Production of Solid Oxide Fuel Cell and Electrolyzer Stacks using HORIBA FuelCon's Sintering Equipment

HORIBA FuelCon製焼結装置を用いた固体酸化物形燃料電池および電解槽スタックの製造

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Fuel cell and electrolyzer solutions will play a major role in the development of the future Hydrogen economy helping to replace fossil fuels. Specifically, high temperature solid oxide cell (SOC) technology has important advantages such as increased efficiencies and the extended range of applications based on its fuel flexibility. The production of solid oxide cells and stacks is a key aspect on the way to an increased number and higher power level of system installations. HORIBA FuelCon provides SOC sintering, reduction and testing equipment that helps to scale-up the production to an industrial level and by that, to minimize the production costs. The present article provides insides on HORIBA FuelCon's solutions based on the specific SOC production steps.

燃料電池と電解槽のソリューションは，化石燃料に代わる将来の水素経済の発展に大きな役割を果たす。特に高温固体酸化物形燃料電池(SOC)技術には，効率向上や燃料の柔軟性に基づく応用範囲の拡大など，重要な利点がある。固体酸化物形燃料電池とスタックの製造はシステムの設置台数と出力レベルを向上させるための重要な要素となっている。HORIBA FuelConはSOCの焼結，還元，試験装置を提供し，工業レベルまで生産をスケールアップすることで生産コストを最小化することに貢献している。本稿ではSOCの製造工程に基づいたHORIBA FuelConのソリューションについて紹介する。

Introduction

The "Paris Agreement" from 2015 that determined to limit global warming clearly below 2 K compared with pre-industrial times motivates the recently raised international activities aiming for reduction of global CO_2 emissions.

Reaching that goal will require to establish a throughout interaction between different energy sectors such as electricity, heat, chemistry and mobility based on alternative energy sources, mainly renewables.

The nature of renewable energy sources like wind and solar power implies the need for seasonal energy storage solutions.

Also, the associated reduction of fossil fuel utilization down to zero will only be successful if there is a way to substitute today's fossil feedstock sources in the chemical industry, the agri-food sector as well as the cement and steel production.

A basic and key and element for the implementation of all three mentioned aspects sector coupling, energy storage and fossil feedstock substitution will be Hydrogen.

A major part of the Hydrogen amounts required will be provided by electrolysis solutions. Amongst different electrolyzer technologies, the high-temperature Solid Oxide Electrolysis (SOEC) shows the highest efficiencies for pure water electrolysis and allows even to utilize CO_2 for provision of a $CO + H_2$ mixture, termed syngas, a major feedstock gas in the chemical industry. Moreover, the efficiency can be increased by heat coupling with subsequent exothermal processes like methanation and ammonia synthesis which play an important role for higher hydrocarbon production as well as for the agri-food sector.

The escalating Hydrogen demand leads to a rapidly rising request for electrolysis facilities, already now. Scaling up the capacities for SOEC cell and stack production requires specifically optimized and fully automated production equipment.

HORIBA FuelCon, as a provider of fuel cell and electrolyzer evaluation and manufacturing equipment for more than 20 years, offers a wide line-up of SOEC testing and production solutions in the full scope from cells to stacks. The same equipment is able to produce and test SOFC fuel cell stacks as well as rSOC reversible solid oxide stacks as these are just two more variants of the solid oxide technology.

The following article gives a detailed overview about solid oxide cell design and stack manufacturing processes. HORIBA FuelCon's associated production equipment will be illustrated providing insides of the applied technologies.

R&D and Quality tests for Cells

Solid oxide cells basically consist of a thin, sintered electrolyte foil that is applied with specific fuel and air electrode materials on each side.

A common electrolyte material is yttrium-oxide-stabilized zirconium dioxide (YSZ), a ceramic material that is gas tight in order to separate the reactants being in contact with the cell. While the electrolyte needs to be a good electrical insulator, it allows O^{2-} ions to pass. Aside from the high temperature that is needed to activate the O^{2-} ion conductivity (min. 600 °C), the O^{2-} ion transport is the main difference to PEM technology which is based on the transport of H^+ ions (protons).

