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# Solid Oxide Development Status at DTU Energy

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Solid oxide fuel cells and electrolysis (SOFC, SOE = SOC) are efficient technologies to link together energy sectors such as power, gas, and heat. They can thus emerge as key technologies in the current energy transitions towards systems based on renewable energy sources. DTU Energy has a long history of research in the areas of SOC and has currently an effort of ca. 35 person-years per year. The presentation will introduce the recent achievements ranging from materials development, cell & stack development, and advanced diagnostics to system analysis and modelling. Examples are significantly improved cells based on state-of-the-art, metal supported cell types, use of alternative fuels such as ammonia and biogas, stack and stack component development, and increased basic understanding aided by phase-field and multi-physics modelling.

## Introduction

The research at the Department of Energy Conversion and Storage at the Technical University of Denmark (DTU Energy) dedicates to developing technologies for the future energy systems based on renewable energy sources. Examples for those technologies are fuel cells (e.g., PEM, SOFC), electrolysis (e.g., PEM, SOEC, alkaline), batteries (e.g., Li-ion, flow batteries), and more. Strong focus lies on methods, such as ceramic processing, detailed electrochemical diagnostics, advanced micro structural analysis, modelling at different levels, combined with materials and integration (cell and stack development, integration analysis into full systems). The research spans thus over a large range of technology readiness levels and is strongly interdisciplinary. Motivated by worldwide goals to achieving low fossil or even fossil-free (for example in Denmark by the year 2050) societies, concepts involving solid oxide cells (SOCs) are considered key technologies. The efforts on SOCs have a long tradition at DTU Energy. Research currently amounts to ca. 35 person-years per year, with projects financed through Danish funding, EU, commercial partners, and funding from DTU.

The contribution presents selected recent achievements in the areas of cell/stack development, innovative manufacturing, lifetime evaluation in tests and through advanced diagnostics, and modelling.

## Recent Achievements

Cell and stack development

State-of-the-art (SoA) SOCs typically consist of Ni/YSZ fuel electrodes, YSZ electrolytes, and LSCF/CGO or LSC/CGO oxygen electrodes separated from the electrolyte by a CGO barrier layer. Despite limitations of this cell type such as redox stability or carbon tolerance, they are currently the cell type in the demonstration units or in commercial units. Through structural optimization together with compositional refinement, it is possible to even further improve SoA type SOCs regarding both performance and lifetime, including improved mechanical properties. The fracture energy of the current DTU Energy SoA NiO-3YSZ fuel electrode supports is already ~200 % higher than that of typical NiO-8YSZ. By introducing Ce as a co-dopant to Y in the zirconia and optimizing the composition for optimum transformability, an even further increase of fracture energy of 50 % was achieved (>300 % tougher than NiO-8YSZ) (1, 2). With the increase of fracture energy, the strength also increases as the two are related. The achieved far higher mechanical strengths are particularly important for the anticipated large systems in power-to-X strategies, requiring larger cell areas and larger stack sizes in order to convert electricity from for example wind turbines at the MW scale. At the same time, improved fuel / water steam electrodes allow for enhanced performance and lower degradation.

Besides SoA cells, manufactured through SoA ceramic processing methods such as tape casting and screen printing, DTU Energy has worked on 3D printing technology of cells/cell layers. This technology promises significant reduction of investment costs, raw materials costs, and it allows for innovative cell and stack architectures. In the frame of the EU funded Cell3Ditor project, DTU Energy is working on the deposition of functional thin layers (< 1 μm) of nanomaterials by inkjet printing and thick supports by robocasting (3, 4). Nanodispersions of NiO, CGO and YSZ have been produced by continuous flow hydrothermal synthesis, a scalable method for the production of large amounts of dispersed nanoparticles (5). These dispersions are converted into inks for inkjet deposition, producing nanostructured layers after sintering. This approach allows depositing functional materials with high surface area, but requires careful study of the sintering process due to the high shrinkage of nanoparticles. Figure 1 shows cross section micrographs of the printed layers after sintering. Nanoparticle-containing inks for inkjet printing were used to print thin layers of nano CGO, YSZ and YSZ/NiO. The YSZ and YSZ/NiO samples were sintered at 800 ºC in air and show uniform layers with nanoporosity on both porous and dense substrates, in the case of printed YSZ and YSZ/NiO respectively. The CGO layer is sintered at 1000 ºC onto a pre-sintered YSZ/NiO anode and is also characterized by nanosized porosity. Challenges to be solved involve cracks due to the shrinkage mismatch between the printed layer and the substrate.

