



Re-activation of degraded nickel cermet anodes - Nano-particle formation via reverse current pulses

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HIGHLIGHTS

- Re-activation of Ni/YSZ SOFC anodes attained via reverse current treatments (RCT).
- Higher Ni/YSZ electrode performance after degradation and RCT than for a fresh cell.
- Ni/YSZ electrode resistance increased from 180 mΩcm² to 390 mΩcm² upon degradation.
- Same Ni/YSZ electrode resistance decreased to 159 mΩcm² upon RCT.
- RCT generates new active sites via nano-particle formation.

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ABSTRACT

The Ni/yttria-stabilized-zirconia (YSZ) cermet is the most commonly applied fuel electrode for solid oxide cells (SOCs). Loss of Ni/YSZ electrode activity is a key life-time limiting factor of the SOC. Developing means to mitigate this loss of performance or re-activate a fuel electrode is therefore important.

In this work, we report a series of five tests on state-of-the-art Ni/YSZ-YSZ-CGO_{barrier}-LSC/CGO cells. All cells were deliberately degraded via gas stream impurities in CO₂/CO or harsh steam electrolysis operation. The cells were re-activated via a variety of reverse current treatments (RCTs). Via electrochemical impedance spectroscopy, we found that the Ni/YSZ electrode performance could be recovered via RCT, but not via constant fuel cell operation. For optimized RCT, we obtained a lower Ni/YSZ electrode resistance than the initial resistance. E.g. at 700 °C we measured fuel electrode resistance of 180 mΩ cm², 390 mΩ cm², and 159 mΩ cm² before degradation, after degradation and after re-activation via RCT, respectively. Post-test SEM revealed that the RCT led to formation of nano-particles in the fuel electrode. Besides the remarkable improvement, the results also showed that RCTs can weaken Ni/YSZ interfaces and the electrode/electrolyte interface. This indicates that finding an optimum RCT profile is crucial for achieving maximum benefit.

1. Introduction

Reversible solid oxide cells (SOCs) have the potential to become an important energy conversion technology in the rapidly developing energy grid, which is accommodating a growing share of intermittent renewable electricity. SOCs can be applied as solid oxide fuel cells (SOFCs) for efficient and flexible electricity generation from chemical energy stored in fuels such as hydrogen, natural gas or biogas. In times of surplus of electrical energy from renewable sources such as wind and solar, the reversible SOC can be used as solid oxide electrolysis cells (SOECs) for storage of energy [1]. The SOEC then produces fuels such as hydrogen when the SOECs are used for steam electrolysis, or syn-gas

when they are used for electrolysis of carbon dioxide and steam (CO₂ + H₂O) [2]. Subsequently, synthetic natural gas or other synthetic fuels can be produced from the syn-gas via well-known catalytic processes [3–6].

By far most of the technological interesting SOC systems rely on cells applying Ni/yttria-stabilized-zirconia (YSZ) based fuel electrodes [7,8]. These electrodes have the advantage of using abundant materials and up-scalable ceramic processing such as multilayer tape casting to produce high performing SOC [9]. These electrodes are therefore employed already for commercially available SOC products. Furthermore, it is required that the Ni/YSZ electrode keeps its high electrochemical performance. In cases where a degradation of the Ni/YSZ electrode has

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¹ The majority of the experimental work was conducted by M. Marchese.

occurred (e.g., due to impurities in the gas stream [11–14]), it will be attractive to be able to recover the electrode performance. A method for improving the fuel electrode performance is via impregnation of electro-catalytically active nano-particles [15,16], a practice which can also be done on already operated SOC stacks [17]. However, this method has the disadvantage that it sets requirements regarding the structure for infiltration. Furthermore, it can be challenging to ensure that the impregnated nano-particles are positioned optimally in the electrode structure to provide largest increase in triple phase boundary (TPB).

An alternative solution is to apply *in-situ* – or even *operando* – methods that generate new nano-structures in the electrode and thereby new TPB sites for the electrochemical reaction in the existing electrode structure. Instead of introducing nano-particles in the electrode structure via infiltration, previous work has also elaborated on the possibility of generating nano-particles via short shift between fuel cell and electrolysis operation of the SOC [18–20]. In the case of a Ni/YSZ-based electrode, a short shift from fuel cell operation to electrolysis and back could lead to partial reduction of the stabilized ZrO_2 at electrochemical active sites. Depending on the conditions, this reverse current treatment (RCT) facilitates intimate reaction of the reduced stabilized ZrO_2 with Ni. Subsequent re-oxidization yields nanostructured TPB regions. The *in-operando* generated nano-particles provide increased electrochemical performance. Initial experimental work has been reported on RCT on small scale Ni/YSZ electrodes [19,21] and more explorative electrolyte supported button-cells based on LCNT/ScSZ/LSM-ScSZ [20].

In this work, we focus on the application of larger scale technological relevant SOC. We investigate the possibilities for increasing the electrochemical performance via RCT for deliberately degraded Ni/YSZ electrodes, but also investigate the limitations of the RCT method. This is attained by exploring the effects of numbers of RCT cycles and of increasing time and increasing current density during the RCT cycles. Additionally we investigate whether a similar Ni/YSZ electrode improvement could have been obtained via constant galvanostatic fuel cell operation of the cell.

