Strategic Electrochemistry Research Center, DSF project 2104-06 -0011
Qualitative report, Annex to the final report, May 29, 2013.

This report describes in 5 pages the main outcomes of the SERC project.

1. Research results

Due to the fact that SERC was a 6 year project with a large budget, many results have been generated. Most of them have already been published in 77 papers and more are to come. A few of the results are listed here.

a) High pressure test set-ups for electrolysis

In order to produce synthetic hydrocarbon fuels from synthesis gas produced by co-electrolysis followed by conversion into e.g. synthetic natural gas, dimethyl ether (diesel substitute) or petrol/diesel it is advantageous to pressurise the gases to 10 – 80 bar since the catalytic conversion of synthesis gas is operated at increased pressure. The pressurisation favours the catalytic conversion of synthesis gas and in addition also favours the electrode kinetics. Construction of high-pressure set-ups for operation of cells and stacks using autoclaves was therefore undertaken. Two high pressure set-ups of 95 bar have been constructed and three more (two 50 bar and one 95 bar) are under construction as part of SERC and associated projects. It was planned to map the effect of higher pressure at various conditions of temperature and gas composition as part of the SERC project but construction has been extremely time-consuming and only limited experiments have therefore been performed as a part of the SERC project. Fortunately, new projects have been awarded for the continuation of this work.
The performance of the solid oxide cells improves significantly in both SOEC and SOFC mode with increasing pressure. When operating the cell at 750°C and 0.4 bar the power density in fuel cell mode is 0.6 W/cm^2 and when increasing the pressure to 10 bar the power density increases to 0.95 W/cm^2 as shown in

Figure 1. The SOEC efficiency is weakly affected by the pressure range in the present study. At -0.5 A/cm^2 the cell voltage at 0.4 bar is 1.29 V and at 10 bar it is 1.26 V due to the fact that the open circuit voltage increases with increasing pressure as predicted by the Nernst equation. The internal resistance of the cell decreases with increasing pressure. Although the ASR is decreasing, the decrease is insufficient to offset the increase in OCV. Therefore there is no noticeable effect on the SOEC efficiency at the current densities measured.

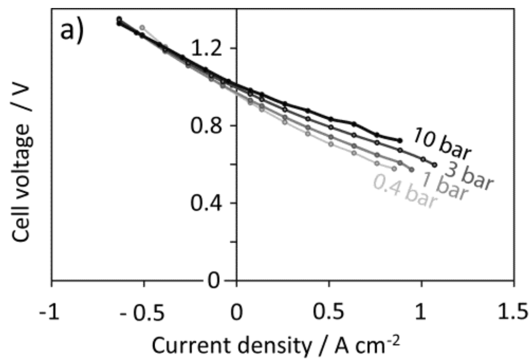

Figure 1. i-V curves measured on a 16 cm^2 planar SOC at 750°C. The i-V curves were obtained with 50% H_2+50% H_2O (24 l/h) supplied to the Ni/YSZ-electrode and 50 l/h O_2 supplied to the LSM/YSZ-electrode.

b) Quantitative image analysis of solid oxide electrodes by focused ion beam 3D reconstruction

The activities in quantitative image analysis and 3D reconstruction in SERC has focused on three main areas: experimental techniques, 3D image segmentation and computational methods for quantifying distances, sizes and connectivity within the segmented structure. The experimental part of the activities has seen major improvements in the quality of the acquired image data. This progress has mainly been obtained through better sample preparation, better programming of the milling macros and tuning of FIB milling current and SEM imaging conditions.

A novel segmentation technique based on a level set method was introduced that makes it possible to better utilize the local 3D intensity structure of the image data to perform more accurate segmentations. The technique utilizes expanding wave fronts that are attracted to the fastest changes in intensity, which typically coincide with the true location of phase interfaces.

The most important results of the SERC activities has been the development of novel and highly accurate methods for quantifying the interface properties of the electrodes e.g. interface areas between phases and triple phase boundary length. It is now possible to perform a full analysis of each TPB site in a reconstructed volume, including its percolation pathway distance through each of the three phases, the bottlenecks in those pathways and the tortuosity of the pathways.

