Combining science and practice in the Danish 'DK–SOFC' program

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Abstract

A three-year solid oxide fuel cells (SOFC) development program completed in 1992 has produced 10 cm^2 cells with area-specific resistances in the range 0.25 to 0.40 Ω cm^2 at 1000 °C. Cathode and interconnect materials were produced in the program. Sintering of electrodes, electrolyte and interconnect was done in air at 1300 °C. Tests with small stacks yielded promising results. Electrochemical investigations have contributed to the understanding of the electrode processes and their kinetics.

Introduction

In the Danish energy planning [1], priority is given to the development of fuel cells as a clean energy technology, having high electrical efficiency and low emission of pollutants. It was decided a few years ago that support from the Danish Government for fuel cell developments should be mainly in the area of solid oxide fuel cells (SOFC). At the same time, the electric utilities took active interest in this development. This provided the basis for the 'DK–SOFC' program with the following goals:

(i) to contribute to the industrial development of SOFC in Denmark, with the emphasis on SOFC conversion of coal gas and natural gas to electricity and heat;

(ii) to develop design, materials and processes in the pre-competitive phase, but with a clear view to industrial exploitation, and

(iii) to conduct fundamental research related to the above technologically oriented development, and in this context to ensure the required scientific education of personnel.

The resulting program has two main lines: (i) development of cell and stack technology, and (ii) fundamental investigations of conventional and new materials, to improve the SOFC performance. This is realized through the combination of different categories of project participants (research institute, university laboratories, industrial companies). Risø National Laboratory is the project managing organization and provides a large part of the project effort. The other participants are: Innovision A/S, Department of Chemistry of Odense University, The Technical University of Denmark (Department of Physical Chemistry, Physical Institute, and Chemistry Department A) and Haldor Topsøe A/S.

The major part of the work in the first phase of this cooperation constituted a three-year program 'DK–SOFC 1990–1992' with a total budget of 43.5 million DKr (~US$ 7 million). The program costs were shared by the Government's program for energy promotion, the electric utility companies ELSAM and ELKRAFT and the

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six project participants. Planning and execution of the work was supervised by a joint committee with representatives from all the organizations sharing the costs. This ensured coordination and agreement between all parties involved.

The major achievements of the 1990–1992 program are presented in the following, with conclusions and perspectives for the follow-on program for the period 1993–1996.

Achievements

SOFC concept

The general concept chosen is that of a planar SOFC. The various components are made of fairly conventional materials:

- Electrolyte: Yttria-stabilized zirconia, YSZ
- Anode: Ni-YSZ cermet
- Cathode: Strontium-doped lanthanum manganite, LSM
- Interconnect: In the early part of the development, strontium-doped lanthanum chromite, LSC, was chosen as cell interconnect material. It appeared, however, that rather high sintering temperatures, say 1650 °C and preferably under reducing conditions, would be necessary for this material. This was considered less realistic from an industrial point of view: expensive high-temperature furnaces would be required and it would be difficult to realize co-sintering of the cell components. As a consequence, the interest was shifted to calcium-doped lanthanum chromite, LCC, as explained in the following.

The design chosen for the tests of this program is shown in Fig. 1. It is based on 'cross-flow', i.e., the streams of fuel gas and air are perpendicular to each other. The manifolding is internal for the fuel gas, with connections to only one face of the stack (front/left in Fig. 1). The air manifolding is external with gas connections to two opposite stack faces (front/right and rear/left in Fig. 1). This enables measurement for individual cells of voltage, gas flow and local temperatures.

Cell and stack development

The technological development was mainly material and process development for the SOFC concept shown in Fig. 1. In the beginning of the work, alternative routes of development were often pursued until the most promising one for a specific application had been identified. Emphasis was always given to processes with potential for industrial upscaling. This meant among other things that sintering temperatures should not exceed 1300 °C.

Raw materials

Some of the powders are available commercially. Tosoh's TZ8Y with 8 mol% Y_2O_3 was selected for the electrolyte. The nickel for the anode was applied as the oxide, green NiO.

For the manganites (cathode) and chromites (interconnect), it was necessary to set up manufacturing procedures on a laboratory scale (say 25 g) for initial development applications.

