



A parameter study of solid oxide electrolysis cell degradation: Microstructural changes of the fuel electrode

Michael Philipp Hoerlein ^{a,*}, Matthias Riegraf ^a, Rémi Costa ^a, Günter Schiller ^a,
K. Andreas Friedrich ^{a, b}

^a German Aerospace Centre (DLR), Institute of Engineering Thermodynamics, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

^b University of Stuttgart, Institute of Energy Storage, Pfaffenwaldring 31, 70569 Stuttgart, Germany



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ABSTRACT

A parameter study of 20 solid oxide electrolysis cells was carried out to systematically investigate long-term degradation each over 1000 h under variation of temperature, humidity and current density. The influence of operating temperature was investigated between 750 and 850 °C, the humidity ranged from 40% to 80% H₂O, and the current density varied between open circuit voltage (OCV) and 1.5 A cm⁻². The progress of degradation was monitored in-situ by electrochemical impedance spectroscopy. Five different contributions to the spectra were identified by calculating the distribution of relaxation times and separated via a complex non-linear square fitting routine. The present work focuses on the degradation of the fuel electrode. From SEM analysis, Ni depletion and an increased pore fraction close to the electrode/electrolyte interface was derived, which is correlated with an increased ohmic resistance of the cells. This unidirectional transport of Ni away from the fuel electrode/electrolyte interface leads to an effective electrolyte extension and is the main source of degradation. Ni depletion is shown to be driven by current density and its extent is shown to be dependent on the complex interplay between the operating parameters current density, anode overpotential, humidity and temperature. It is particularly pronounced for *p*H₂O larger than 0.8 atm and temperatures above 800 °C. Furthermore, the fuel electrode electrochemistry also exhibits degradation in the high-frequency region around 10⁴ Hz.

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1. Introduction

The transition to a more renewable electricity generation is accompanied by the challenge of an increasing mismatch between production and demand, which leads to a growing electric energy storage demand. In this regard, the solid oxide electrolysis cell (SOEC) promises high efficiencies towards the conversion of water into hydrogen and is therefore considered particularly environmentally friendly. However, especially at high current densities degradation limits its lifetime thus hindering commercialization. Several degradation processes on both fuel and air electrode have been identified and investigated [1,2].

On the fuel electrode, one common degradation phenomenon in SOEC is the segregation of impurities such as silica at the triple phase boundary (TPB) [3,4]. Impurities can partially be removed by

reversible operation in SOFC mode [5]. Furthermore, Ni agglomeration is a common degradation phenomenon in Ni/YSZ electrodes of solid oxide cells operating at high fuel gas humidity, which leads to a reduction in TPB length [6–9]. This is partially due to a minimization of free surface energy according to Ostwald ripening but can also be correlated to a high Ni mobility due to Ni(OH)_x formation [7,8,10,11]. At high current densities and large overpotentials Ni relocation has been shown to lead to irreversible Ni migration away from the electrolyte and to Ni depletion of the most inner few micrometers close to the electrolyte [10–13]. This leads to the shift of the reaction zone away from the electrolyte and essentially represents an effective extension of the electrolyte. At a higher temperature of 950 °C, the Ni migration has been observed to be directed towards the electrolyte and has led to a clogging of the pores close to the electrolyte [7]. Furthermore, Ni depletion at the fuel electrode/electrolyte interface has also been observed in solid oxide fuel cell operation, possibly driven by a similar mechanism [6,14,15]. Recently, this process was suggested to be driven by potential and humidity gradients [10]. However, the underlying

* Corresponding author.

E-mail addresses: Michael.Hoerlein@fst.com (M.P. Hoerlein), Matthias.Riegraf@dlr.de (M. Riegraf).

mechanism is still not fully understood.

Despite the increasing progress achieved in the identification and mitigation of degradation processes, a systematic investigation of the influence of key operating parameters on the extent of degradation is still missing. In the present work, SOEC degradation of 20 state-of-the-art LSCF|CGO|YSZ|Ni/YSZ fuel cells is systematically analyzed during 1000 h testing in order to establish a clear correlation between degradation processes and operating conditions. Three parameters, namely the operating temperature, the current density and the fuel gas humidity, were identified to be most revealing and the experimental matrix shown in Fig. 1 was devised to separately identify the influence of each parameter and gain insights into the nature and extent of the occurring degradation processes. This work mainly focuses on the microstructural changes of the fuel electrode. The degradation of the other cell components will be published elsewhere.

2. Experimental

In the present work, commercially available anode-supported fuel cells (ASC) supplied by CeramTec (Marktreidwitz, Germany) were used. They are supported by a 290 μm fuel electrode layer, which is a composite of Ni and 8YSZ produced by warm pressing using a so-called Coat-Mix material and pre-sintered at 1230 $^{\circ}\text{C}$. The active electrode of the cells consisted of a porous composite with an 8–10 μm thick Ni/YSZ active layer. The electrolyte was a tape-casted 8YSZ layer with a thickness of 10 μm sintered at 1230 $^{\circ}\text{C}$. The air electrode consisted of 30 μm thick $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF-6428). In addition a 3–4 μm thick screen-printed GCO diffusion barrier layer was employed to reduce reactivity between the 8YSZ electrolyte and the LSCF-6428 oxygen electrode. The active area of the planar cells was $4 \times 4 \text{ cm}^2$ with a total area of $5 \times 5 \text{ cm}^2$. The setup for cell testing enables the characterization of up to four cells simultaneously and was already illustrated and described in a similar configuration in detail elsewhere [16,17].

