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Recent highlights of solid oxide fuel cell and electrolysis research at DTU Energy

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Research on solid oxide concepts has a long tradition at the Department of Energy Conversion and Storage (DTU Energy) of the Technical University of Denmark. It spans from fundamental topics such as materials & electrode development over methodology development for example in micro structural & electrochemical characterization, up to the applied level, where integration of SOC with up- and down-stream processes becomes important. Significant funding from National and European programs supported this research. The presentation will introduce highlights of recent achievements in the areas of (i) materials & electrode development to reach higher activity and better durability, (ii) cell & stack development for lowering costs and increasing robustness, (iii) power to X concepts with special emphasis on X= fuels, (iv) lifetime & diagnostics approaches for accelerating durability studies, and (v) modelling from materials to stack levels aiding lifetime evaluation and designing of stacks & systems.

Introduction

A successful Green Transition requires efficient, and cost competitive technologies for converting & storing energy from renewable sources and for providing energy to the stationary and the transport sector. Solid oxide fuel cells and electrolysis (SOFC, SOE - SOC) provide high efficiencies for electricity generation and production of storage media / fuels, respectively. In addition, they are flexible and versatile, which makes them attractive in many different application areas and energy scenarios.

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In addition to actual research, the past ca. 1.5 years have been devoted to moving the department to the new premises at the main DTU campus in Lyngby (see Figure 2) and to re-establish the equipment.

Figure 2. Main building of DTU Energy at Lyngby campus (a). Electrochemical test lab (b), (c).

**Materials & electrode development**

As Co is needed for batteries and availability could be challenged and the mining of it raises ethical questions, the oxygen electrodes without Co would be desirable. With the aim to reduce use of critical raw materials in SOCs, Co-free oxygen electrodes were developed based on lanthanum, strontium, and iron containing perovskite materials (LSF) applying a nano engineered hybrid catalyst coating via co-infiltration in the Danish project EP2Gas. LSF electrodes with infiltrated (target) Pr$_2$Ni$_{1-x}$Cu$_x$O$_4$ particles were shown to have a significant performance enhancement. Infiltration of Pr$_2$Ni$_{1-x}$Cu$_x$O$_4$ with $x=0.3$, 0.4 and 0.5 resulted in a decrease of the polarization resistance to 0.161 $\Omega$cm$^2$, 0.127 $\Omega$cm$^2$ and 0.192 $\Omega$cm$^2$ from 0.980 $\Omega$cm$^2$ at 650°C for the reference, respectively (1,2).
Cell & stack development

Work on developing and evaluating metal supported cells (MSCs) has been continued. They are expected to be cheaper and more robust, particularly against thermal cycling / thermal gradients. DTU Energy’s MSC concept is based on scalable processing methods like tape-casting, lamination, screen printing, and infiltration. MSCs with two anode versions were tested recently: (i) MSC1, an all-ceramic anode with 95% LSFNT (La0.4Sr0.4FeO3-Ti0.94O3) / 5% ScYSZ and (ii) MSC2 with (55% LSFNT/40% FeCr/5% ScYSZ), both infiltrated with Ni/CGO. Common for both MSCs is the tape casted metal support layer (ferritic stainless steel alloy (Fe22Cr)), a ScYSZ electrolyte, and the LSC oxygen electrode. Figure 3 shows the iV curves in hydrogen fuel at low temperatures in comparison to SoA cells with Ni/YSZ anodes (from ref. (3)). The MSC with the all-ceramic anode shows the best performance under those conditions, demonstrating the potential of these cells. Challenges occur when using methane containing fuel, which requires internal reforming. Due to the lower Ni content in the anode compared to SoA Ni/YSZ anodes, the reforming activity is low and thus fuel starvation occurs early in the iV curve, at low current densities. Improvement through infiltration of more Ni into the perovskite backbone is in progress. On the other hand, recent tests showed that the water gas shift reaction is occurring, which opens the possibility to operate MSC with reformate from hydrocarbon fuels (e-gas, e-fuels).

