STACKING OF PLANAR SOFCs

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ABSTRACT

In the Danish SOFC programme major emphasis is placed on R&D leading towards manufacture and test of a 1/2-1kW stack based on the planar cross flow design. Small stacks have been built and tested. A number of challenges are encountered when building planar stacks. Two are being dealt with in the present paper: (i) attaining operational seals for electrodes and manifolds and (ii) minimizing the difference in thermal expansion between the yttria stabilized zirconia-electrolyte and the LaCrO₃-based interconnect material.

INTRODUCTION

The Danish Solid Oxide Fuel Cell Programme (DK-SOFC) is a national programme with participation of university laboratories (The Technical University of Denmark: Department of Physical Chemistry, Physics Department and Chemistry Department A, Odense University: Department of Chemistry), industrial partners (Innovation A/S and Haldor Topsøe A/S) and the Materials Department at Risø National Laboratory (project managing). The current phase of the programme has a budget of 90 MDKK (~15 M US$) over the years 1993 to 1996. The main purpose of the programme is to establish technologies for making solid oxide fuel cell stacks. One of the milestones is the manufacture and test of a ½-1 kW stack based on the planar cross flow design. Consequently, a major activity is devoted to experimental studies on stacking of planar cells, and a number of small stacks have been built and tested (3-5 cell stacks). The planar cross flow design with external manifolding and the materials used in the DK-SOFC programme are illustrated in Fig. 1.

This paper addresses two of the major problems encountered during experimental studies on stacking: (i) Sealant performance and (ii) Thermal expansion mismatch between electrolyte and interconnect material. Both subjects were introduced in (1).

SEALANT PERFORMANCE

Advantages of using a glass or glass containing sealant

During operation of the SOFC bipolar flat plate design with external manifolding (Fig. 1) it is necessary to prevent oxidant gas and fuel gas from mixing (1). Consequently seals are required both at the electrodes and at the manifolds.
It is commonly accepted that a glass or a glass-ceramic seal are to be preferred in favour of ceramic materials because:

- A glass/glass-ceramic seal is relatively easy to place due to its softness at elevated temperatures.
- Stress introduced during stack manufacture or during operation by thermal gradients or by differences in thermal expansion may be relaxed at the operation temperature.
- At lower temperature the glass based seal will be rigid and thereby contribute to the coherence of the stack, thus limiting the risk of damage during stack handling.
- Cracks formed in glass seals by handling or by thermal cycling may be healed by a subsequent heat treatment.
- Unlike most crystalline materials glasses do not have fixed stoichiometries. Modification of component concentrations are therefore permitted within certain limits, which enables continuous changes of glass properties, e.g. thermal expansion coefficient (TEC).

Requirements to glass sealing materials
Sealing materials will be in intimate contact with stack components during operation at a partial oxygen pressure in the range 0.2 to $10^{-18}$ atm. This results in a number of requirements to the seal material:

- High chemical stability in air and in fuel gas (with high steam content) in the whole temperature range 25-1000°C.
- Little if any chemical reactivity towards other stack component materials
- Wetting capability against other stack components (electrolyte, interconnect and manifold)
- Low vapour pressure in relevant gases and in the entire temperature range to minimize loss by vapourisation.
- Suitable viscosity at operating temperature, i.e. deformable but able to withstand a slight overpressure.
- A TEC that matches that of the other stack components. If the TEC does not match, the strength of the seal must be less than that of the surrounding stack components, provided that cracks in the seal can be regenerated at elevated temperatures.
- If crystallization is desired or cannot be prevented, the crystalline phases must also meet the above requirements and should not have any phase transformations that causes volume changes.

Experimental development of sealing materials
Within the DK-SOFC programme, pure glasses, glass-ceramics and glasses with ceramic filler materials are investigated extensively as potential candidates for electrode- and manifold seals. Glass formers $B_2O_3$, $P_2O_5$, $SiO_2$ and mixtures hereof have been included together with additives which modify the glass network. Major activities in the R&D are:

- Test on the substrates (a) yttria stabilized zirconia (YSZ) and (b) lanthanum chromite (LC) based interconnect material in relevant atmospheres to determine wetting ability and possible reactions between glass and YSZ or LC. Test atmospheres are air or a fuel gas mixture consisting of 9% hydrogen and 91% nitrogen with a fixed water content (in the following referred to as wet fuel gas). Samples are analyzed with XRD, optical and electron microscopy including chemical analysis with EDS.
- Thermogravimetric analysis (TGA) to determine high temperature stability with respect to the atmospheres mentioned above.
- Determination of glass points by DTA and by dilatometry.
- Measurement of thermal expansion coefficients (TEC) by dilatometry.
- Optimization of nucleation and crystallization properties by DTA and XRD.
- Electrochemical, structural and XRD analysis of seal interaction with electrodes and assessment of possible consequences of such interaction upon electrode performance.
- Test of sealants in real stacks.