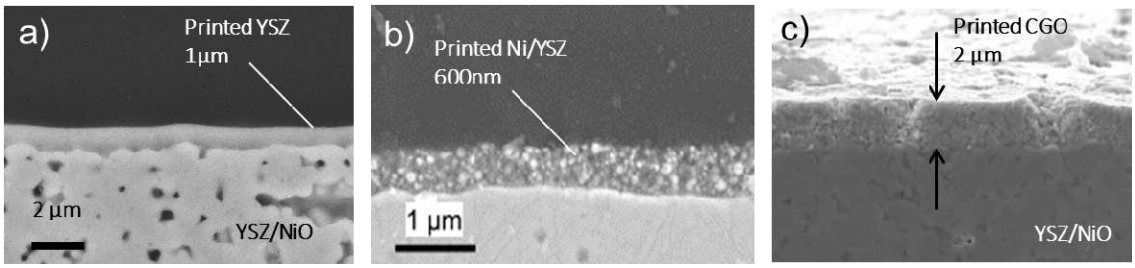


Figure 1. SEM Micrographs of cross sections of layers deposited by inkjet printing, taken after sintering. a) YSZ electrolyte (6), b) Ni/YSZ anode (3), c) CGO barrier layer (4, 5).

An enhanced focus on stack and stack component development has led to the discovery of improved oxygen electrode contact layers and glass sealings. The contact layer between the oxygen electrode and the interconnect is a critical interface in the SOC stack, as it is typically made by perovskites similar to that of the oxygen electrode itself. The challenge is to sufficiently sinter the contact layer *in-situ* in the stack, such that it bonds well with the adjacent components, without exposing other stack components to too high temperatures for too long time periods. Thus, the SoA contact layers typically have a fracture energy in the order of ~1 J/m$^2$. At DTU Energy, the toughness of the contact layer has been drastically increased by use of *in-situ* reactive oxidative bonding. In this approach, metallic particles (Co-Mn, Cu-Mn) are deposited, which through the assembly of the stack oxidize to well conducting spinels. The oxidative reaction through the forming of the spinels assists the sintering process and increases the adherence by a factor 5 or 10 for the CoMn and CuMn contact layers, respectively (1, 7). This research is undertaken in the EU project LOWCOST-IC and the plan is to test these contact layers together with novel coating and steel compositions in stacks from the companies SOLIDpower and Sunfire.

The glass sealing is another critical interface in the SOC stacks, which is prone to failure. In recent works we have shown that the fracture energy of these interfaces is not only dependent on the glass-ceramic itself, but also on the coatings, the glass is adhering to (8). Using an in-house developed glass-ceramic material, denoted V11, together with an in-house produced alumina coating on Crofer 22 H, we have shown that the fracture energy of this assembly can be enhanced by a factor of 5 as compared to SoA (1).

## Lifetime of SOCs

Durability studies to identify and counteract degradation mechanisms. SOFCs based on SoA compositions, i.e. Ni/YSZ anode support, Ni/YSZ anode, YSZ electrolyte, CGO barrier layer, and LSCF/CGO cathodes, have achieved a high degree of maturity and are used for degradation studies and identification of safe operating windows. These studies include tests over long durations to establish baseline durability values and assess microstructural evolvements after operating times close to realistic periods. A SOFC test in hydrogen fuel at 700 ºC is approaching five years with a degradation rate below 1%/1000 h in the last 10000 hours of operation, which is a viable value for commercial application (see Figure 2).

