

Water and steam electrolysis: status, challenges and prospects

Water electrolysis with proton exchange membrane (PEM) electrolyzers

Renewable energy is expected to account for 86 % of global electricity generation in 2050. However, this is threatened by dynamics beyond renewable energy generation and is therefore critically dependent on successful advances in energy conversion, such as green hydrogen generation with proton exchange membrane (PEM) water electrolyzers.

Unlike alkaline electrolysis, the PEM concept is designed as a compact system, delivers pure hydrogen, and can be operated dynamically, which fits well with the requirements of the green energy sector.

In PEM water electrolysis, noble metals are used as catalysts for the electrode, while a solid proton-conducting membrane composed mainly of perfluorinated and polysulfonated polymers separates the cathode and anode. Numerous research activities aim at reducing the content of noble metals (e.g. iridium, platinum) used as catalysts and at the same time increasing the activity of the anodic oxygen evolution reaction (OER) of these electrodes. State-of-the-art catalysts for the anode made of pure iridium or iridium oxide, used with high loadings, arose from the goal of developing a PEM water electrolyzer with maximum power and minimum degradation rate.

Despite their market accessibility and development, PEM water electrolyzers are still considered very expensive compared to hydrogen production from fossil fuels, and more expensive than alkaline, which is an additional limit to market penetration.

In PEM stacks, the bipolar plates are a major cost component and are designed for multiple functions that require advanced materials to be coated on titanium. Bipolar plates need to be fundamentally changed in the near future as they play an important role in improving performance and durability as well as reducing cost.

For the heart of the stack, the catalyst-coated membrane and the use of platinum group metal catalysts account for a large portion of the cost. While iridium is one of the scarce catalysts that is stable as a mate-

rial in the electrolyzer operating environment, some approaches have shown to be promising in enhancing the performance. Advanced structures such as nanowires and nanostructured thin films, as well as catalyst support, are key to stabilizing the surface area and minimizing catalyst loading.

In addition, more reliable methods for testing these catalysts are needed to predict long-term performance. Finally, it is essential that testing and standards of comparison be consistent across the community, especially at earlier stages of development, to more quickly identify promising avenues and avoid conclusions based on differences in testing conditions or cell designs.

Steam electrolysis with solid oxide electrolysis cells (SOECs)

Electrolysis using solid oxide cells was tested in the 1960s for regeneration of oxygen from CO₂ for space missions. In the 1970s and 1980s, high temperature steam electrolysis was investigated by GE, Dornier, Westinghouse, and other companies, mainly with tubular stack designs. Due to the high cost and lack of industrial perspective at that time, R&D activities of solid oxide cells (SOCs) were focused on solid oxide fuel cell (SOFC) mode, with which a high efficiency power generation with carbon-containing fuels could be achieved. With rapid growth of the renewable energy and increasing demand on CO₂ reduction worldwide, SOEC technology has drawn more attention within the last 15 years.

The development of SOECs has benefited from the long experience in SOFC development, since the same cells and stacks can be operated basically in fuel cell and electrolyzer mode.

Compared to PEM and alkaline electrolyzers (PEMEL, AEL), which generally operate below 100 °C, state-of-the-art SOEC stacks operate between 700 °C and 850 °C, depending on the type of the cells used. The high operating temperature is necessary for the solid oxide electrolyte (e.g. yttria-stabilized zirconia) to reach sufficient ionic conductivity. Due to the large temperature difference to PEMEL and AEL, SOEC has the following features:



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- Thermodynamically the electrical energy demand for H₂ production decreases with increasing temperature, because a larger part of the required energy is supplied as heat. For this reason, SOEC is most suitable for large scale industrial applications where waste heat is available.
- Higher temperature means also a fast reaction kinetic. No noble metal catalyst is necessary for SOCs. Due to the negligible activation loss in the electrodes, the operation voltage of SOEC is much lower than that of PEM or Alkaline electrolyzers, which results in a lower electricity consumption.
- Solid oxide electrolytes are dense. There is no crossover of H₂ through the electrolyte in the normal working conditions.
- Higher working temperature means also a longer start-up, especially for a cold start from room temperature. SOEC is therefore not suitable for applications, where fast and frequent start-ups are desired.
- SOECs can be used not only for H₂ production (i. e., steam electrolysis) but also for a direct generation of various syngas mixtures by co-electrolysis of steam and CO₂. Furthermore, SOECs are applied for CO production by CO₂ electrolysis (e. g. eCOs™ from Haldor Topsoe). Although SOECs with a proton conducting electrolyte are still in the early R&D stage, the production of NH₃ in such cells is becoming another promising application. Therefore, SOEC can play an important role in Power-to-X, where X can stand for H₂, gas, fuel, and chemicals, etc.
- As mentioned above, SOCs can operate in either fuel cell or electrolyzer mode. This unique feature provides the possibility and flexibility in power generation or power storage using the same system.

