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Electrochemical Impedance Spectroscopy study on ammonia-fed Solid Oxide Fuel Cells

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Abstract. The use of ammonia as a fuel is one of the promising pathways to decarbonize the energy sector. When ammonia is converted into power in the so-called “Ammonia-to-Power”, the most interesting technology is the Solid Oxide Fuel Cell (SOFC) that can operate directly with ammonia and reach high performance in terms of efficiency. SOFCs are a high-efficiency and, potentially, low-cost technology, but still suffer from degradation issues related to internal losses. An innovative experimental technique to evaluate losses evolution caused by degradation is electrical impedance spectroscopy (EIS), followed by measurement data post-processing through the Distribution of Relaxation Times (DRT) analysis. In this study, a single SOFC is studied with a combined EIS and DRT methodology, when operating with a gas mixture of hydrogen, nitrogen and ammonia. The results identify the contribution to DRT of fuel dilution and the internal ammonia decomposition reaction.

1. Introduction

Ammonia is considered an innovative fuel for the decarbonization of society. In particular, in the *ammonia as a fuel* paradigm, green ammonia is produced from renewable energy sources (RES) and used as a fuel in power systems for power production. Ammonia is a versatile fuel and can be used in all energy systems based on hydrogen technologies since ammonia can be decomposed into a mixture of hydrogen and nitrogen. In particular, the use of ammonia in Solid Oxide Fuel Cells (SOFCs) is promising to achieve a high level of power conversion and low emissions. In SOFCs ammonia is easily decomposed in the fuel electrode, due to the presence of nickel as a catalyst and high operating temperatures. Once hydrogen and nitrogen are produced, hydrogen reacts in the cell with the typical advantage of the SOFC technology where electrochemical reactions allow to reach high efficiency and zero emissions. Recent studies of system design, based on SOFC operating with NH₃ as a fuel, report net efficiencies at the system level up to 52.1 % in the one-stage process [1] and up to 72% for enhanced system design with hydrogen membrane separation [2].

SOFCs operation is usually evaluated considering the polarization curve: the variation of voltage as a function of current density at fixed or variable inlet fuel conditions. Recently, electrochemical impedance spectroscopy (EIS) has been introduced to identify the contribution of internal processes to polarization losses. In this sense, EIS and the further elaboration called Distribution of Relaxation Times (DRT) allow investigating separate contributions of different cell components. The application of the DRT analysis to SOFC is under development and several aspects are still being investigated. The DRT analysis allows to generate the spectrum of relaxation times as a function of the EIS excitation frequency, obtained with a mathematical elaboration of EIS experimental data [3]. Therefore, the DRT spectrum is characterized by a series of peaks at different frequencies. Previous



research tried to couple each peak to a specific physico-chemical phenomenon occurring in the SOFC operating process. **Table 1** reports typical frequency value ranges corresponding to single phenomena according to the literature [4]–[7]. Note that the literature has not a unique interpretation of the results of the DRT analysis and the table is a synthesis of the main outcomes. Moreover, depending on the specific set-up, frequencies may be shifted compared to what is reported in the table. The peak at higher frequencies ($> 10^4$ Hz), corresponds to oxygen ions transport in the electrolyte. The peak at lower frequencies, around 10^3 Hz, is related to the anode charge transfer at the triple phase boundary (TPB) level. Going to c.a. 10 Hz, literature considers the main phenomenon the oxygen diffusion and exchange. In this range of frequencies, some studies attribute fuel diffusion to the DRT peak. Conversely, the 10^{-1} Hz peak is debated for being associated with anode reactant diffusion, as reported in the table, and a combination of both anode and cathode diffusion. Finally, in the case of low air partial pressure, a fifth peak is identified at 10^{-2} Hz related again to the air diffusion phenomenon.

Table 1 Frequency ranges and relative phenomenon identified by DRT analysis

| Frequency range | Component | Phenomenon |
|-----------------|-------------|---------------------------------------|
| $> 10^4$ Hz | Electrolyte | Oxygen transport |
| 10^3 Hz | Anode | Charge transfer |
| 10^1 Hz | Cathode | Oxygen diffusion and exchange |
| 10^{-1} Hz | Anode | Reactants diffusion |
| 10^{-2} Hz | Cathode | Air diffusion at low partial pressure |

When feeding the cell with a fuel mixture, chemical reactions may occur in the fuel electrode. Such phenomenon was investigated in [7], where a SOFC was fed with mixtures of methane and steam (achieving the internal reforming of methane) and with syngas (simulating the result of an external reforming process). The DRT study shows a new peak in the very low-frequency range, namely 1 Hz for the case analyzed in [7].