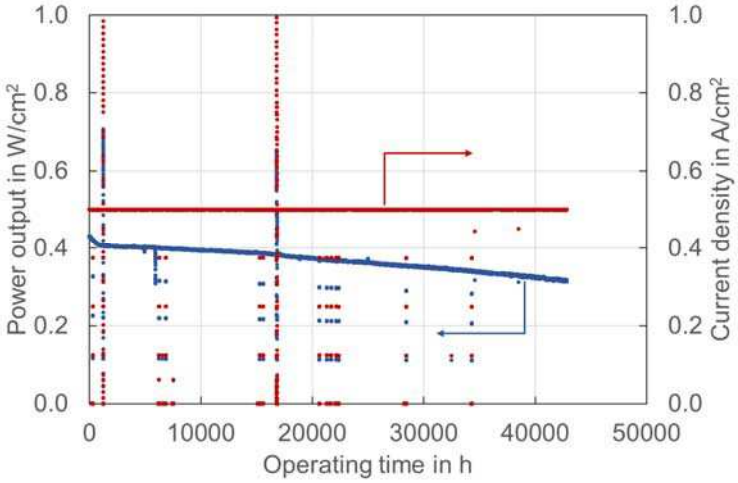


Figure 2. Baseline durability test in hydrogen fuel at 700 °C, 0.5 A/cm$^2$, cell with Ni/YSZ anode support and anode, YSZ electrolyte, CGO barrier layer, and LSCF/CGO cathode with 16 cm$^2$ active area.

Methane containing fuel. SOFC have the unique advantage of fuel flexibility. Systems in stationary applications typically use natural gas. In the future, sustainable systems, e-gas – the product of power-to-X using renewable electricity sources and electrolysis – is an attractive opportunity for high density fuels stored and transported through an existing infrastructure. New cell generation comprise metal supported cell (MSC) types, which promise higher mechanical robustness and lower costs. To fully exploit their potential, those cells should be able to work on hydrocarbon fuels, as well. So far, results have been obtained with hydrogen fuel. MSCs typically contain less nickel in the fuel electrode as compared to SoA Ni/YSZ, and thus the activity for internal reforming of methane and other hydrocarbons might be limited. Other intrinsic catalytic reactions like the water gas shift/reverse water gas shift reaction might run differently and the postulated equilibrium fuel compositions can be different from the case of SoA fuel electrodes. Furthermore, the lower operating temperatures by ca. 100 °C might lower the rates of the catalytic reactions. The MSC generation tested with methane and steam as fuel contained a smaller amount of Ni (< 1 mg/cm$^2$ of cell area), which was infiltrated on a backbone of lanthanum strontium iron nickel titanate (LSFNT), instead of having Ni in the SoA Ni/YSZ cermet. Indeed, tests with this MSC version revealed for the first time that the methane reforming reaction occurs also with the lower amount of nickel in the fuel electrode (see Figure 3); however, the conversion is not complete – as it is the case on SoA Ni/YSZ. In the iV curve characterization, the lower conversion is visible through the lower than expected open circuit voltage (OCV). In the current test, the OCV should be above 1000 mV. For the current MSCs version, the conversion amounts to ca. 17% (9). It is still possible to operate the MSCs over several hundred hours with methane and steam as fuel and thus, MSCs can operate on e-gas, once the reforming function is further optimized.

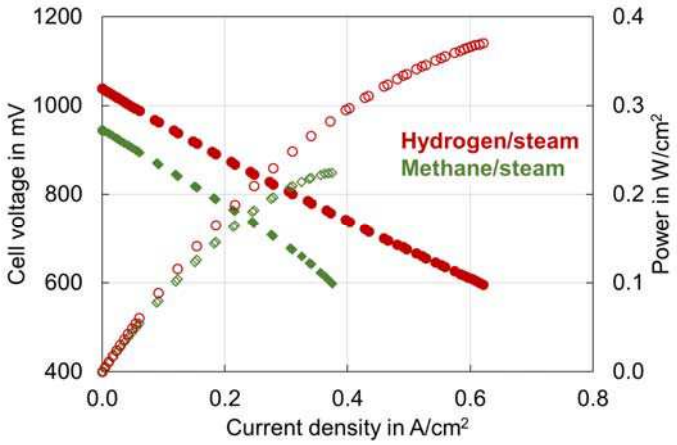


Figure 3. Performance of a MSC with a lanthanum strontium iron nickel titanate backbone and infiltrated Ni/CGO anode, and LSC cathode at 650 °C in hydrogen or methane containing fuel (9).