Currently, most of the SOEC stack developers are focusing on the planar design because of its higher current density comparing to the tubular one. The features of different stack and cell designs, including electrolyte-supported cells (ESCs) and fuel electrode supported cells (FSCs), are summarized in the following:

- The most widely used cell materials, including yttria-stabilized zirconia (YSZ) electrolyte, Ni/YSZ or Ni/GDC (gadolinia doped ceria) fuel electrode, and lanthanum strontium cobalt ferrite (LSCF) or lanthanum strontium cobalt (LSC) air electrode, have shown satisfied reversibility between SOFC and SOEC mode in the temperature range of 700 °C and 850 °C.
- In case of co-electrolysis, CO₂ is converted to CO through the reverse water gas shift reaction (RWGS) chemically. In case of a direct electrochemical CO₂ reduction the electrode polariza-

tion is slightly higher and no special catalysts are required.

- The output composition of syngas (i. e., ratio of H₂ and CO) can be well predicted by steam electrolysis and RWGS, taking into consideration the thermodynamic equilibrium.
- The syngas composition can be well adjusted by tuning H₂O/CO₂ ratio, operating temperature and current density.
- There is no evidence of increased degradation through reversible operation between SOFC and SOEC mode. Whether the alternating operation may prohibit the degradation in electrolysis mode still needs more investigations.
- There are no difficulties for SOEC to follow dynamic variations in the load profile or feed gas composition. Fast switching between SOFC and SOEC is not restricted by the electrochemical process, but more limited by a sufficiently fast supply of the required steam or fuel in the system.

The long-term stability of the SOEC stacks can be referred to SOFC stacks to certain extent, which has been demonstrated for up to 100,000 hours. In SOEC mode, operating time of more than 20,000 hours with a voltage degradation rate of 0.6%/kh was demonstrated with a short stack at Forschungszentrum Jülich, which also confirmed that Ni-migration (or Ni-depletion) in the functional layer of the fuel electrode is one of the most critical degradation mechanisms for Ni-based electrode. At the system level, there are only a few reports showing operating time up to 10,000 hours.

Europe is currently leading the development and industrialization of SOEC worldwide. Among others, the German company Sunfire GmbH, headquartered in Dresden, has demonstrated the world's biggest steam electrolyzer in 2017 in the frame of the EU-project GrInHy. The system had a power of 150 kWAC, producing 40 Nm³/h H₂ with an electrical efficiency of up to 82% LHV. This system was integrated into the infrastructure of Salzgitter's iron-and-steel works and was operated for approximately 13,000 hours. In the follow-up project GrInHy2.0, a larger system of a power of 720 kWAC producing 200 Nm³/h H₂ (18 kg/h) will be demonstrated with an electrical efficiency of up to 85% LHV until the end of 2022. In parallel to GrInHy2.0, three other MW-projects (i. e., MegaSyn, MultiPLHY and e-CO2Met) will be commissioned in 2022 and 2023, respectively.

Although SOEC has reached MW-scale, further cost reduction as well as further system demonstrations with large power and long operating time are necessary for market penetration. A comprehensive study of the manufacturing cost of 5 kW stacks, using the stack designs at Forschungszentrum Jülich for instance, has shown that the manufacturing cost for lightweight cassette design stacks can be reduced to ~500 EUR/kW for a production capacity of 25 MW per year. More than one third of the total cost would be caused by the interconnect material Crofer22 APU. By replacing Crofer22 APU with other possible cheaper steels, the manufacturing cost will be further reduced.

SOEC has demonstrated its highest electrical efficiency with additional heat supply. The unique capabilities of co-electrolysis and reversible operation make SOEC a key player in Power-to-X and sector coupling. SOEC is on the way of industrialization, with more demonstrations of MW-production approaching.

Further R&D topics will be focused on understanding of the degradation mechanisms, cost reduction by alternative materials (especially metallic interconnect) and optimized manufacturing techniques. Furthermore, the availability and stability of the BOP components in SOEC or rSOC systems need to be improved and confirmed through more long-term demonstrations.