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Evaluation of the stability of Ni/CGO-based electrolyte-supported cells in co-electrolysis

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The Authors did not wish to publish their full contribution in this proceedings and have published it in a journal.[1] Please contact the Authors directly for further Information.

Abstract

The electrochemical conversion of steam and CO₂ into syngas and their subsequent upgrade has attracted growing interest over recent years as a potentially economically viable route to the sustainable production of e-fuels. For this pathway, the use of high temperature solid oxide cells represents a promising option, since they allow the simultaneous electrolysis of both carbon dioxide and steam in one reactor. While solid oxide cells have been historically developed and optimized in fuel cell mode, their operation in electrolysis mode entails new boundary conditions that trigger different predominant degradation mechanisms. For example, increasing cathodic polarization of the fuel electrode leads to irreversible Ni migration away from the electrode/electrolyte interface. Moreover, carbon deposition has to be carefully avoided by the choice of safe operating conditions. Since these phenomena are governed by the complex interplay of temperature, operating conditions, fuel electrode microstructure and electrode materials, the assessment of their individual contributions remains challenging.

Ni/Gadolinium-doped ceria (CGO) electrodes are prominent candidates to alleviate these issues due to the high electro-catalytic activity and potentially carbon mitigating effect of the ceria phase. Furthermore, the electrolyte-supported cell architecture might be more suitable to prevent carbon deposition due to the higher operating temperature and lower risk of local reactant starvation.

In an attempt to explore these possibilities, this work presents an investigation of commercial electrolyte-supported cells in co-electrolysis mode under various operating conditions. Cells with both *state-of-the-art* Ni/CGO and Ni/Yttrium-stabilized zirconia (YSZ) fuel electrodes were electrochemically characterized by means of chronopotentiometry and electrochemical impedance spectroscopy and compared to each other with regards to their performance and long-term stability (>=1000 h). Both cell types were operated close to the thermodynamic carbon formation regime to assess their respective susceptibility towards coking. *Post-mortem* analysis was carried out with scanning electron microscopy (SEM) to correlate the observed degradation phenomena with microstructural changes. Furthermore, the importance of a gas stream free of impurities such as silica is underlined as a key parameter to achieve low degradation rates.

[1] Amaya-Dueñas et al., *Chemie Ing. Tech.*, 92, 45 (2020).

Introduction

Co-electrolysis of steam and CO₂ in solid oxide electrolysis cells (SOEC) allows the production of tailor-made syngas compositions that can be used to produce renewable synthetic fuels or chemicals in further downstream processing. However, degradation phenomena such as Ni migration away from the electrode/electrolyte interface, carbon deposition and poisoning by fuel gas impurities restrain SOEC lifetime.

SOC exist in multiple cell architectures. The planar cell design has so far received most of the attention since it is used in most commercial applications for fuel cell operation. Two different architectures are used: the electrolyte-supported cells (ESC) or the fuel electrode-supported cells known as anode-supported cells (ASC) in fuel cell applications (Figure 1).[1-4]

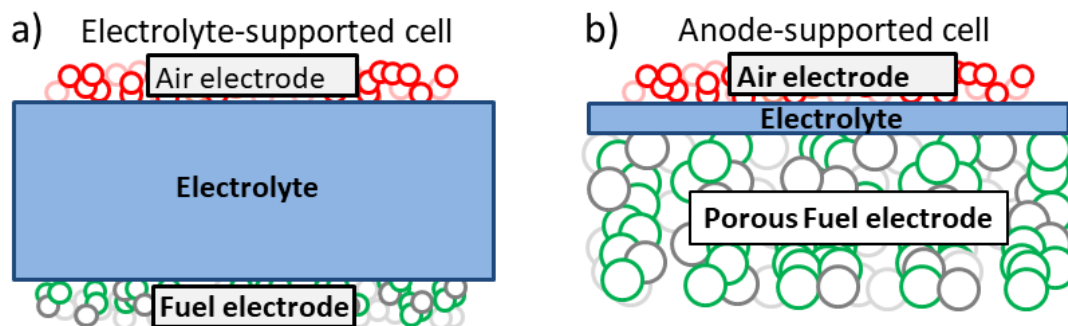


Figure 1: Schematic illustration of an ESC (a) and an ASC (b).[20]