The fuel and air electrode materials are highly porous allowing the reacting gases to reach the three-phase boundary (electrolyte, electrode and gas). Also, a good electrical conductivity is desired to lead the electrons being released when O_2 split into O^{2-} ions. In order to assure the electrodes staying attached at the electrolyte when operating at high temperatures, the thermal expansion coefficients (TEC) of the electrodes need to be aligned to the electrolyte's properties.[1]

Commonly, the fuel and air electrode materials are printed on the electrolyte (e.g. by screen printing or tape casting) in form of a paste or slurry. After printing, the materials need to dry before they will be sintered at 1,000-1,400 °C. The materials being typically used are Nickel for the fuel electrode and lanthanum strontium manganite (LSM) for the air electrode.[1] Their main job is to catalyze the reactions, O^{2-} ion generation on air side and oxidation of the supplied fuel on the fuel side. In order to increase the electrochemical active zones and for TEC optimization, both electrodes are provided as a composite (cermet = ceramic + metal) of the basic materials mentioned above and electrolyte material (YSZ).[1]

To provide mechanical support to the cell, one of the layers need to be made thicker and by that representing a distinctive feature of the cell concept. Most manufactures use one of these 3 common cell types:

- Electrolyte supported cells (ESC, e.g. IKTS, Sunfire)
- Anode supported cells (ASC, e.g. Topsoe, Elcogen) or
- Metal supported cells (MSC, e.g. Ceres Power)

HORIBA FuelCon's cell test equipment accommodates all these cell types by using the integrated, fully ceramic cell

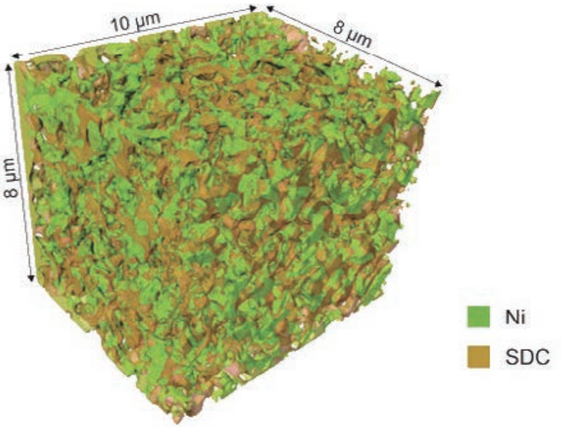


Figure 1 3D example of a Ni/SDC cermet, Gregor Kapun, Ljubljana.[3]

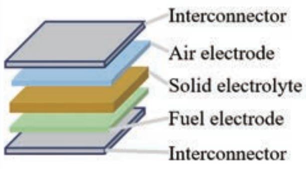
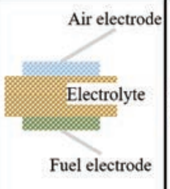
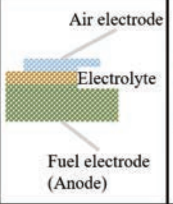
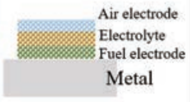
Cell type	Electrolyte Supported Cells (ESC)	Anode Supported Cells (ASC)	Metal Supported Cells (MSC)
			
Example	IKTS, Sunfire	Topsoe, Elcogen	Ceres Power

Figure 2 SOC cell types.

housing for standard 5 × 5 cm cell designs as well as button cells. The all-ceramic cell housing approach provides a clean testing environment avoiding impurities. Mirror-finishing the ceramic surface improves the adhesion between ceramics. Thus, there is no need to use gaskets or glass sealing which allows to operate the cell in another test run or to apply academic examinations using HORIBA Scientific's wide range of sophisticated equipment such as Raman Spectroscopy.

Cell tests are supported by a number of proprietary features including a direct injection humidifier providing steam with a minimized noise or a direct combustion humidifier with zero noise, both for fuel cell and electrolysis operation at up to 100% steam.

Desulfurizer and reformer units being available for integration in HORIBA FuelCon's test stations allow for reformat fuel cell tests while a number of diverse supply media, such as H_2, CO_2, CO, CH_4, NH_3, support reformat simulation as well.

Electrolysis and reverse SOC operation based on steam and/or CO_2 is just another operation mode as the integrated 2-quadrant load provides smooth changing through the current origin.

Specific cell properties are determined by the integrated high-performance impedance spectrometer (EIS).

Stack Sintering

In order to receive an adequate power output for a specific SOFC/EC application, the single cells are piled on top of each other. The so called "stack" provides a higher voltage, equivalent to the number of cells, while the current through the complete stack is identical with the one applicable to a single cell.

In most cases, the cells are stacked in a bipolar manner meaning that the anode of one cell faces directly to the cathode of the next cell. The advantage of that method is a very simple electrical interconnection. However, since both air and fuel electrode need to be supplied with air and fuel gas just at the point of common contact, an additional interconnector layer is required to separate the two gas sections.