Results and discussion

A number of compositions developed for high temperature coatings with B$_2$O$_3$ as glass former were tested. Compositions that contained B$_2$O$_3$ as the only glass former showed extensive reactions with the LC interconnect both in air and wet fuel gas, and up to 20% weight loss was observed. Modifications by addition of alkaline metal earth oxides and small amounts of P$_2$O$_5$ did not increase the stability. However, it increased the wetting on LC (2).

Experiments were performed with P$_2$O$_5$ based multicomponent glasses (3-5 components) with and without small quantities of SiO$_2$. Various oxides were added as stabilizers (e.g. alkaline metal earth oxides, Al$_2$O$_3$). In an attempt to decrease the reactivity towards LC interconnect, La$_2$O$_3$ and Cr$_2$O$_3$ were added to some of the glasses.

Stability experiments revealed that the major problem with glasses purely based on P$_2$O$_5$ as glass former is loss by volatilization, a loss that in all cases leads to surface nucleated crystallization. When a certain amount of P$_2$O$_5$ is lost, the surface composition moves away from the compositional region permitting glass forming and, hence, crystallization takes place. The crystalline phases usually formed are meta- or pyrophosphates, and these phases have generally a low stability at high temperature in wet fuel gas. The meta- or pyrophosphates will decompose further into stable orthophosphates, as exemplified with Mg-phosphates in reaction [1]:

\[
\text{Mg-P}_2\text{O}_3 \text{ glass} \rightarrow \text{Mg(PO}_3\text{)} + P_2O_5(\text{g}) \rightarrow \text{Mg}_2\text{P}_2\text{O}_7 + P_2O_5(\text{g}) \rightarrow \text{Mg}_3\text{(PO}_4\text{)}_2\ 
\]

Since the glass forming regions unfortunately do not extend into the orthophosphate stability areas, it is necessary to find ways to decrease the phosphate content, and simultaneously increase the glass forming ability and the stability of the glass structure, the latter to ensure a stronger bonding of P$_2$O$_5$. The approach chosen has been addition of various stabilizing oxides. Early experiments showed the importance of choosing oxides that are stable in the entire pO$_2$ range. A number of oxides were selected by a simple thermodynamical calculation of the equilibrium pO$_2$, these were added in small quantities (2-10 mole%). In all cases an increase in stability was seen, but a substantial number of the oxides promoted bulk crystallization (including Cr$_2$O$_3$ and La$_2$O$_3$). Only SiO$_2$ and ZrO$_2$ were found to increase the chemical stability and decrease the crystallization tendency. These experiments resulted in a number of very stable 4-5 component glasses, which showed no reaction with YSZ or LC. The glasses, however, have TEC values around 5-7x10$^{-6}$ °C$^{-1}$, while a reasonable target value for development would be close to that of YSZ, ~10.8x10$^{-6}$ °C$^{-1}$. Experiments were performed with glasses added up to 10 mole% alkaline
metal oxides to increase the TEC. Experimental results such as substantial weight loss and severe reactions with LC showed that addition of alkaline metal oxides is detrimental to the high temperature stability due to their depolymerisation of the glass structure and the consequent decrease in viscosity.

It has been possible to develop stable compositions in phosphate based systems, but these systems have a TEC which is too low. Fortunately the strength of these glasses has proven relatively weak. Cracks, therefore, tend to occur in the glass seals rather than in the YSZ.

Compositions based on silica as the main glass former have so far provided the best seals. Stable electrode seals that do not crystallize after several hundred hours at 1000°C and with a perfect TEC match with YSZ have been developed and tested with success in two stacks. A composite manifold seal with ceramic filler has also been developed and tested successfully.