The Pechini process [2] was not suitable for production of LSM. It was difficult to control and excessive conditioning of the powders was necessary. An alternative process was developed, based on continuous drip pyrolysis of solutions of organic metal complexes [3]. With this process, 10 kg lots of LSM and LCC powders are now produced routinely, reproducibly and with the desired compositions. Only a minimum

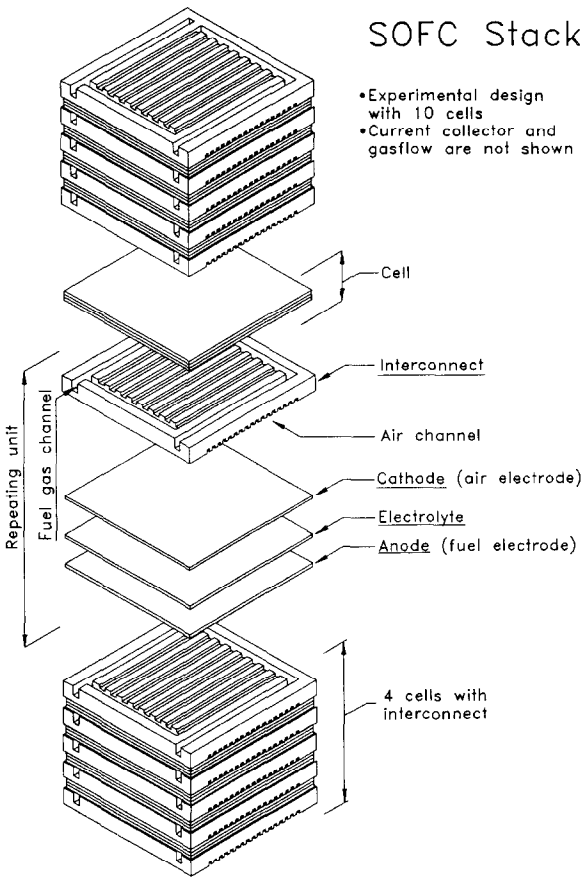

Fig. 1. Planar SOFC concept.

conditioning of the resulting products is required in order to obtain the desired powder characteristics. Figure 2 illustrates the morphology of one of the LSM powders produced.

Cell manufacture

As a technique for shaping thin, ceramic plates, tape casting is attractive because it is cheap, it can be scaled up and it can be automated. In the present context, tape casting was chosen for the manufacture of YSZ electrolyte plates. Slip recipes were developed and procedures for casting, drying and sintering of the resulting tapes were established. Dense YSZ plates are now produced routinely and at near-zero defect rate in large quantities, with the adopted standard dimensions for cell manufacture and testing: 45 mm×45 mm×160 μm; sizes up to 80 mm×80 mm have also been made. The sintering temperature is 1300 °C and the linear shrinkage rate is about 23%. Release agents have been identified which enable casting and drying on polyethylene foil, as required in industrial mass production. The rate of densification can be controlled by heat treatment of the as-delivered YSZ powder, this is important in studies of the co-sintering of cell components.

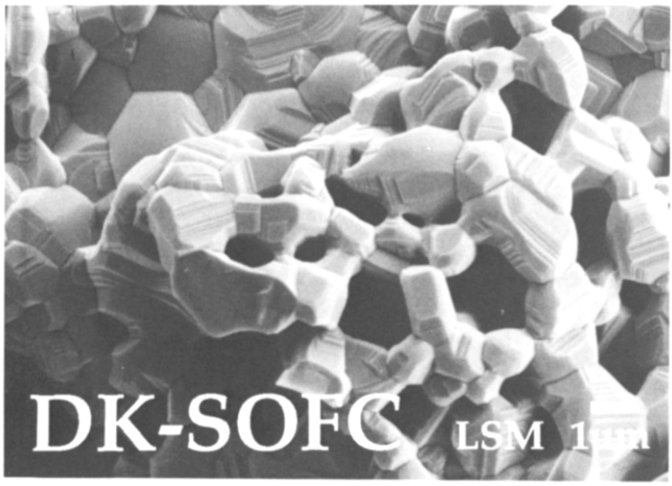

Fig. 2. LSM powder morphology.

Part of the tape casting development was carried out within the NORDTAPE* project, a joint development with companies and research laboratories in the Nordic countries and with support from the Nordic Industry Fund [4].

The cathode and anode layers are deposited on the YSZ electrolyte plates by airspray 'painting'. This is a low-cost technique which can easily be upscaled and automated. It can be used on 'green' or sintered substrates. The resulting electrode can be composed of a number of thin layers thus providing a graduated change in composition across the electrode thickness.

The LSM cathode has a thin, electrochemically active layer deposited directly on the electrolyte. On top of this there is a 50 to 200 μm porous layer primarily for the transport of air and electrons. This double-layer concept provides a good adhesion to the electrolyte of the thick, outer layer. The sintering temperature is 1300 °C. A typical value of the polarization resistance is 0.07 Ω cm^2 (1000 °C in air) at a polarization of 45 mV.

A simple four-point method for measuring the in-plane conductivity at room temperature of the cathode layer was used in the development. This is a fast technique which is well suited for quality control in mass production. Electrochemical measurements were carried out with methods described in ref. 5.

