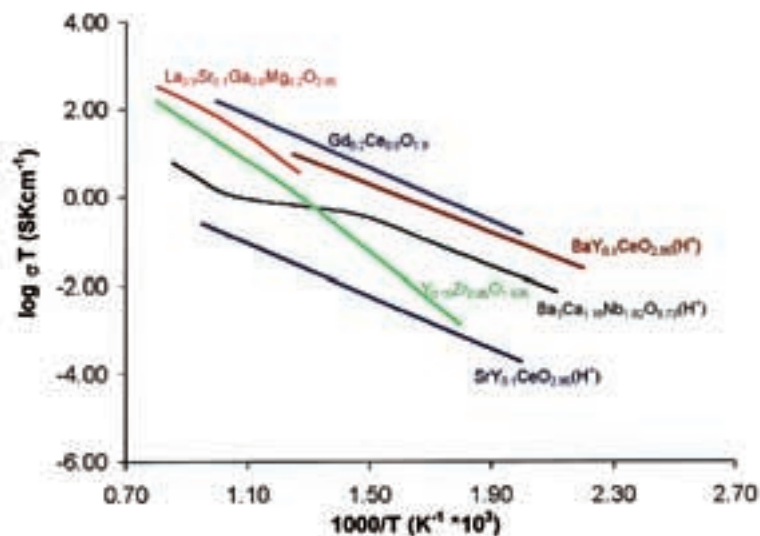
Typical Solid Oxide Fuel Cell planar design



This cracking reaction is even more problematic with higher hydrocarbons, which also are present in natural gas.

In the next generation of SOFC devices, there is considerable emphasis on moving to lower temperatures of operation as this will reduce sealing problems and allow cheaper and interconnect materials to be used. The initial problem to be addressed is finding a suitable electrolyte material that performs well at lower temperatures; good progress has been made using thin film YSZ electrolytes or alternative oxygen-ion conductors such as scandia-stabilised zirconia, lanthanum gallate-based perovskites or gadolinia cerium oxide. Another, highly attractive alternative may be to use proton conducting electrolytes such as the perovskite  $\text{BaCeO}_3$  or perovskite-related materials such as  $\text{Ba}_3(\text{Ca}_{1+x}\text{Nb}_{2-x})\text{O}_{9-d}$  to provide good ionic conductivity in the temperature range 500-750°C. In order to use these alternative electrolytes systems, new or improved electrode materials with suitable electrochemical properties for operation at lower temperatures, i.e. < 850°C are required.

The requirements for efficient fuel electrode operation are many, so the search for alternative materials is not a simple task. These materials must be stable both at the low oxygen partial pressures prevalent in the fuel gas and at the more oxidising conditions at the fuel outlet. Fuel electrodes must also exhibit suitable catalytic and electrical properties and they must also be structurally and mechanically compatible with the electrolyte up to operating temperatures.



There is growing interest in high temperature fuel cells for transport applications and the use of alternative fuels such as biogas for power generation. Recently a number of car manufacturers have developed prototype vehicles using hydrogen powered fuel cells. Despite these advances, hydrogen is not an ideal fuel due to potential safety hazards and difficulties in distribution. Attention is, therefore moving towards hydrocarbons with initial developments focusing on methanol; however further development is likely to move towards more energy rich fuels such as dimethyl ether, gasoline and diesel, especially if the methanol is to be derived from fossil fuels. High temperature fuel cells offer considerable promise for working with more complex fuels, such as gases derived from gasification of biomass, waste and coal or reformed higher alkanes, as their high temperature of operation facilitates reforming engineering. Reforming systems typically require temperatures of 600°C and thus can easily be integrated into a high temperature fuel cell stack.

Comparison between proton and oxide ion conductivities of potential electrolyte materials for high temperature fuel cell electrolytes

SOFC technology may be also used for high temperature electrolysis of water and carbon dioxide, which results in synthesis gas as the product. From synthesis gas several valuable compounds, e.g. methanol or dimethyl ether, may be produced. This technology could eventually be developed for the transport of renewable energy such as hydropower from remote areas or for better distribution of energy from gasfields to urban areas.