Looking at the use of ammonia in SOFCs, literature reports experimental test on single cells where the two-steps reaction was clearly assessed: 1) ammonia is decomposed into hydrogen and nitrogen in the cell and, subsequently, 2) hydrogen electrochemically reacts to produce power [8]–[10]. In recent studies, the EIS technique was used to evaluate the effect of ammonia compared to hydrogen [11], [12]. The EIS was used to evaluate and compare degradation caused by ammonia with degradation caused by hydrogen.

This paper aims to study, for the first time in literature, the use of ammonia in SOFCs through DRT analysis. In detail, this study has two main objectives at both the technological and the methodological levels. Looking at the technology, i.e. the use of ammonia in SOFCs, the study aims to identify the impact of ammonia in each specific phenomenon identified with the DRT analysis. Regarding the method, the main purpose is to identify the chemical reaction contribution to peak distribution and magnitude in the final DRT spectrum. Since the only chemical reaction occurring in the cell is ammonia decomposition, the single contribution of the reaction should be identified when comparing the ammonia operation with equivalent mixtures of hydrogen and nitrogen. To pursue these targets, a SOFC single cell is operated with mixtures of hydrogen, nitrogen and ammonia. Then, DRT is applied to deconvolute EIS experimental data obtained with different anodic mixtures and operating temperatures. The impact of nitrogen and ammonia in the feeding gas mixtures is finally investigated.

2. Material and methods

The tests are performed on a commercial anode-supported SOFC with Ni/8YSZ anode, 8YSZ electrolyte and LSFC bilayer cathode. The cell is housed in a metal set-up with mica and glass seal at the anode and only mica at the cathode. The current is collected with a crofer mesh at the cathode and a nickel mesh at the anode. The set-up is located in a thermal controlled furnace and the cell is fed employing digital controlled gas flow meters, namely with hydrogen, nitrogen and ammonia at the

anode, and air at the cathode. Current is collected from the metallic pipes and controlled with a power supply and an electronic load. EIS measurements are performed with a Potentiostat/Galvanostat provided by BioLogic© (measurement ranges 0-1,5 V, 0-4 A, 10^{-2} - 10^5 Hz). Temperature and voltage sensors allow sampling operating conditions of the cell during operation.

The test campaign aims to evaluate the effect of ammonia, when used as a fuel in SOFC, through EIS/DRT analysis. After the start-up and the validation, the cell runs under a specific operating condition as defined in the test campaign and the EIS study was performed at Open Circuit Voltage (OCV). DRT was obtained with a free MATLAB toolbox DRTtools [13].

The experimental campaign is divided into two different phases:

- Phase 1: a study of nitrogen dilution in SOFC. Since ammonia decomposes at low temperatures in presence of steel, many studies indicate that the decomposition occurs in the system components before the cell [12], [14], [15]. This means that the cell operates with a mixture of nitrogen and hydrogen. The study of nitrogen dilution is a preliminary mandatory phase, before the real study on ammonia;
- Phase 2: a study of ammonia. At lower temperatures, ammonia may decompose inside the cell. Phase 2 aims to identify if ammonia decomposition can be detected using the DRT method.

For each study two parameters, temperature and anodic gas flow rate (H_2 , N_2 , NH_3) are set. Cathodic gas flow rate is kept constant in all studies at 39.82 NI/h for all the tests performed.