Hydrogen carrier: ammonia. Ammonia has gained renewed attention as a well-proven medium for storage and distribution of energy from renewable sources with high energy density. One motivation is that it might be challenging to extract sufficient carbon to produce needed fuels for aviation and shipping. With ammonia, the feedstock is readily at hand most places in the world. When using ammonia in a SOFC, electricity production without local emissions of $CO_2$ are possible. Therefore, DTU Energy participates in the SOC4NH3 project, with the objective to further investigate the implications of using ammonia as an energy vector in the society. The compatibility with state-of-the-art SOFC technology was previously successfully demonstrated on cell level. In fact, ammonia is completely cracked into hydrogen and nitrogen under SOFC operating conditions and the performance and durability behavior is the same as if hydrogen is fueled (10, 11). This applies for the initial performance and the durability as well (see Figure 4).

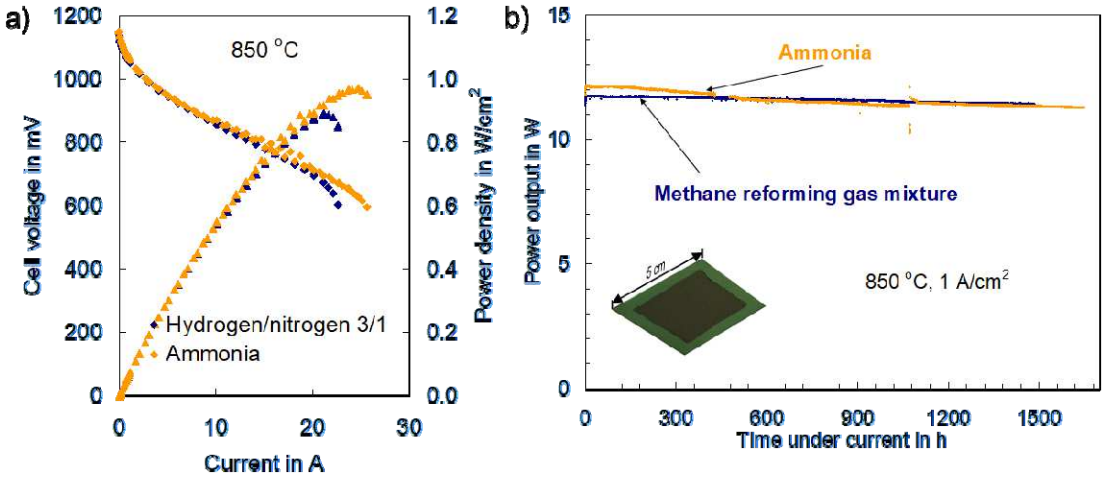


Figure 4. Use of ammonia as fuel. (a) iV curve at 850 °C with a mixture of nitrogen / hydrogen (blue curves) of 1/3 and pure ammonia (orange curves), (b) Long-term test at 850 °C, 1 A/cm$^2$ with ammonia fuel (orange curve) and with methane reforming gas mixture fuel (blue curve). From ref. (10).

Use of biogas. Biogas is another attractive sustainable fuel. This mixture of $CO_2$ and methane forms through anaerobic digestion of organic matter. It is worldwide a large resource from wastewater treatment or landfill. $CO_2$ in the biogas is an internal reforming agent of methane, which helps to avoid the carbon formation, which otherwise would deposit in the pipes for fuel delivery and lead to fatal degradation of SoA SOFC anodes. In order to avoid the thermodynamically preferred carbon formation, the addition of more reforming agent is required. This is easily achieved through anode recirculation. It was demonstrated at cell level, that this approach is feasible (see illustration of the principle and test results in Figure 5).