ESC (Figure 1a) typically employ a thick zirconia-based electrolyte (65–200 μm), which provides the mechanical strength to the cell. ESC are operated at high temperature (typically above 800°C) in order to obtain sufficiently high ionic conductivity and to reduce the ohmic losses related to the large electrolyte thickness. As electrocatalyst for the fuel electrode, the cermet Nickel / Ce_{1-x}Gd_xO_{2- α} (CGO) has attracted a lot of attention due to increased redox stability, coking resistance and high tolerance towards potential sulfur-containing impurities in CO₂ sources.^{5–10} The reason is believed to be that the electrocatalytic activity of CGO that shifts the reaction zone of the cermet electrode away from the triple phase boundary (TPB) between metal/ceramic/gas phase to the double phase boundary between CGO surface and gas phase.[10-13] Thus, Ni/CGO shows the potential to alleviate the issues of carbon deposition.

In the ASC design (Figure 1b), a thin zirconia-based electrolyte (5–15 μm) is supported by a thick porous cermet substrate. This substrate which is about 300 to 500 μm thick is typically made of a nickel/yttria-stabilized-zirconia (Ni/YSZ) cermet providing the mechanical stability to the cell. Compared to ESC, the thin electrolyte allows reduced ohmic losses which improves the overall performance at lower operating temperatures (700–800 °C). For these reasons, the use of the ASC architecture is considered very promising in co-electrolysis and was widely investigated.[14-17] However, the ASC design faces critical challenges due to the thick porous support layer (in SOFC mode the anode, in SOE the cathode). In particular, this leads to low tolerance towards redox and thermal cycling. Moreover, it has recently been shown that the possible high operating current densities and corresponding large fuel electrode overpotentials can lead to Ni migration away from the electrode/electrolyte interface in Ni/YSZ fuel electrodes causing severe degradation.[17-19] Also, since the Boudouard reaction is thermodynamically favorable at lower operating temperature and is readily catalyzed by nickel, carbon formation in the porous electrode can become a problem at high local CO concentrations.

In contrast to that, the use of electrolyte-supported cells (ESC) in co-electrolysis operation offers several potential benefits to alleviate cell degradation that can counteract the increased materials' degradation at higher operating temperatures, typically above 800 °C.[20]

First, the higher operating temperatures are thermodynamically more favorable to prevent carbon deposition and impurity poisoning. Second, the higher temperatures generally lead to decreased electrode overpotentials which is likely to prevent or diminish Ni migration.[18] Third, the absence of diffusion limitations in the thin fuel electrode layers may have a beneficial effect on carbon deposition due to the facilitation of CO transport away from the electrode/electrolyte interface and the avoidance of the formation of local non-equilibrium gas phase compositions that trigger carbon deposition.[15] Fourth, the ESC design opens up the possibility to employ Nickel/Ce_{1-x}Gd_xO_{2-α} (CGO) fuel electrodes that have been suggested to display increased coking resistance and high tolerance towards potential sulfur-containing impurities possibly present in CO₂ sources[5,6,8] due to the electro-catalytic activity of CGO.[11-13]

Therefore, the present work shows an investigation of Ni/CGO-based ESC to explore the effect of these potential benefits on SOEC degradation in co-electrolysis operation.

Experiments

In this contribution, we exclusively focus on the operational aspects of the co-electrolysis on state-of-the-art ESC in oven environments, in which cells are investigated. The ESC consisted of a ~90 μm 3-YSZ electrolyte coated with a CGO layer of about 5 to 10 μm in thickness on both sides. The fuel electrode consisted of a 15 μm thick Ni/CGO cermet and a thin (~10 μm) nickel-rich contact layer for current collection. The air electrode was a 20 to 25 μm thick porous La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF)/CGO layer with an LSCF current collector layer. The cells had an active surface area of 16 cm². The fuel gas humidification was achieved with a direct evaporator. The steam was mixed to the feed gas at 120°C and then heated to nominal operating temperature in the oven. Two different steam to carbon (S/C) ratios were investigated. Mixture 1 consisted of 63.7 % H₂O, 31.3 % CO₂ and 5 % H₂ and thus, had a S/C ratio of 2. Mixture 2 consisted of 63.7 % H₂O, 21.3 % CO₂ and 15 % H₂ with a S/C ratio of 3. The test bench for cell testing was already illustrated and described in a similar configuration in detail elsewhere.[6,21]