Phase 1: nitrogen dilution

The aim of the nitrogen dilution study is to investigate, through DRT analysis, the contribution of nitrogen in the anodic mixture. When ammonia is completely decomposed, the gas results in a mixture of $N_2:H_2$ in the ratio 1:3. To have a complete study of the phenomenon, four gas mixture compositions were studied as reported in Table 2, from pure hydrogen (#1) to a mixture $N_2:H_2$ 3:1 (#4). Fully decomposed ammonia corresponds to mixture #4. Different nitrogen concentrations can be obtained following two different approaches, both analysed in this study. In the first case, called constant volume (CV), the total volume flow rate of anode inlet gas is kept constant to the value of 10.14 NI/h. Consequently, in CV studies, the dilution is obtained by substituting part of the hydrogen flow rate, initially 10.14 NI/h, with nitrogen. Consequently, the hydrogen flow rate is reduced when the concentration of hydrogen reduces. The second approach, called constant hydrogen (CH), obtains same nitrogen concentrations, increasing total inlet gas flow. Starting from 100% hydrogen with a flow rate of 10.14 NI/h, an increasing amount of nitrogen is added to the inlet gas flow to obtain the target compositions. In this case, the hydrogen flow rate entering the anode is always the same. Note that the pure hydrogen mixture (#1) is the same for both CV and CH studies. Both constant volume and constant hydrogen investigations are performed at a constant furnace temperature of 750 °C.

Table 2 Compositions of nitrogen diluted mixtures

| # | N_2 (% _{vol}) | H_2 (% _{vol}) | $N_2:H_2$ (vol:vol) |
|---|---------------------------|---------------------------|---------------------|
| 1 | 0 | 100 | 0 |
| 2 | 25 | 75 | 0.33 |
| 3 | 50 | 50 | 1 |
| 4 | 75 | 25 | 3 |

Phase 2: ammonia

This second phase aims to compare ammonia with a mixture of hydrogen and nitrogen in the ratio $N_2:H_2$ 1:3, equivalent to fully decomposed ammonia. In this case, only two gas mixtures are considered: 6.76 NI/h of ammonia (NH_3 composition) and a mixture of hydrogen and nitrogen 10.14 NI/h and 3.38 NI/h respectively (H_2N_2 composition). The study was performed at furnace temperatures

of 750, 700 and 650°C. In this case, a detailed investigation of temperature is introduced, because the principal phenomenon under investigation is expected to be more affected by temperature, as it decreases. Moreover, the eventual identification of a temperature threshold for SOFC internal decomposition is of primary interest.

3. Results

DRT curves of the first phase of the study are reported in Figure 1 a and b for CV and CH studies respectively. In both investigations, the impact of nitrogen can be clearly identified in the peak at lower frequencies, in the 10^{-1} :10 Hz range. The introduction of nitrogen moves the peak to lower frequencies, achieving a higher magnitude. Considering current knowledge shared by the scientific literature, as discussed in the introduction, this frequency range corresponds to the anode diffusion phenomenon. When nitrogen is mixed with hydrogen, the partial pressure of hydrogen decreases and the diffusion of hydrogen in the anode is reduced. In constant hydrogen study, the peak reaches higher values. This could be related to the increase of total pressure in the anode due to the increase in total anodic flow rate.

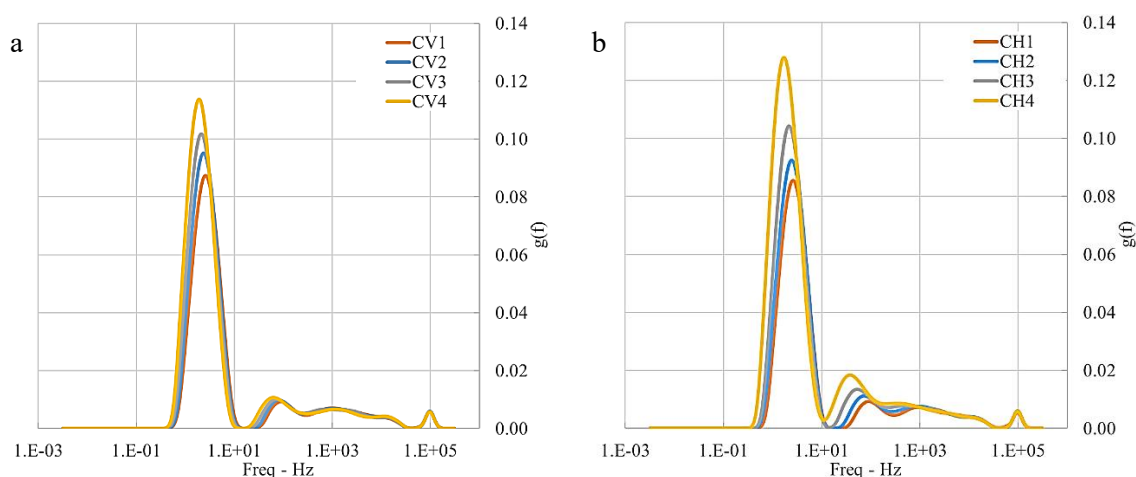


Figure 1 DRT of hydrogen diluted in ammonia at a constant total flow rate (a) and constant hydrogen flow rate (b)