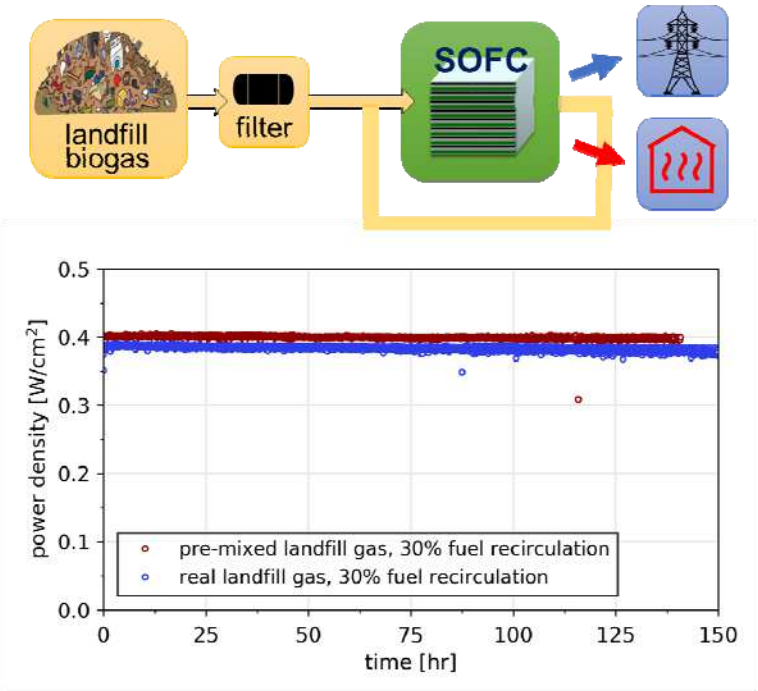


Figure 5. Use of landfill biogas. Upper: Illustration of principle. Lower: SOFC test with fuel recirculation on pre-mixed biogas (red curve) and real landfill biogas (blue curve), (12).

Dynamic SOEC operation. SOEC can utilize electricity from renewable sources such as wind or solar, which are fluctuating by nature. Degradation mechanisms might differ when running SOEC (steam or co-SOEC) under load following conditions as compared to constant operation. This question was one of the major topics in the EU funded ECo project for the case of co-SOEC of steam and $CO_2$. A real wind profile was modified and put into SOEC test conditions (see Figure 6). When testing cells or stacks according to such a dynamic profile, the cell voltage degradation, i.e. increase of voltage, was similar to the values obtained at constant conditions and similar current densities. This result indicates that no additional degradation occurs due to the dynamic operating profile and that the durability is mainly determined by the applied current density.

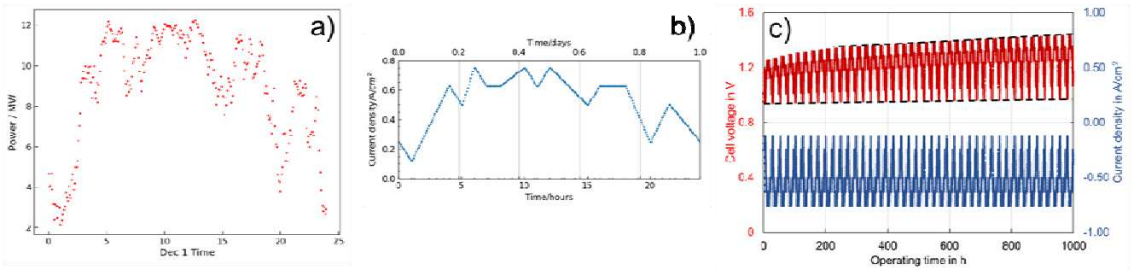


Figure 6. (a) real data of electricity from wind turbines, (b) operating profile for cell and stack test, (c) cell test of SoA type cell with improved fuel electrode following the profile shown in (b) at 750 ºC using co-SOEC with 65%vol $H_2O$, 25%vol $CO_2$, 10%vol $H_2$.

## Electrochemical diagnostics

Diagnostics of faults. Durability and reliability are major issues for market introduction of Solid Oxide Fuel Cells (SOFCs). The development of online diagnostic tools for state-of-health (SoH) estimations of an operating stack addresses this concern by identifying critical failures and thereby avoiding premature stack degradation. Some of the activities target a signal-based diagnosis approach. Hereby, conventional stack signals (e.g. stack voltage or gas/stack temperatures) and electrochemical impedance spectra were recorded during designed fault experiments. Specifically, fuel starvation and carbon deposition failures were primarily considered as realistic faults for system operation. The different system responses were analyzed to extract applicable 'fault metrics' indicating deviations from nominal operating conditions.