2. Experimental

2.1. Cell specifications and test set-up

The cells are Ni/YSZ supported Ni/YSZ-YSZ-CGO_{barrier}-LSC/CGO (lanthanum-strontium-cobaltite and gadolinium-doped-ceria) based cells produced at DTU Energy, Risø Campus [9]. An overview of cell and test specifications is given in Table 1. The cells comprises of a ~10 μm thick Ni/YSZ fuel electrode with a ~300 μm thick Ni/YSZ support layer, a ~15 μm thick YSZ electrolyte, a 2 μm thick CGO barrier layer and a ~40 μm thick LSC/CGO oxygen electrode and ~30 μm thick LSC contact layer [22]. Zirconia stabilized with 8 mol percent Y_2O_3 was used for the electrolyte and the active fuel electrode layers. Zirconia stabilized with 3 mol percent Y_2O_3 was used for the support layer. For all applied Ni/YSZ cermets the quantities of NiO and YSZ were scaled to provide a Ni/YSZ volume ratio of 40/60 after reduction of NiO. The active fuel electrode was produced as dense as possible leading to a pore fraction of approximately 22% after NiO reduction. For the production of the support layer, active fuel electrode and electrolyte layer successive tape casting i.e. a multilayer tape casting (MTC) process and lamination process was applied [9]. The three MTC layers of the tape were cut into 16 × 16 cm² pieces and co-sintered at 1315 °C [23]. Then the CGO barrier layer was applied by pulsed vapor deposition (PVD) and then cut into 53 × 53 mm² cells. The oxygen electrodes (40 × 40 mm²) and LSC contact layers were applied by screen-printing. For cell C the oxygen electrode and contact layer was masked during screen printing to an area of only 4 × 0.6 cm² to accommodate reverse current treatment at higher current density. All tested cells reported in this work originated from the same casted tapes, barrier layer was added by PVD in one go for all cells and are therefore

referred to as “sister cells”. The set-up for single cell testing was illustrated and described in detail previously [11,24], and a set-up close to the one illustrated as “Cell assembly 2” in the work by Ebbesen and co-workers was applied. However gold seals on anode side and seal less cathode assembly [11].

2.2. Test procedure and reverse current treatment (RCT)

The cells were heated (1 °C/min) to 850 °C for sealing. The NiO was then reduced by leading 20 l/h of dry 9% H_2 in N_2 to the fuel electrode for 2 h followed by 1 h of 20 l/h dry H_2 to the fuel electrode while air was led to the oxygen electrode. Hereafter performance characterization via iV-curves and electrochemical impedance spectroscopy (EIS) was conducted. EIS was conducted both at different temperatures, gas compositions and at OCV and under current load. The Ni/YSZ electrodes were then deliberately degraded and subsequently the RCT was conducted as specified in Table 1. This is further illustrated in supplementary material (Fig. S1). During the RCT EIS were recorded first at OCV and during fuel cell operation (air to the oxygen electrode, 4 and 20% H_2O in H_2 to the fuel electrode). To keep the time at FC test conditions short during the RCT, the EIS recorded at 1 A cm⁻² only lasted 8 min and were recorded down to 2 Hz. RCT were done via a direct switch from 1 A·cm⁻² to -1 A cm⁻². During the fast switch between fuel cell and electrolysis cell operation of the cells, the gas composition to the fuel electrode was kept at 4% H_2O in H_2 . The cell voltage was logged at a rate of 2–3 measurements per second. Cell voltages reached approximately 2.1 V during each 10 s RCT. For Cell C even higher voltage was measured during the electrolysis shift (see supplementary material, Fig. S1).

2.3. Electrochemical impedance spectroscopy (EIS)

A Solartron 1255 frequency analyzer was used for recording EIS both at OCV and under current load applying a set-up as described by Jensen [25]. Impedance spectra (IS) were recorded with 12 points/decade from 97 kHz to 0.1 Hz during initial characterization and down to 2 Hz during RCT. In-house developed Python-based software was used for plotting and analysis of the impedance data [26]. In this work, experimentally obtained IS are depicted as inductance corrected data in Nyquist and Bode plots. Furthermore, plots of distribution of relaxation times (DRT) are provided. The DRT plots are used to illustrate and highlight frequency ranges for different processes contributing to the total impedance response [27,28]. To enable a quantitative analysis of the IS complex-non-linear-least-squares (CNLS) method was used to fit an equivalent circuit model to the impedance data. For a quantitative break-down of losses via IS the equivalent circuit based on the work reported by Kromp et al. [29] and the work by Ramos and others [30] was used. Table 2 provides an overview of the different resistance contributions included in the equivalent circuit model for impedance analysis and their interpretation. The electrochemical impedance response from the Ni/YSZ electrode was approximated by two RQ-elements. The higher frequency impedance arc (RQ)_{ionic} at ~10–25 kHz has previously been ascribed to ionic transport through the ionic conducting matrix in the electrodes. For the applied cells (Ni/YSZ-YSZ-LSC/CGO) with the mixed ionic electronic and highly conducting LSC based oxygen electrode, the majority of the resistance R_{ionic} can be expected to originate from the Ni/YSZ electrode. The (RQ)_{Ni/YSZ,TPB} at a summit frequency of ~1–15 kHz is ascribed to the charge transfer reaction at the triple phase boundaries (TPBs). These two contributions to the overall impedance of the cell can also be described using a transmission line model (TLM) [28,31,32]. In the “Supplementary Material” a comparison of the application of the two models is given (see Fig. S2). The impedance response from the LSC/CGO oxygen electrode has been approximated by a Gerisher-type response [22]; having a characteristic frequency of ~300 Hz. Furthermore; gas diffusion and gas conversion resistance contributions have been approximated by two RQ-circuits

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