The interconnector plate has multiple functions as it needs to assure an optimal electrical contact and conductivity between the cells, provide main gas channels and stabilization to the stack and carries contacting and tightening elements. The interconnector material should have a high thermal conductivity to keep the temperature gradients inside the stack low and, at the same time, its thermal expansion coefficient (TEC) needs to meet the associated cell properties to prevent mechanical stress.[1] Finally, the interconnector's surface needs to build a tight oxide layer being protected from further oxidation and evaporation of metal contents while still keeping a good electrical conductivity in reducing and oxidizing atmospheres. A proven and widely used material for all these purposes is Crofer22APU, a ferritic high-temperature stainless steel.[1]

To contact the interconnector plate to the anode and cathode electrodes, additional materials are desired to fill the space between the rough surfaces of electrodes and interconnector.[1] Nickel foam or grids provide good results in reducing atmospheres at the fuel electrode.

The oxidizing atmosphere at the air electrode does not allow to use similar metal foams or grids due to their large active surface. A common solution is using electrically well conducting oxide ceramics with perovskite or spinell structures. Elements like manganese, lanthanum, strontium, chromium, kobold, copper or iron are part of these structures to obtain the required properties like the

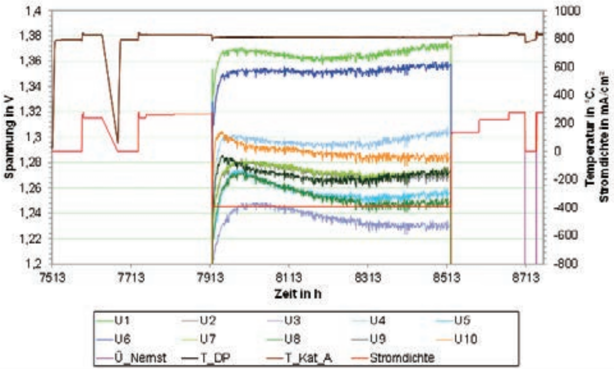


Figure 3 SOEC cell voltages @ 10...20 g/min steam over 600 h, IKTS.

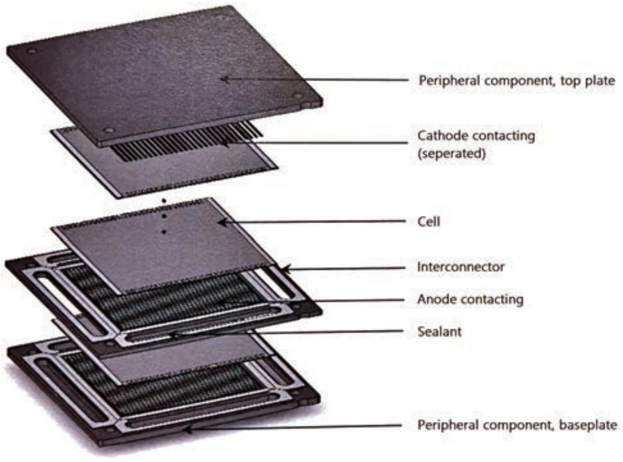


Figure 4 Explosion view of a planar, bipolarly assembled stack.[1]

good electrical conductivity.[1]

Usually, these contacting materials are applied in green state to the interconnector plate or to the air electrode where they build ceramic contacting bars. In this way, the oxide ceramics also represents a favored local barrier between interconnector and cathode that complicates evaporated chromium to reach the air electrode where it would harm the long-term cell performance.[1]

The air electrode connecting bars have contact to the opposite side after stack assembly already. Depending on the stack concept, they will be sintered (substance-to-substance bonds) or pressed with high pressure (force-fit bonds) at the next step.[1]

Before sintering can take place, the interconnector plates and the cell electrodes need to receive a sealant to keep the air and fuel gas inside the channels. Commonly, a glass solder, a special glass composition that allows to achieve the optimal TECs, is applied to the interconnector plate as a foil or paste. Beside sealing, the glass provides a leveling effect between the cells.[1]

Using HORIBA FuelCon's sintering stations, the stack is heated above typical operating temperatures up to 1.000 °C while air is supplied to both fuel and air side. During the sintering process, the stack releases organics coming from the glass solder binders which need to be removed safely. HORIBA FuelCon integrates purging and trace heating features as well as exhaust incinerator solutions.