In Figure 7, possible 'failure indicators' for detecting fuel starvation from a conventional signal, more specifically, the variance of the stack voltage and EIS, i.e. area specific resistance (ASR) of the gas-conversion impedance, are presented. These two metrics clearly demonstrate the possibility to differentiate between nominal considered FU (i.e. 77%) and abnormal FU operation. However, whereas diagnosis based on conventional signals may be easier to implement, it shows to be limited to specific operating conditions. On the contrary, the identified EIS metric allows differentiating between nominal and 'abnormal' state in both cases. Such approaches can be implemented in stacks and systems.

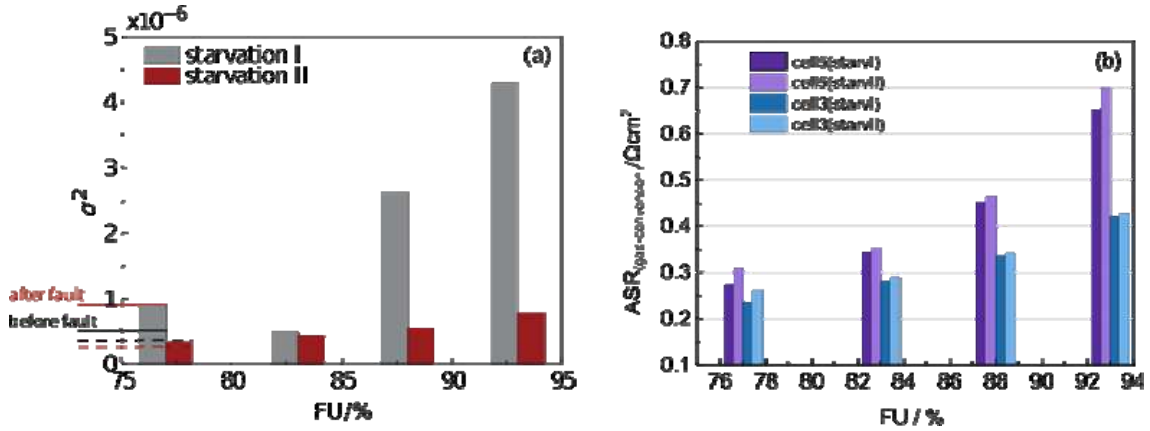


Figure 7. Variance of the voltage signal (a) and ASR of gas-conversion impedance of two repeating units (b) while stepwise increasing the fuel utilization from 77% to 93% under constant current (starvation I) and under constant power (starvation II) operation, from ref (13).

Effect of fuel impurities. SOFC are proposed to run on biogas fuel, or other renewable fuels, which can contain impurities. Particularly the effect of $H_2S$ on performance and durability of SOFCs has received extensive attention. Most relevant are cases, which consider methane containing fuel, because this is a realistic case for a sulphur containing fuel, where, furthermore, sulphur affects the reforming reaction as well as the electrochemical processes. The typical approach is operating the SOFC at constant conditions, adding a specific $H_2S$ concentration to the fuel, observing the changes of cell voltage after steady state is reached, adding the next concentration and/or removing $H_2S$ and observing recovery. The main response parameter is the cell voltage drop. This approach is time consuming and bears the risk of degradation of the SOFC overlapping with the short term and reversible effects of adding $H_2S$. To avoid this risk, fresh calls are used for each different operating condition, which is both time consuming and expensive. A new methodology of analyzing the tolerance of a specific SOFC towards $H_2S$ in the fuel was developed based on iV curve measurements (illustration see Figure 8). It delivers cell voltage drops due to sulfur coverage of active sites in the Ni/YSZ anode, which are well known from traditional steady state studies and it provides the opportunity of prediction of cell voltage drops for a large range of operating conditions in short testing times and allows for predicting safe operating windows (14). This methodology can be applied to all poisons, which adsorb on the active sites in the SOFC electrodes.