Figure 3. iV-curves of SoA cell with Ni/YSZ anode (green curves), MSC1 (red curves) and MSC2 (blue curves) at (a) 650 °C (2), and (b) 620 °C in 50/50 hydrogen/steam and air to the cathode. Results obtained in the project EU NewSOC. From J. O. Christensen et al. in ref. (3).

SOEC Ni-YSZ fuel electrodes are degrading at an undesirable rate, when exposed to higher current densities (4). While current operation could be limited to lower degradation and stable operation, it is appealing to aim for the higher current densities to achieve thermo-neutral operation inside the SOEC stacks. It was shown that the degradation rate at 800 °C and −1.25 A/cm² could be limited to 66 mV/kh as opposed to that of the reference cell with a degradation of 699 mV/kh by infiltration of CGO nanoparticles (see Figure 4 from ref. (5)).
Figure 4. Decrease of cell voltage degradation rate of CGO infiltrated cells (Cell B1 and B2) as compared to reference SoA (Cell A), from S. Ovtar et al. in ref. (5).

Power to X concepts

A novel and efficient route for producing green methanol was demonstrated by use of residue from the agriculture (see Figure 5). A 6 kW SOEC stack unit produced hydrogen, which was combined with syngas from a thermal gasifier operating on straw in a downstream methanol reactor. This concept was successfully demonstrated (6). Methanol is a widely used chemical and is considered a promising green fuel for the transportation sector, although biomass may limit the possible production volumes to certain uses.

Figure 5. Synfuel project concept (financed by the Innovation Fund Denmark), where gasification and SOEC have been demonstrated together with a catalytic conversion unit to produce methanol.

Ammonia is becoming an accepted alternative fuel if biomass is limiting or when zero emission power production is desired. For the production of ammonia, the excess heat from the Haber Bosch loop can be used in the SOEC for an overall higher efficiency. Vice versa, when using ammonia as a fuel in an SOFC, the excess heat from the electro-chemical reactions can be used in the endothermic cracking of ammonia. As Ni based solid oxide fuel electrodes can catalyze the cracking of ammonia, this reaction can even be conducted as internal reforming (7). Identical iV curves in either ammonia or hydrogen/nitrogen fuel confirm the ammonia cracking activity of SoA Ni/YSZ fuel electrodes (see Figure 6 from ref. (7)). With the two thermal couples both the production and during usage, the ammonia
fuel can be considered to come with “build-in thermal storage”. This could potentially result in a very high round trip efficiency, higher than what is possible with hydrogen.

Figure 6. Current-voltage curves for the use of ammonia or a corresponding hydrogen/nitrogen mixture (3/1 ratio) as fuel at (a) 750 °C and (b) 850 °C, recorded on SoA anode supported cells, data from A. Hagen et al. in refs. (7,8).

SOC technology is capable of operating in dynamic mode and reversible mode, i.e. it can store electricity through electrolysis forming hydrogen from renewable sources and produce electricity from the stored hydrogen through fuel cell operation. It was shown for commercial state-of-the-art cells with fuel electrode supported configuration that such reversible operation does not lead to increased degradation as compared to operating under constant current load (see Figure 7 from ref. (9)).
Figure 7. Durability single cell tests operated at 700°C, 40% FU, 0.4 A/cm² and −0.6 A/cm², respectively in SOFC and SOEC mode. Dry H₂ during SOFC operation for RND8 SOFC mode and H₂O/H₂:50/50 for RND14-low (both modes) while H₂O/H₂:90/10 was applied for RND8 in SOEC mode. Synthetic air to the oxygen electrode. Results obtained in the EU REFLEX project. From A. Hauch et al. in ref. (9).