The furnaces provided by HORIBA FuelCon come with multi-zone control to assure optimal heat distribution and can be arrange to accompany multiple stacks. Once the desired temperature is reached, the proprietary mechanical load design applying compression forces from above or from below the stack allows to compress the stack uniformly in order to secure the intended stack geometry. The maximum force level depends on the specific stack design and can reach up to 40 kN which is kept safely by HORIBA FuelCon's load concept, even at power outage or emergency shut down.

It is important to calculate the optimal glass amount, in order to receive optimal electrical contact after sintering without having surplus glass entering other parts of the stack. Using an open air side concept allows to waive the glass sealant at the air electrode which simplifies air side contacting as the green connecting bars described above can be sintered onto the air electrode, directly.[1]

Partly glass crystallization during the sintering process shifts the TEC toward the value of the cell. In addition, by crystallization, the glass viscosity increases by magnitude which provides the stack with the desired mechanical stability even at maximum operation temperatures.[1]

Stack Reduction

In preparation to the first real stack operation after sintering, the fuel electrode must be reduced using Hydrogen. The catalytic component, a nickel-containing material, forms nickel oxide (NiO) in air, although the nickel compound must be in the metallic state. Reduction with Hydrogen reduces nickel oxide to nickel. The reduced fuel electrode must have enough porosity to transfer the fuel gases. Good electrical conductivity is needed for decreasing the area specific resistance.

The time allowed to conduct the overall anode reduction process is a critical variable in stack production as this step may causes thermal and mechanical stress to the single cells and to the interconnection with other cells. Thus, Hydrogen is commonly diluted with nitrogen in order to control the speed of reduction and by that to protect the stack integrity.[1]

Using HORIBA FuelCon's sintering and reduction stations, the operator can control both the Hydrogen dilution and the flow rate of Hydrogen mixture in a well-defined way. A typical starting ratio is 20 % H_2 and 80 % N_2.[4] The test stand automation allows to control the duration and a continuous increase of Hydrogen content perfectly in accordance with manufacture's requirements.

The reduction process takes place at furnace temperatures between 700 - 800 °C which is below the sintering temperature. The sintering station's multi-zone furnace control follows the given temperature curves and limits precisely.

Stack Test

After sintering and reduction, one important test is to verify the stack's gas tightness. The glass sealant between cells and interconnectors needs to provide reliable leak protection.

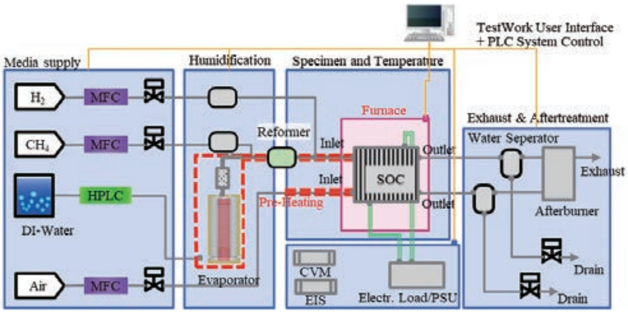


Figure 5 Overview of an SOC evaluation system.

HORIBA FuelCon's test stations offer diverse methods for leak testing. One is the fully automated online leakage test allowing to check for fuel and air electrode and for cross-over leakages during hot operation, depending on stack design. Another method is injecting noble gas like helium to fuel and/or air side. Helium traces found in the opposite gas compartment does indicate a cross-over leakage.

Once Hydrogen is supplied by 100 %, the OCV provides a more detailed picture about successful gas channel sealing as the OCV level highly depends on cross-over leak tightness. HORIBA FuelCon's sintering stations allow to measure the overall stack voltage as well as potentials of single cells or cell groups by multiple cell voltage measurement (CVM) options. By this means, manufacturing quality can be checked down to each single cell. High voltage measurement accuracy by superior input resistances for a large number of cells is the basis.

Polarization tests are a standard to receive quick information on the stack performance after manufacturing.[2] Typically, these tests are conducted under part load of the stack's nominal power. Depending on the intended application, the stack is operated in either fuel cell, electrolysis or reversible mode.

HORIBA FuelCon's sintering stations support all these operation variants in one rig. In most cases, focusing on Hydrogen and steam provision is sufficient for quality checks. If required, additional gases are available, e.g. NH_3 and CH_4 for ammonia and carbon fuel operation or CO_2 for co-electrolysis.

HORIBA FuelCon's proprietary direct injection humidifier provides large amounts of steam with a minimized noise. Together with the fully integrated 2-quadrant load concept, the stations support to change smoothly between fuel cell and electrolysis mode.