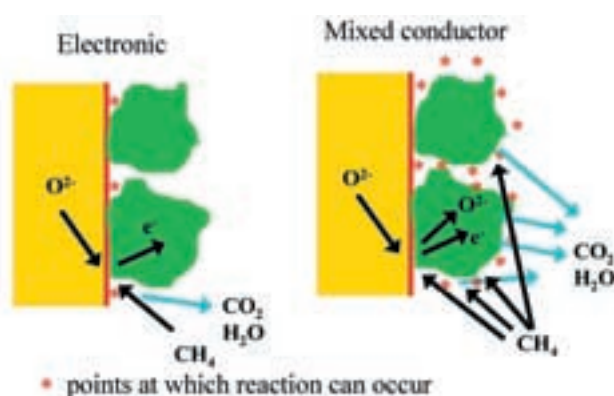
Intimately linked with fuel cell technology is electrocatalysis. In developing new fuel cell anodes, catalytic activity for hydrocarbon oxidation is very important. Electrocatalysis at solid electrolytes is a topic of growing importance and is

potentially an excellent tool for the partial oxidation of hydrocarbons, e.g. in the preparation of olefins from alkanes. Catalytic processes at solid electrolytes are of great interest to the chemical industries as they offer improved yields and selectivity. An important phenomenon, the Non-Faradaic Modification of Catalytic Activity (NEMCA) effect can give rise to substantial increases in catalytic activity due to small changes in the electrode potential at a solid electrolyte. These phenomena are not well understood and provide a fruitful area for basic investigations.

## Research topics and methodology

### Transport properties

Underlying the electrochemical activity of an electrode material is the ability of charged species to migrate from the electrolyte to the surface and their availability at the surface to perform electrochemical reactions. If an electrode can transport both electrons and ions from electrolyte to the surface, then it will allow electrochemical reactions to occur across the complete electrode surface, not just at the three phase boundaries between electrode, electrolyte and gas phase, figure 2. This affords much better activity and may be viewed as a catalytic effect. One of the major topics to be discussed and investigated during this programme is charge transport.  $O^{2-}$ ,  $H^+$  and  $e^-$  conductivity will be investigated as functions of temperature, atmosphere and composition. The extent of mixed conductivity will be investigated using concentration cells, ion blocking and



Comparison between electrode activity of a purely electronically conducting electrode with that of a mixed conducting electrode

permeation techniques. Bulk transport and surface exchange will be investigated using diffusion techniques such as secondary ion mass spectrometry. Modelling will be used to compare theoretical and observed characteristics.

### Catalytic activity

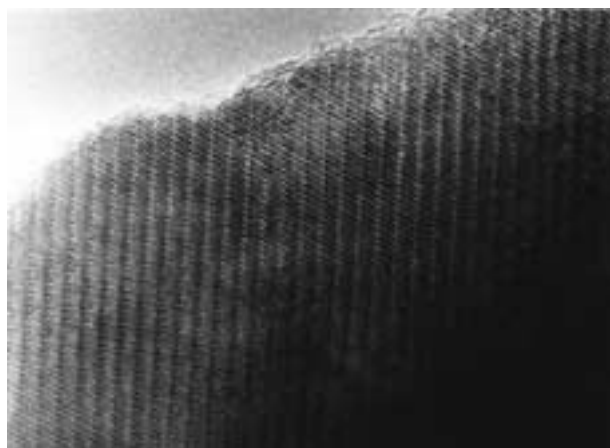
Another major activity of this programme relates to catalytic activity. The ability of potential electrode materials to oxidise, dehydrogenate or reform a wide range of hydrocarbons will be investigated using temperature-programmed techniques with GC and mass spectrometric analysis. Sensitivity to sulphur and other impurities will be tested. Electrocatalysis will be investigated both in fuel cell and reactor operational modes. For fuel cells I-V characteristics will be investigated in association with evolved gas analysis. The possibility of gradual reforming of natural gas in SOFCs using a methane steam reforming catalyst coated onto an anode material will be studied. For electrochemical reactors hydrocarbon gas will be fed across the fuel electrode and the conditions required to optimise partial oxidation or dehydrogenation determined.

### Structure and microstructure

*In situ* and *ex situ* techniques such as X-ray, electron and neutron diffraction, EXAFS, Raman and NMR spectroscopy will be used to perform basic structural studies on candidate electrode materials. The resulting information will provide details of structural changes that occur on changing temperature, atmosphere and polarisation. Post-mortem studies will also be performed to investigate degradation on operation.