A glass sealant may affect an electrode chemically over a short range through solid state reaction or over long distances through reactions involving vapour phase transport of decomposed glass components. Reactions are to be expected in areas where the seal is in intimate contact with the electrode. If reactions are limited to such areas the overall electrode performance will not be influenced significantly. If the reaction is associated with decomposition of the sealant followed by vapour transport of previous glass components, large areas of the anode may be affected and severe performance losses may result.

Interface (short range) reactions have been studied by heat treatment of mechanical mixtures (1:1) of powdered anode and phosphate or silica based glasses. The samples were analyzed with XRD to reveal reaction phases after a heat treatment for 100h at 1000°C in wet fuel gas. The phosphate based glass showed extensive reaction: All Ni had reacted to form nickel phosphide and zirconiumoxyphosphate had formed, too. With respect to silica based glass no reaction products between glass and anode were found.

The experimental setup used to analyze the influence of potential sealant vapour phases on the anode performance (long distance) is shown in Fig. 2. Samples are analyzed by microscopy and impedance spectroscopy after heat treatment at 1000°C in wet fuel gas. Fig. 3a-c shows microstructures of a reference anode, an anode which has been exposed to P2O5 based glass and an anode which has been exposed to SiO2 based glass, respectively. Little difference is seen between the reference anode and the SiO2 treated one, but the anode exposed to P2O5 based glass shows an extensive reaction; the structure is entirely changed, and there is little remaining porosity. The large white particles were determined by EDS to be nickel phosphide and no elementary nickel remained in the sample after 360 hours. For obvious reasons impedance spectroscopy was not performed on structures similar to that of Fig. 3b. Preliminary results from samples with silica based glasses have not indicated a dramatic degradation on the anode performance (3). However, more experimental work remains in this area.

MATCHING OF THERMAL EXPANSION

Residual stresses will exist in a stack cooled to room temperature in case of differences in thermal expansion between the stack components. If the TEC of the interconnect is lower than that of the electrolyte, the relative weak YSZ will be brought into a state of tension during
cooling. Part of the interest in chromites for interconnect material is associated with the possibility of obtaining reasonably high electric conductivities in relevant atmospheres. This is achieved by doping with Ca or Sr. Mg has been reported as dopant, too, (4) but is less attractive due to poor conductivity in reducing atmospheres. Selection of the amount of Ca-dopant represents a compromise between desired properties. LaCrO$_3$ with a high Ca amount attains good sinterability, a relatively high TEC and a high electrical conductivity. However, increasing Ca contents will increase a volumetric expansion on reduction (5), the temperature for a orthorhombic-rhombohedral transformation (6) and the quantity of liquid phase present in samples at operation temperature after the transient liquid phase sintering (7). According to Srilomsak (8), Sr is a more favourable dopant that Ca with respect to some properties. Sr increases the TEC and decreases the temperature of the orthorhombic-rhombohedral transformation.

A number of compositions with concentration of Sr in the range 16-28 mole percent, in some cases with small amounts of vanadium as sintering aid (9) have been examined. Chromite powders (Table 1) were made by continuous drip pyrolysis of solutions of organic metal complexes (10). Bars were uniaxially pressed and sintered for 8 hours at 1500°C. The thermal expansion and structural stability were analyzed by dilatometry. The analyses were performed in air in the range 25-1300°C. Resulting TEC values are listed in Table 1 together with values for YSZ and LC for comparison. Expansion curves are shown in Fig. 4 and TEC as function of Sr content is shown in Fig. 5. The LSC data are only reported for a temperature range from RT to 1000°C because deformation of the samples occurred at higher temperatures. Within the experimental accuracy addition of a small amount of vanadium does not have any influence upon the expansion characteristics. To acheive a good TEC match with YSZ the amount of Sr dopant should be approximately 24%. In addition the orthorhombic-rhombohedral transformation does not take place (cfr. Fig. 4). However, other properties such as expansion on reduction need to be taken into consideration. This aspect is discussed elsewhere in the present proceedings (5).

Future work should include isothermal dilatometric studies (1000°C) on the rate of dimensional changes as a function of pO$_2$. Furthermore, the creep rate of both LSC and YSZ should be measured at 1000°C to allow a more complete analysis of the stress distribution in a SOFC stack.