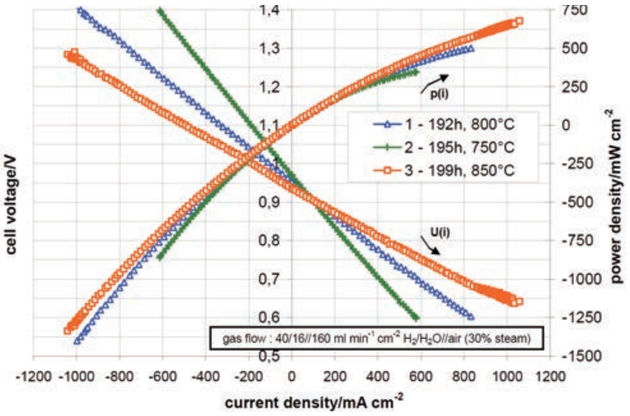


Figure 6 Polarization and i-p curves for reversible SOC operation at different temperatures.[2]

For all sintering and testing steps, HORIBA FuelCon supports closed stack concepts as well as open air or fuel side stack designs by proprietary furnace solutions that take care about chromium and silica prevention at the same time. Exhaust gases are cooled down and led to outside the station safely while sample ports allow manufacturers to check gas compositions continuously using gas analyzers from HORIBA. Defined exhaust interfaces enable operators to remove exhausts or to connect to sub-sequent processes.

Scaling-up Stack Production

The worldwide increasing CO_2 reduction goals will motivate the fuel cell and electrolyzer manufacturers to scale-up their production, rapidly. This concerns the cell and stack production in equal measure.

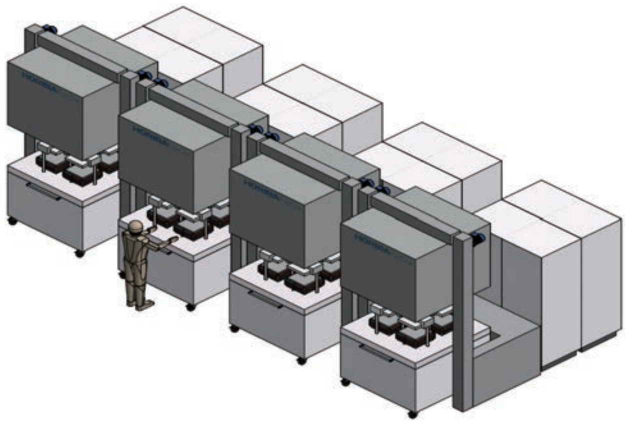


Figure 7 HORIBA FuelCon's Multiple Sintering Stations with 4-fold trolleys.

Higher volumes can be reached by installing additional production capacities. Optimizing the manufacturing processes and logistics does need to take place at the same time in order to increase the output of one production line to an optimum.

HORIBA FuelCon does provide next generation sintering and reduction stations, already now. Larger furnaces with space for multiple stacks are just a first step.

HORIBA FuelCon's proprietary trolley concept supports manufacturers with a movable and universal multi-stack platform that can be used for the whole range from stack assembly down to stack sintering, reduction and testing. As the trolleys include mechanical load systems for each single position, the assembled stacks can be pre-compressed for safe stack transfer. Prepared like that, a trolley is in pool position for docking with the next allocated sintering station once the previous trolley is ready. That might be the case even if the cool down procedure has not finished yet as a quick cool down by furnace opening and stack transport may be acceptable at intermediate temperatures already to shorten the station's occupation time. Moreover, docking the trolley to HORIBA FuelCon's multiple sintering stations is conducted without manual help as they come with an automated docking solution. The described handling covering a number of compatible stack trolleys does allow to reduce the setup and production time to a minimum.

Conclusion

A detailed outline of solid oxide technological principles with HORIBA FuelCon's associated testing and production equipment and their upscaling concepts has been provided.

Solid oxide cell technologies comprise a number of sophisticated methods on cell and stack level, developed over the last decades. Diverse manufacturing steps are required, specifically differentiated according to the concrete SOC type and its fuel cell or electrolyzer application.

HORIBA FuelCon provides proven and progressive sintering, reduction and testing solutions for the broad range of existing SOC variants. Cell and stack manufacturers receive strong support for SOC production and for their upscaling strategy - saving time and resources.

* Editorial note: This content is based on HORIBA's investigation at the year of issue unless otherwise stated.

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