Lifetime & diagnostics approaches

The long lifetimes—both required and achieved—of mature SOC generations make it necessary to develop new approaches for degradation studies and lifetime assessment. With the aim to harvest gained results from single cell durability testing over the last ca. 20 years at DTU Energy, a database was established allowing for a new evaluation of durability behavior. The database contains data from 2135 tests comprising a large variety of cell generations (materials, structures), test setups (sealings, contacting layers, etc.), and operating modes (short & long term, SOFC & SOE modes, constant & dynamic conditions, etc.). The database makes it possible to apply machine learning routines to reveal linear and non-linear correlations and single & combined effects of operating parameters on durability over a large range of tests. The aim is to identify accelerating testing approaches and establish lifetime prediction. From a statistical point of view, both a large variation of the dataset (i.e. range of temperatures, current densities, etc.) and a large number of data points at each test condition is desired in order to be able to identify outliers and establish models. Figure 8 shows the results of this analysis using the database for the examples of four operating parameters: oxygen partial pressure at fuel electrode inlet (pO₂_in), fuel utilization, operation temperature, and current density for fuel cell durability tests (from ref. (10,11)). The histograms reveal that fuel cell durability tests were done over large ranges of the given four operating conditions, however, with only limited repetitions (reproducibility), which is common for the current state of SOC testing. Such information aids identifying missing test data and revealing the validity range of models. Currently, degradation values are related to input parameters and combination of those.
Based on those degradation data, means to accelerate degradation are desired to design tests on component level, at shorter times or in cheaper environments than full stacks. One step towards this approach is to treat SOCs in steam environment to the fuel electrode, as steam has a well-known effect on the Ni particle structure leading to degradation. This approach is pursued by DTU Energy in the European project Ad Astra (see Figure 9). Two commercial SOC cell designs were studied: Anode supported cells (ASC) and Electrolyte supported cells (ESC) in terms of the effect of steam to the fuel electrode both without (ex situ) and with (in situ) applying a current load in fuel cell or electrolysis mode. The degrading effect of increasing steam content in hydrogen fuel and increasing temperatures was confirmed under ex situ aging conditions. A quantification and validation with field tested samples, including evaluation of the micro structural changes are in progress (12).
Figure 9. Approach of selection of potential accelerating parameters for aging treatments of SOC by DTU Energy in The EU Ad Astra project. ESCs and ASCs are aged both with applying polarization (in situ) in fuel cell or electrolysis mode and without (ex situ). The electrochemical properties and the micro structure are analyzed and compared to field tested samples.

Modelling

To further optimize the operation of an SOC and avoid degradation, a time dependent 3D stack model describing the degradation over the entire lifetime has been developed (13). Simulation of all the coupled physical phenomena will take in the order of 10 hours for a full stack, using a simplified interconnect geometry (14). Thus, for this to be computational feasible, the model was built using the multi-scale, multi-physics homogenization concept. Here the complex geometry of the interior of the stack is considered in a sub-model and the effective behavior of this is transferred to the model of the full stack. In the model of the full stack the detailed geometry is thus represented by these effective parameters from the exact geometry. Doing so a vast number of computational elements (control volumes or finite elements) can be omitted by only including this through an effective media (15). This makes it possible to simulate 40,000 hours of operation for a full 3D stack in one hour and 15 minutes (16).

The same modelling concept was also utilized to describe local mechanical failures by use of a sub-model for the mechanical stress concentrations near assembly points inside the stack (17). The detailed geometry of the interior of the stack is again modelled by a sub-model, which provides effective parameters for the full stack model (Figure 10a). However, in this work the sub-model is also used to determine the interior high local stresses to examine for failure inside the stack (Figure 10c). The average (macroscopic) stresses can be extracted from the full-scale stack model (Figure 10b) and be applied on the boundaries of the sub-model (Figure 10c) to represent that specific region inside the stack in detail. This can in principle be done for all regions inside the stack efficiently using a computer cluster, as the individual calculations for each sub-model can be done independently of each other – while being connected through the full-scale model. However, in (17) an analytical expression was derived to obtain the local energy release rate locally in the sub-model for any stress combination in the full-scale stack model (Figure 10c). Doing so the local energy release rate can be determined at all points using the analytical expression and hereby not increasing the computational load (Figure 10d).
A full-scale 100 cell stack model with the analytical expression investigating for local failures can be simulated in 3 minutes for each operating condition.

Figure 10. Multi-scale simulation concept including a) a multi-physics full-scale simulation with electrochemistry and relevant transport equations, b) a mechanical full-scale model to determine average (macroscopic) stresses, c) a sub-model to determine local energy release rate ‘G’ through the J-integral, c’) an alternative analytical expression to determine ‘G=J’ for any average stress combination ‘σ’, d) obtained energy release rate for any point inside the full-scale model to investigate for failure.

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