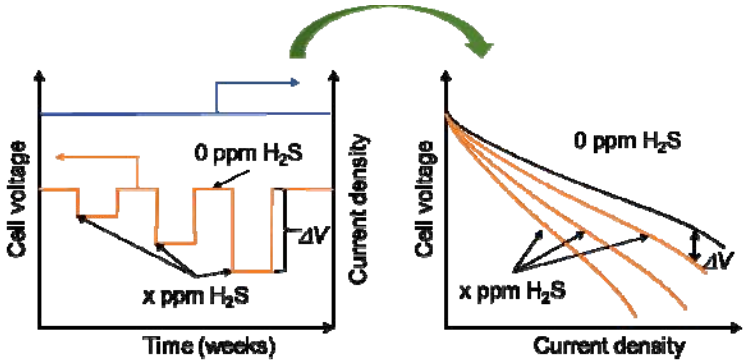


Figure 8. Approaches for analyzing $H_2S$ poisoning: left: typical, addition of $H_2S$ concentrations under constant operating conditions (one current density, one temperature, one gas composition), right: new based on iV curves for each $H_2S$ concentration and $H_2S$-free fuel (current density range, one temperature, one gas composition).

## SOC integration

Solid oxide cells enable integration of large shares of electricity from renewable sources in the energy systems by balancing the incoming fluctuating electricity through load following SOEC-operation and by reversible SOFC-SOEC operation. Furthermore, the coupling with gasification to produce electro-fuels / synthetic fuels is an option, which allows for favorable thermal and gas integration for achieving higher system efficiencies. Several activities have been devoted to this topic.

## Modelling

To develop new SOC stack concepts, to investigate the local conditions in an SOC stack for a wide range of operational conditions to avoid failure, and to investigate the long-term response of SOC stacks, computational efficient multi-physics models are needed. One challenge with the current SOC stack modelling concepts is that many geometric details are included, with a corresponding high computational demand. Simulating the full stack is in some cases not possible and sweeping over a large number of operational conditions or long-term simulations highly unlikely.

At DTU Energy a new multi-scale modelling concept is therefore pursued. The main idea is to simulate full stacks in 3D (see Figure 9), but without including the geometric details explicitly in the mesh of the model. The geometric details are embedded by a mathematical treatment, so-called homogenization, where the effect of the particular geometry is embedded into the material model, and the interior of the stack is just a homogeneous media in the model. This increases computational speed by approximately a factor of hundred as compared to the SoA models (15, 16).

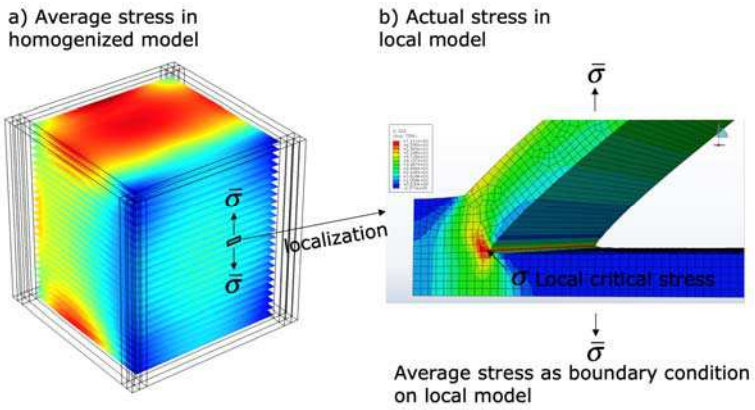


Figure 9. Example of a) stresses in 3D homogenized stack model and b) a local model to calculate the critical stress, responsible for failure (here loss of contact between cell and interconnect).

The local details, leading to degradation (e.g., activation overpotentials) or failure (e.g., tensile stress in the electrolyte) can still be retrieved from the homogenized model by another mathematical treatment, so-called localization. For many cases the local conditions can be determined as a function of the average conditions (in the homogenized models), e.g., the stress in the electrolyte from the average stress, and be expressed with simple closed form solutions. The local conditions can thus be obtained for any point in the stack model in every simulation without any loss of computational efficiency. This approach thus contemplates a strong tool to investigate for local failures in a full 3D stack at wide range of operational conditions, and in the future also for long-term operation.

To further understand a main degradation mechanism in electrolysis operation, the Ni migration and agglomeration, phase-field modelling of the phenomenon was undertaken. The phase field model is able to describe coarsening and migration of the Ni in a 3D microstructure. The model thus predicts a decrease of Ni surface area, TPB length, and Ni/YSZ area. The model also predicts that that the initial coarsening is faster. The model is currently being used to study strategies for minimizing the degradation, such as different modifications of the processing approaches (17).

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