Results

The cells were investigated in co-electrolysis operation at 770°C, 800°C, 830°C and 860°C with two different steam to carbon (S/C) ratios (2:1 and 3:1) to evaluate the influence of the gas composition on the electrochemical behavior of the cell. The open circuit voltage (OCV) was ~20 mV above the Nernst potential for every temperature. Such difference of the OCV from the Nernst potential may be linked to a small deviation of the gas composition from the nominal one. This might be due to small leakages in the cell housing. The current-voltage characteristics of the cells are shown in Figure 2.

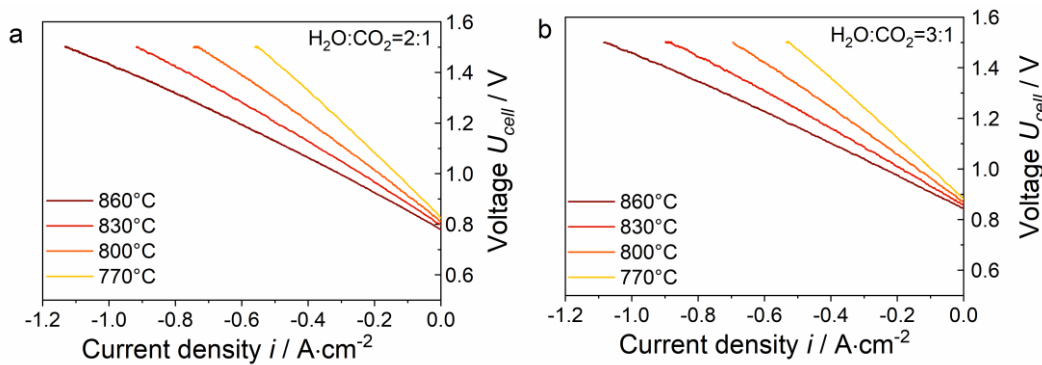


Figure 2: Polarization curves of ESC recorded at different temperatures in co-electrolysis with a (S/C) of 2 (a) and 3 (b).[20]

Furthermore, electrochemical Impedance Spectroscopy (EIS) spectra were recorded at 860 °C both at OCV and -0.6 A·cm⁻² in gas mixture 1 with S/C = 2. Both curves show comparable characteristics (Figure 3). The ohmic resistance ASR_{Ω} was determined to be 0.55 $\Omega\cdot\text{cm}^2$ with or without applied current. Comparison of the two spectra shows the influence of the current density mostly on the middle and low frequency region (< 100 Hz). The polarization resistance was determined to be 0.23 $\Omega\cdot\text{cm}^2$ and 0.1 $\Omega\cdot\text{cm}^2$ at OCV and at -0.6 A·cm⁻², respectively. This leads to a total polarization resistance of 0.78 $\Omega\cdot\text{cm}^2$ at OCV and 0.65 $\Omega\cdot\text{cm}^2$ at -0.6 A·cm⁻². Upon an increase of temperature, a clearly distinguishable flattening of the polarization curves at high current densities is observed.

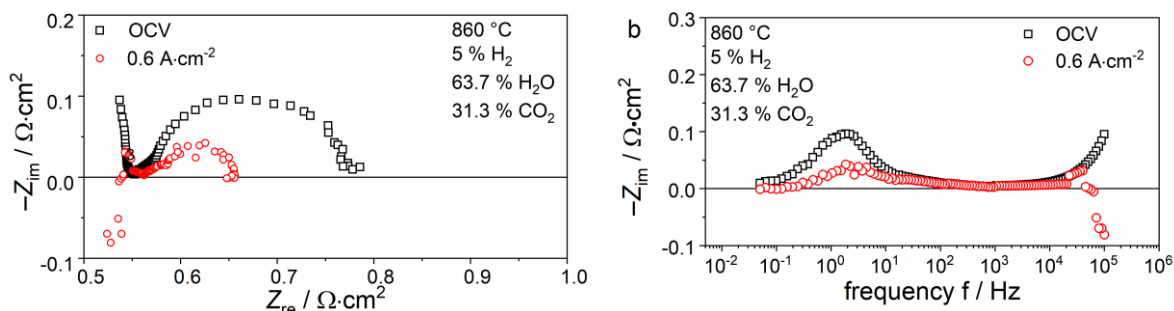


Figure 3: Nyquist and imaginary impedance plots of EIS measurements recorded at different current densities at 860°C in co-electrolysis operation with S/C = 2. [20]