SUMMARY

A major research area in the Danish DK-SOFC programme is the development of sealing materials. Experiments revealed B$_2$O$_3$ to be inapplicable as glass former, alone as well as together with P$_2$O$_5$. Stability experiments with P$_2$O$_5$ based compositions demonstrated that the phosphate component is volatilized in as well oxidising as reducing environments at the operating temperature, and that this generally leads to surface crystallization. Optimized phosphate based multicomponent glasses showed no reaction with YSZ and LC. However, generally the compositions have TEC values below that of other stack components and the glasses are weak. Experiments on interaction with Ni-anodes in hydrogen showed severe short range and long range chemical reaction, all Ni was converted to NiP which killed the anode functions completely. Stable SiO$_2$ based electrode- and manifold seals with a perfect TEC match to the stack components have been developed and tested successfully in real SOFC stacks.
Experiments on interaction with Ni-anodes did not indicate reactions.

The emphasis has moved from Ca-doped to Sr-doped lanthanum chromite as interconnect material, major problems with the Ca-compounds being low TEC and instability. Chromites with high Sr contents have been examined with respect to TEC and phase transformation. A good TEC match to YSZ and absence of phase transformation has been obtained with 24% Sr doping in LaCrO₃.

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| Composition                  | Thermal expansion coefficient 25 - 1000°C (x10^-6 °C^-1) |
|-----------------------------|-----------------------------------------------------------|
| La_{0.86}Sr_{0.16}CrO_3    | 10.3                                                      |
| La_{0.80}Sr_{0.20}CrO_3    | 10.6                                                      |
| La_{0.76}Sr_{0.24}CrO_3    | 10.7                                                      |
| La_{0.72}Sr_{0.28}CrO_3    | 11.0                                                      |
| La_{0.84}Sr_{0.16}Cr_{0.97}V_{0.03}O_3 | 10.4                                          |
| La_{0.80}Sr_{0.20}Cr_{0.97}V_{0.03}O_3 | 10.5                                          |
| La_{0.76}Sr_{0.24}Cr_{0.97}V_{0.03}O_3 | 10.7                                          |
| La_{0.72}Sr_{0.28}Cr_{0.97}V_{0.03}O_3 | 11.0                                          |
| La_{0.79}Ca_{0.22}CrO_3    | 10.0*                                                     |
| YSZ Tosoh TZ8Y              | 10.8*                                                     |
| Tape casted electrolyte plate |                                           |
| YSZ Tosoh TZ8Y              | 11.0*                                                     |
| Large pellet                |                                                           |
| Spinel manifold (ref. 11)   | 10.6*                                                     |

Table 1. TEC values for a number of LSC compositions, values for other SOFC components are listed for comparison.

* Determined by Gurli Mogensen, Haldor Topsøe A/S. The Haldor Topsøe and Risø dilatometers are calibrated with the same standards, thus the values are directly comparable.
Fig. 1. Bipolar flat plate design and materials used in the Danish SOFC programme.

Fig. 2. Schematic drawing of a glass-anode sample. The glass is placed close to the anode, but without being in direct contact, hence allowing a study of reactions caused by vapour phase transport of glass components.
Fig. 3a,b,c. These figures represent cross-sections of three kinds of anodes taken by optical microscopy, all at magnification x800. Fig. 3a is a structural reference anode used for comparison. Fig. 3b shows an anode, heat treated with a phosphate based glass. A substantial change in anode structure is evident. The white areas contain the Ni as NiP with a much larger particle size than seen with Ni particles in the reference anode (Fig. 3a). There is no contact between the large NiP particles. Fig. 3c similarly shows an anode, heat treated with a silica based glass. The slightly enlarged Ni-particle size relative to Fig. 3a is probably due to reproducibility problems in the anode manufacturing process.
Fig. 4 Linear thermal expansion of La$_{1-x}$Sr$_x$Cr$_{0.97}$V$_{0.03}$O$_3$ and La$_{0.78}$Ca$_{0.22}$CrO$_3$. Orthorhombic to rhombohedral phase transformation is seen at around 250°C for the LCC sample whereas no transformations is seen for the LSC material.

Fig. 5 TEC values from 25-1000°C for La$_{1-x}$Sr$_x$Cr$_{0.97}$V$_{0.03}$O$_3$ as a function of Sr amount.