The SERC activities have sparked a wealth of possible future application areas e.g. modeling of physical properties on the reconstructed microstructure and utilization in a diverse set of different technologies.

c) Local, in situ scanning probe microscopy for electrochemical measurements

Two controlled atmosphere high temperature scanning probe microscopes (CAHT-SPM) where a fine tip is used to probe local electrical/electrochemical surface properties at temperatures and atmospheres relevant for solid oxide cells have been built by in cooperation with DME Danish Micro Engineering A/S during the project. The microscopes have been used for testing of gold and cathode microelectrodes by microimpedance spectroscopy. It was possible to obtain reproducible spectra at a number of relevant conditions including low pO_2 and polarisation. The microscopes have also been used to study dynamic surface processes such as break up of a gold film and in situ reduction of a NiO-

YSZ cermet by hydrogen. The entire process from introduction of hydrogen to complete surface reduction could be mapped between 300 and 525 °C while scanning the surface. An incubation period previous to onset of reduction, much discussed in the literature, was identified and a mechanism suggested. Activation energies could be calculated and showed the retardation by water in humidified experiments and two temperature regimes for the dry reductions. Furthermore, high temperature Kelvin probe microscopy, where surface potential distributions can be mapped have been successfully tested.

d) Methods of analysing impedance spectra

Solid oxide cell (SOC) performance is limited by various processes. One way to investigate these processes is by electrochemical impedance spectroscopy. In order to quantify and characterize the processes, an equivalent circuit can be used to model the SOC impedance spectra. Unfortunately, the optimal equivalent circuit is often unknown and to complicate matters further, several processes contribute to the SOC impedance - making detailed process characterization difficult. Analyzing differences in a series of impedance spectra measured at operating conditions that only affects a few of the processes can assist the analysis. An example is spectra that were measured during electrolysis operation which only affected the Ni/YSZ-electrode of the cell and not the other electrode or the electrolyte. Differences between the spectra can be modeled as a change in the Ni/YSZ electrode impedance, i.e. it can be modeled with a model that does not involve the other parts. This makes the model much simpler and makes it possible to distinguish between two equivalent circuits, the Cole-Cole element (*RQ*) and the modified Gerischer (*Ge*) element.

e) Internal reference oxygen sensor (IROS)

An oxygen sensor with an internal reference electrode was developed in the SERC project. The IROS is potentiometric and uses the equilibrium pO_2 of the binary mixture of Ni/NiO as the reference pO_2. The sensing electrode of the IROS was made of metallic Pt or the composite of $(La_{0.75}Sr_{0.25})_{0.95}MnO_{3\pm\delta}$ (LSM25) and 8 mol % yttria stabilized zirconia (8YSZ), with/without samaria doped ceria (SDC) impregnation. The composite sensing electrodes were verified to be superior to Pt in terms of a lower polarization resistance and an extended working temperature range. Cell performance evaluations show high accuracy, good stability for more than 6600 h, fast response, good tolerance to thermal and pO_2 cycling and easy recoverability when Ni is depleted. Both cell fabrication and performance show good reproducibility. Apart from the excellent performance, the IROSes are fabricated by an inexpensive and flexible method. A patent application has been filed and proof-of-concept funding has been received to develop a sensor with an integrated furnace for commercial application. Dansensor, a SERC project partner, is quite interested in the sensor and will perform tests later on.

f) Density functional theory

Density functional theory (DFT) is a quantum mechanical calculation method that has its strength in finding trends of many materials properties as a function of a variety of parameters. One example was the calculation of the thermodynamic properties of transition metal oxide perovskites (AMO_3, A = Y, La, Ca, Sr, Ba; M = transition metals from Ti to Cu) as a function of atomic number and the underlying change in electronic structure, i.e. correlation with the differences in d-band centers of La/Y and M.