The development of the Ni–YSZ anode has been published elsewhere [6]. Also here the quick check of in-plane conductivity (after reduction) at room temperature was found very useful. In accordance with the general strategy, the sintering temperature was limited to 1300 °C. The polarization resistance (1000 °C, H_2 with 3% H_2O) is typically 0.06 Ω cm^2 at a polarization of 45 mV.

Cell testing

Development of material composition for electrodes and evaluation of fabrication process parameters require measurements of single cell performance. This should preferably be conducted in an environment which excludes stack-related problems such as variations in local gas composition and chemical interaction with interconnect

*NORDTAPE: Nordic Project for Tape Casting of Ceramics.

and sealing materials. For this purpose, a test stand design has been developed with the features summarized below. Details have been published elsewhere [7].

A SOFC cell is placed horizontally between two alumina tubes inside a furnace which can operate up to 1100 °C. Sealing between cell and tubes is accomplished by gold rings which also form part of the current collection. The maximum current is 20 A. Compression of the seals takes place at the operating temperature (usually 1000 °C) by applying an axial force of 100 to 500 g. The diameter of the rings defines a test area of 10 cm^2. Fuel gas and air are fed through central alumina tubes equipped with plates shaped for radical distribution. The materials chosen will prevent cracking in tests with hydrocarbons. Current collector networks of platinum and/or gold are screen printed onto the electrode surfaces in a pattern corresponding to the design (contact area, channel width) of the interconnect plates. This minimizes the influence of in-plane resistance of the electrodes.

A.c. impedance spectroscopy is used to obtain the differential resistances at increasing load and in order to separate the polarization resistances of the electrodes from the pure ohmic resistances. The measurements were carried out with 200 mA sinusoidal a.c. at 0.1 Hz–10 kHz, superimposed on different d.c. loads in the range of 0 to 6 A/10 cm^2.

A large number of cells manufactured as described in the previous section have been tested at 1000 °C. The fuel gas was usually 9% H_2 in N_2 to eliminate explosion hazards. The gas was saturated with water at room temperature (corresponding to a theoretical OCV value of 930 mV). Area-specific cell resistances in the range of 0.25 to 0.40 Ω cm^2 were obtained routinely. The results from a typical cell test is shown in Fig. 3 [7]. These results compare favourably with the current 'state-of-the-art'.

Stacking

With the design concept of Fig. 1, the LCC interconnect material must be shaped into plates with a thickness of several mm. The powder produced consists of agglomerated crystallites in nanometer size; the specific surface (say 33 m^2/g BET) is too large for shaping by wet methods due to excessive requirements for organic additives. However, it is possible to reduce the particle size in a controllable manner by calcination. For the shaping, hot pressing with various binder systems has been investigated. It was found possible to produce acceptable interconnect plates with the channels for internal

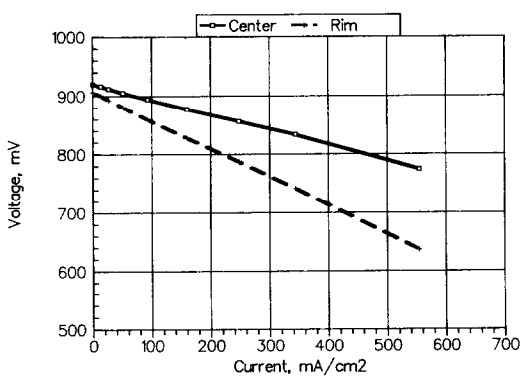

Fig. 3. Cell voltage (measured at cell centre and rim in the Risø test setup) as a function of current density at 1000 °C.

manifolding by one of these pressing techniques combined with sintering at 1300 °C in air.

A large number of glasses has been synthesized and evaluated for sealing between the stack components. Glasses based on silicon were considered undesirable in order not to affect the cell performance unfavourably. Possible candidate materials were screened by simple tests with heating to 1000 °C for a few hours: (i) in air or hydrogen and in contact with interconnect material, for check of interaction, and (ii) in steam for check of oxidation (weight loss).

Candidate materials have been identified and used in the stack tests conducted so far.

The initial stack testing revealed difficulty in obtaining a sufficiently good electrical contact between electrodes and interconnect. Slurries are being developed which will act as a 'glue' when assembling the stack components. The cathode/interconnect contact resistance has been reduced to an acceptable level below 0.025 Ω cm^2, whereas the anode slurry still needs improvement.

The initial stack testing involved experiments with one or two cells, including LCC end plates. The following problem areas were addressed in these tests:

(i) ohmic resistance between electrodes and interconnect;
(ii) ohmic resistance between LCC end plates and metallic conductor;
(iii) dimensional changes of interconnect during reduction;
(iv) gas channel dimensions, and
(v) application of sealing materials.