Anode and cathode were contacted with nickel and platinum meshes, respectively, and gold was used as the sealant between the anode and the cathode side, thus avoiding the use of silica-containing materials. In all tests, cells were operated at a constant total fuel flow rate of 2 SLPM (standard liter per minute) for each cell. The air electrode was operated with air at a constant flow rate of 2 SLPM. These large flow rates were chosen to keep gas

conversion below 20% for all degradation measurements thus reducing gradients across the length of the cell and consequently minimizing the emergence of local degradation effects. The fuel gas humidification was implemented with a “Controlled Evaporator Mixer” (CEM) in combination with a liquid water mass flow controller (Cori-Flow™, Bronkhorst, Netherlands).

The cells were heated (3 K/min) to 900 $^{\circ}\text{C}$ and reduced. The OCV was checked before starting the tests and confirmed to be higher than 1.20 V at 900 $^{\circ}\text{C}$ in pure hydrogen and air (each 1 SLPM) for all investigated cells, assuring proper gas tightness. Consecutively, the operating temperature was changed to 800 $^{\circ}\text{C}$ and initial characterization was carried out with a polarization curve in fuel cell mode with a $\text{H}_2/\text{H}_2\text{O}$ (96/4) mixture. Subsequently, electrochemical impedance spectroscopy (EIS) measurements were conducted with 4% H_2O at OCV and 60% H_2O at OCV and -0.5 A cm^{-2} , respectively, in order to characterize the initial state of the cells. After this initial characterization the degradation experiment was started. During the experiments, the current of all cells was interrupted approximately every 168 h (weekly) for intermediate cell characterizations. In order to gain comparable data humidification and temperature were adjusted to 60% molar humidity (MH) and 800 $^{\circ}\text{C}$, respectively for all impedance spectroscopy measurements. These were conducted at -0.5 A cm^{-2} . After the impedance measurements, the operating conditions were applied again and the degradation measurement was continued. At the end of the degradation experiment after approximately 1000 h a final characterization was carried out before the cells were cooled down. Besides the investigated parameters all other parameters were kept constant for all degradation measurements. Furthermore, deviations between the respective measurements were minimized by conducting all experiments in the same test rig and using commercially available, highly reproducible cells of the same batch. A fresh cell was used for each of the 20 parameter combinations displayed in Fig. 1.

For electrochemical impedance spectroscopy measurements, an electrochemical workstation (Zahner® PP-240 with Thales software) was used in a typical frequency range from 500 mHz to 100 kHz. The amplitude of the current stimulus was 500 mA and chosen in order to achieve a voltage response not higher than 10 mV. A representative example for a fitted spectrum is depicted in Fig. A1, where values for fitting error as well as uncertainty of each fitting parameter are presented.

The distribution of relaxation times (DRT) was calculated with a modified Levenberg-Marquardt algorithm adapted from Ref. [18] SEM images were recorded with a Zeiss Ultra Plus SEM (Oberkochen, Germany). In order to separate percolated from non-percolated Ni, measurements at low acceleration voltage were conducted without prior carbon deposition, according to the procedure in Ref. [19].

3. Results and discussion

3.1. Initial cell characterization

Initially recorded current-voltage characteristics of one of the cells in fuel cell mode are exemplarily depicted in Fig. A2 (800 $^{\circ}\text{C}$, 96/4 $\text{H}_2/\text{H}_2\text{O}$, air). At 1.5 A cm^{-2} the cell voltage is still at 0.73 V, demonstrating the cell's high performance.

To separate the occurring processes and obtain information about their characteristic frequencies, the DRT was calculated. A typical DRT plot of a cell in its initial state measured at 800 $^{\circ}\text{C}$ and 60% MH is presented in Fig. A3. Including the ohmic resistance, it shows the existence of five rate-limiting processes. Their characteristic frequencies are approximately one order of magnitude apart and are roughly at $2 \cdot 10^4$, 10^3 , 10^2 and 10 Hz, respectively. Based on a variation of operating parameters (temperature T ,

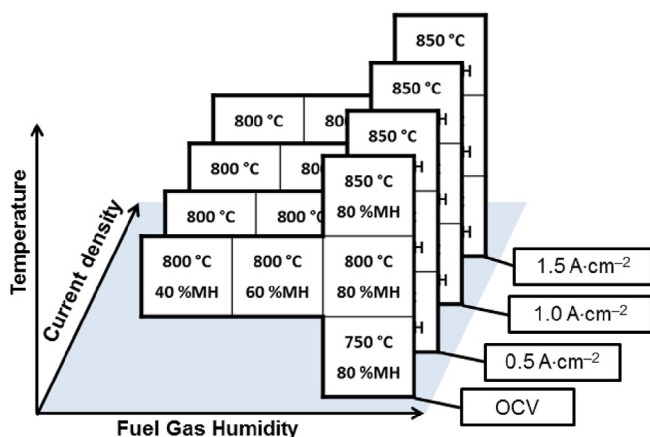


Fig. 1. Testing matrix of the present study consisting of three temperatures, three molar humidities and four current densities devised to separately identify the influence of each investigated parameter on cell degradation in SOEC operation. At each displayed operating condition a long-term experiment over a duration of 1000 h was conducted.

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