All these families of perovskites exhibit a systematic linear scaling between their energetics and the atomic number of M. The scaling was previously revealed by experiments only for some La perovskites at 1273 K. This behavior was found for other families of perovskites, and the insight allows the following generalization: the slope of the lines is determined by the oxidation states of A and M. Therefore, these compounds could be divided into two groups: perovskites with the same oxidation state for A and M (+III for $A'MO_3$; A'=Y, La), and perovskites in which their oxidation states differ (+II and +IV for $A''MO_3$; A''= Ca, Sr, and Ba). The former are more stable than the latter and their stabilities along the 3d series decrease more slowly. Such data are very useful for selecting new electrode materials for improved solid oxide cells.

2. Industrial and societal results

The synergy between the projects has been inherent for SERC as all work has been dealing with similar types of cells and establishment of new refined methods for studying these cells. Three companies are especially in focus concerning the synergy between SERC and the industry. These are Haldor Topsøe A/S, Topsoe Fuel Cell A/S and Dansensor A/S. According to SERC participants John Bøgild Hansen (HTAS) and Niels Christiansen (TOFC) the SERC activities such as development of advanced characterization methods, e.g. the 3D image analysis, result in a valuable tool for development of SOEC and SOFC. TOFC has a significant interest and commitment to follow and participate in the leading development in this field ensuring long term competitiveness. Ultimately they want to implement the results in future SOFC and SOEC components. Dansensor A/S benefits from the knowledge obtained through SERC. This concerns both new electrode materials and the general design of the oxygen sensor. A new oxygen sensor has been developed in one of the Ph.D. projects and Dansensor has a strong interest in this. A patent application has been filed and the Ph.D. student has acquired proof-of-concept funds for further development, and the objective is to fabricate a handheld device to be tested by Dansensor A/S.

3. Research education

The Strategic Electrochemistry Research Center has implemented its scientific objectives mainly through the education of Ph.D. students and postdocs. Furthermore, some M.Sc. projects and a bachelor project were included. Below is a list of the theses outcome from these projects.

8 Ph.D. theses
4 M.Sc. theses
1 B.Sc. thesis

As a part of the SERC center, all Ph.D.s and postdocs have presented their work at the SERC meetings twice a year and written short reports to be published on the website. Longer reports were written for the benefit of the students allowing them to evaluate their work regularly in cooperation with supervisors and other interested partners, and to improve their scientific writing as the first step in writing journal publications. 152 months of postdoc training were undertaken during SERC.

4. Collaboration, including cross-institutional, interdisciplinary and international cooperation

The SERC partners include 8 Danish companies who have regularly attended the SERC meeting, sometimes given presentations, and have also been involved in the Ph.D. and postdoc projects.
DME Danish Micro Engineering and DTU Energy Conversion has been working in close collaboration on the controlled atmosphere high temperature scanning probe microscopes in order to refine the second proto type microscope (CAHT2) to both ensure the development of the microscope to a commercial level and to document its capabilities to perform advanced in situ analyses.

Six university institutes have participated actively in the SERC project contributing with a budget, some of them hosting a Ph.D. student or postdoc.

SERC had from the beginning three supportive international universities. Two of them have been active and three more have been acquired.
John Irvine and coworkers from University of St. Andrews have been to DTU Energy Conversion as part of SERC cooperation three times and Henny Bouwmeester from University of Twente have been there once, both giving talks at the SERC meetings.
DTU has together with Klaus Lackner from University of Columbia, NY, USA via SERC cooperation started a series of yearly workshop on capture and conversion of CO_2 into sustainable hydrocarbon fuels . Now 5 workshops have been held. Christopher Graves, one of Klaus Lackner's Ph.D. students spent a large part of his time (1½ year) at DTU Energy Conversion doing most of his experimental Ph.D. study at DTU Risø Campus. Christopher is today employed as researcher at DTU Energy Conversion.
Annika Utz, a Ph.D. student from Karlsruhe Institute of Technology visited DTU Energy Conversion for 3 month doing work within SERC. This resulted in a common journal article.