The experience thus gained was used to build and test a three-cell stack at the end of the program period. Each anode had its own, controllable gas flow. The air flow was through external alumina manifolds. The stack current was collected through gold plates in contact with the LCC end plates.

The test was conducted at 1000 °C with wet hydrogen (composition as in cell testing) and lasted 408 h (test termination was caused by break-down of the external gas supply, not by stack failure). The OCV obtained was 2.73 V (theoretical value 2.79 V) during the entire test period. The maximum power was 3.2 W (2.11 A, 1.53 V) and the effective area was 9 cm^2 for a single cell, giving a specific power density of 0.12 W/cm^2. The internal cell stack resistance was 189 mΩ/cell, corresponding to an area specific resistance of 1.7 Ω cm^2. This compares reasonably well with published results.

Fundamental research

The main aim of the research work was to support the technological development. In addition, new anode materials with potential for direct oxidation of methane were investigated.

Conventional electrode materials

In a paper describing the current state of electrode performance and the level of mechanistic knowledge, it is stated that there is only little understanding of the electrode mechanisms and their kinetics [8]. Cathode and anode investigations in the DK–SOFC program aim to improve the understanding of the electrode processes. Fundamental research is under way on the relations between structure, oxygen stoichiometry, composition and oxygen partial pressure, and on the effect of these parameters on the electrical and electrochemical properties of the electrode materials. The experimental methods used include: impedance spectroscopy; cyclic and linear sweep voltammetry; chronoamperometry; thermogravimetry; dilatometry; X-ray diffraction, and electron microscopy.

Results for the LSM cathode are summarized as follows [5]:

(i) three rate-limiting steps are indicated: O−O bond breaking; surface diffusion of oxide intermediates, and oxide ion transfer;

(ii) at 1000 °C, a reaction order varying between 0 and 0.3 with respect to oxygen was found when the oxygen partial pressure varied between 0.01 and 1 atm, and

(iii) the length of the gas/YSZ/LSM three-phase boundary is a parameter of major importance.

The main findings of the studies of the hydrogen oxidation on the Ni–YSZ cermet anode are [9]:

(i) two processes contribute to the hydrogen oxidation resistance: proton transfer from Ni to YSZ, and reaction of the resulting hydroxyl ions to water, and

(ii) the reaction order with respect to hydrogen of the above hydroxyl ion reaction varied from about 1 at a H_2 partial pressure of 0.1 atm to 2 at 1 atm H_2 pressure.

New anode materials

It is not possible to convert hydrocarbons on a Ni–YSZ anode. This is because nickel acts as a cracking catalyst and causes deposition of carbon in the electrode. It was demonstrated, however, that direct methane oxidation is possible using a CeO_2-based anode [10]. This presumably because this type of material is a mixed oxide ion and electron conductor. In order to be able to optimize the electrical properties, their dependency on dopant type and concentration must be known, this has necessitated extensive characterization. Also, it was shown that good adhesion to the electrolyte could be achieved using a 'neutral' oxide as interlayer. Reduction of pure CeO_2 is accompanied by a volume increase, this can to a large extent be suppressed by the addition of gadolinium. Sintering of CeO_2 and $Ce(Gd)O_2$ requires temperatures around 1600 °C which is unacceptable high as already noted. Process development is continuing to enable sintering temperatures around 1300 °C.

Conclusions and perspectives

1. A three-year program focusing on materials and process development for a planar SOFC concept has been completed. The major achievements include the following:
- production of 10 kg lots of cathode (LSM) and interconnect (LCC) materials with specified composition and powder characteristics
- routine manufacture of 10 cm^2 cells with area-specific cell resistances in the range of 0.25 to 0.40 Ω cm^2 at 1000 °C. Electrolyte and electrodes are sintered at 1300 °C
- dense sintering of interconnect plates at 1300 °C in air
- tests with small stacks with promising results

2. Electrochemical investigations of cathode (LSM) and anode (Ni–YSZ) materials have contributed to the understanding of the electrode processes and their kinetics.

3. CeO_2-based materials have been characterized extensively, aiming at new anode materials for direct oxidation of methane.

4. The three-year program has established a good basis for the further development for commercialization. Although the major part of the program was 'practice' (i.e., technological development), the combination with the 'science' line was found very useful.

5. A new four-year program 'DK–SOFC 1993–1996' is well under way, with a cost sharing similar to the previous program and total budget of 90 million DKr

(~US$ 15 million). The technological development includes stack building and testing in the 0.5–1 kW range, as well as smaller stacks specially instrumented to identify operational limits, to study internal reforming of natural gas, and to provide data for model verification. The fundamental research continues in general along the lines of the previous program. It is usefully supplemented by a CEC (Commission of the European Communities) project carried out by Risø with six partners; the main objective is here the development of new materials, in particular electrodes, for operation at 850 °C.

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