To investigate thermal effects at dynamic operation on SOEC performance, current-voltage characteristics in co-electrolysis at 860°C were measured together with the cell temperature evolution for each condition. The results are shown in Figure 4. The polarization curves show a nearly linear evolution up to an inflection point that is correlated with a change in the temperature evolution profile. Above the inflection point, the slope of the polarization curve decreases which results in a flattening of the curve at high current densities. At low current densities the endothermal nature of the co-electrolysis reaction is not balanced by Joule heat production. Therefore, the cell temperature decreases. This cooling effect lowers both the ionic conductivity of the electrolyte and also the electrode kinetics. Above the thermoneutral voltage the cell is heated due to the exothermal operation, thus increasing ionic conductivity and accelerating electrode kinetics. A comparison of the temperature evolution profiles depicts a more pronounced cooling at low current densities for the co-electrolysis experiment with S/C = 2, which also results in a lower slope of the corresponding polarization curve. The reason for this effect is very likely related to the thermodynamics of CO₂ and steam electrolysis. The experiment with S/C

ratio of 2 contains the highest ratio of CO₂. Since CO₂ electrolysis is more endothermic than steam electrolysis, these results in a more pronounced cooling effect. As a consequence, it can be anticipated that dynamic operation of a stack in co-electrolysis mode will generate significant thermo-mechanical stress gradients within the stack. Therefore, mechanical robustness of cell and stack is of the utmost importance.

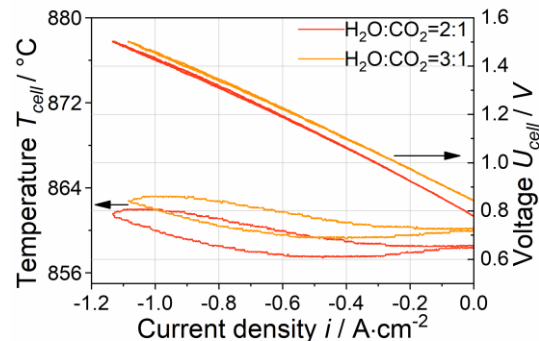


Figure 4: Cell temperature evolution (left axis) and polarization curves (right axis) for ESC in and co-electrolysis at 860°C.[20]

Especially for the fuel electrode, impurities in the feed gases could adsorb on the active sites and slow down the reaction kinetics. In the long term, similarly to what is observed with sulfur species in SOFC mode, this could lead to enhanced and irreversible cell degradation that is detrimental for the system durability.

In the electrolysis process, steam may come from different sources. It could be from direct water evaporation or from industrial steam sources and thus, may be of different quality. SiO₂ impurities in the water are known to be easily transported in the vapor stream and can be deposited on the active sites for the co-electrolysis, leading to an accelerated degradation of the electrochemical performance. Furthermore, since cell voltage is a direct function of gas composition, a constant flow of steam free of any liquid water has to be maintained to avoid unwanted voltage oscillation. Therefore, to increase the durability of the electrochemical reactor, high quality steam with the lowest amount of impurities should be provided.

In the co-electrolysis process, CO₂ represents a potential source of impurities. This is true especially for CO₂ streams originating from industrial or combustion processes of heavy fuels. Independently from the nature of impurities that may contaminate CO₂ streams, further investigation regarding the sensitivity of co-electrolysis process towards CO₂ impurities are necessary to identify the required purity, allowing economically viable exploitation of the co-electrolysis process.

Summary and conclusions

State-of-the-art Ni/CGO-based electrolyte-supported cells were investigated in co-electrolysis mode under various operating conditions. The cells were electrochemically characterized by means of chronopotentiometry and electrochemical impedance spectroscopy and promising performance was demonstrated. Furthermore, operational aspects with regards to feed gas impurities were discussed.

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