### Thermodynamic properties and stability

Weight and volume changes as functions of gas composition and temperature will be investigated. Oxygen exchange will be investigated in atmospheres relevant to SOFC anodes and electrochemical oxidation



Transmission Electron  
Micrograph of  
Layered Perovskite  
Titanate

cells, e.g. exchanges from isotopically labelled water, CO<sub>2</sub> etc. Chemical compatibility between electrodes and electrolytes will also be investigated after co-firing using microscopy and diffraction techniques to analyse for reaction products.

### Electrochemistry

Techniques such as voltammetry and ac impedance spectroscopy will be used to study reactions occurring at electrode interfaces. Both point and macroscopic electrode geometries will be used. Experiments will be performed in different gases and compositions with the aim of resolving different stages of the electrochemical oxidation processes and relating this to the catalytic and electrical properties of the electrodes.

### Materials

The systems of interest are based on a range of electrolytes including yttria-stabilised zirconia, various lower temperature fluorite and perovskite oxide conducting electrolytes and proton conducting materials. A wide range of electrode materials is of interest including cermets (including Ni/zirconia), composites and oxides. Various powder-processing routes such as sol-gel and combustion synthesis will be used to prepare better powders

for cell preparation. Cells will be fabricated using a range of techniques such as ceramic processing of bulk electrolytes, e.g. tape and slip casting, thick film electrolyte deposition and slurry coating and screen printing of electrodes.

Normally static compaction techniques are used to densify powders of solid electrolytes, applying a constant pressure for a certain period of time. Dynamic compaction uses a pressure pulse with a typical duration of microseconds. The pulse results in a pressure wave that travels through the sample. Both Explosive Dynamic Compaction and Magnetic Pulse Dynamic Compaction are relatively

low-temperature densification techniques which result in high densities and special microstructures. These densification techniques are available to the participants of the ESF-OSSEP programme.

### **Systems**

Work will also be performed in order to test systems for use in SOFCs, electrolysis systems and electrochemical modification. This will involve fabrication and testing of partial and complete single cells, but not, generally cell stacks.

## **ESF OSSEP programme**

### **Workshops**

One or more topical workshops will be held each year involving researchers from the participating laboratories. Each workshop is expected to last for 2-3 days and involve 20-30 participants. The workshop will be comprised of contributed oral papers, round table discussions and overview presentations. The Workshop Programme is detailed below:

- *Optimisation of Solid State Electrochemical Processes for Hydrocarbon Oxidation*  
St Andrews, Scotland, 22-24 June 2000
- *Solid Oxide Fuel Cell Materials and Mechanisms (jointly with IEA)*  
Les Diablerets, Switzerland,  
16-19 January 2001
- *Synthesis and Processing*  
Madrid, Spain, November 2001

- *Fuel Cells based upon Proton-Conducting Electrolytes*

Risø, Denmark, April 2002  
(to be confirmed)

- *Electrocatalytic Processes*

- *Novel Materials and Processes for Hydrocarbon-Fuelled High Temperature Fuel Cells*

- *Electrochemical Oxidation of Higher Hydrocarbons*

### **Grants**

The ESF programme supports individual short-term visits of one to two weeks (mainly for senior researchers) between partner laboratories. Priority will be given to senior scientists involved in the programme collaboration.

The Programme also supports longer term collaborative research projects for younger researchers of up to three months duration or occasionally for six months. The latter involves researchers spending two three-month spells working on a collaborative project at two laboratories involved in the OSSEP Programme.

Selection is based on the quality and appropriateness of the applicant's previous research and the quality of the proposed research project. Short-term fellowships require that the applicants already have some relevant experience, although it is important that they can also expand their expertise as a result of the visit.

For the latest information on this programme consult the OSSEP home page at: <http://www.esf.org/ossep>

An electronic newsletter will be circulated two or three times per year.

To subscribe to the OSSEP mailing list, please send an email as shown below:

To: [ossep-list@esf.org](mailto:ossep-list@esf.org)

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Cover picture:  
Oxygen vacancy in fluorite  
lattice.

October 2000

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