A significant difference between the two tests is related to the peak in the 10^2 Hz frequency range. While in the CV study the peak is constant, in the CH study the peak increases and moves to lower frequencies when nitrogen is added. This aspect seems correlated to the only increase in total flow rate. In this case, the evidence from the scientific literature does not support the interpretation of this trend, since it is unlikely that the peak behaviour could be related to the cathode (see **Table 1**) since air flow is kept constant.

The results of the second phase are reported in **Figure 2**. Specifically, the DRT graph is reported at the three investigated operating temperatures 750, 700 and 650°C. In the graphs, the ammonia mixture, NH_3 , is compared with the equivalent H_2N_2 mixture.

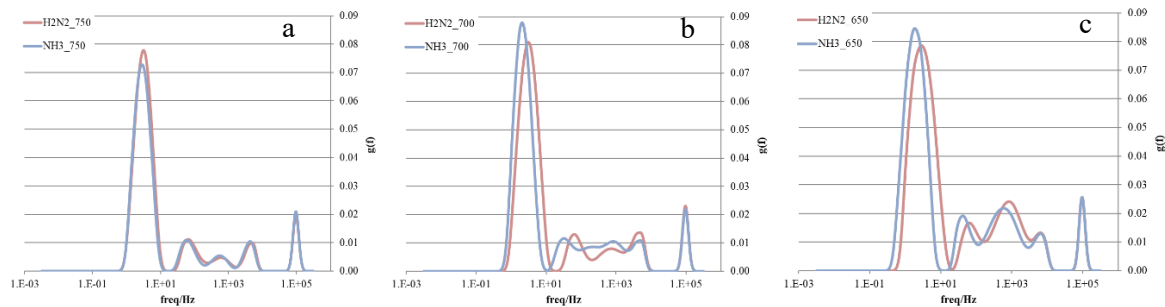


Figure 2 DRT of H_2N_2 and NH_3 mixture at 750°C (a), 700°C (b) and 650°C (c)

At 750°C the two graphs are equivalent due to the complete decomposition of ammonia. When the temperature decreases, the ammonia conversion ratio is lower and a difference between the two mixtures can be identified. In particular, the peak in the frequency range $10:10^{-1}$ Hz shows higher values for the ammonia mixture. Moreover, the peak increases compared to the H_2N_2 spectrum, when temperature decreases. In general, there is a shift of the values to higher frequencies. Note that in this case ammonia is compared with a mixture of hydrogen and nitrogen and the final concentration of nitrogen is the same. Moreover, the low-temperature graph shows a shift of the valley at 10^{-1} Hz to higher values of frequencies. The introduction of ammonia in the cell and the following decomposition can cause several local phenomena. Ammonia reacts producing hydrogen and nitrogen with a behaviour similar to the equivalent mixture. If ammonia is not completely decomposed, the remaining NH_3 is inert and causes diffusion losses similar to nitrogen dilution. Finally, ammonia cracking is an endothermic reaction, causing a local reduction of temperature. The latter case is very unlikely since the oxygen transport peak, in the 10^5 Hz range, is the most sensitive to temperature variation and in all the three graphs reported in **Figure 2**, there is no difference between NH_3 and H_2N_2 .

4. Conclusions

A SOFC single cell was studied with DRT methodology to evaluate the effect of ammonia on the different internal processes. A preliminary study highlighted how the introduction of nitrogen, inert in the electrochemical reaction, impacts the higher frequency peak increasing the peak value and shifting it to lower frequencies. In case of a corresponding increase in total anode flow rate, also the 10^2 Hz peak shifts to higher frequency values. Looking at ammonia operation, the study shows how at 750°C the DRT spectrum of ammonia and equivalent hydrogen nitrogen mixture has no difference. Conversely, when moving to lower temperatures (down to 650°C), the ammonia spectrum is shifted to lower frequencies for all peaks, except for the oxygen transport peak that remains constant.

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