



Negative differential resistance and steady state multiplicity in solid oxide fuel cells



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ABSTRACT

Nonlinear dynamics play a vital role in electrochemical systems and there are many examples in the literature of systems which exhibit interesting behaviour such as multiple steady states and autonomous oscillations. Within the fuel cell community nonlinear dynamics of proton exchange membrane fuel cells have been studied in depth, however other types of fuel cell have not received nearly as much attention. Since fuel cell systems are characterised by a wide variety of physicochemical processes operating on multiple time scales, it is crucial that the nonlinear effects are understood in order to better design and operate them. This work presents the first experimental results on global negative differential resistance and steady state multiplicity in solid oxide fuel cells operating on hydrogen under high fuel utilisation, alongside a basic prototype model that has been adapted from the literature in order to explore the origins of this behaviour. Results are discussed within the context of theoretical predictions from the literature and the prototype model presented within.

1. Introduction

Hydrogen-based energy systems are increasingly being endorsed by governing bodies worldwide due to the renewable nature of the fuel and the ability to utilise it efficiently whilst keeping harmful emissions to a minimum. Production of hydrogen via electrolysis and conversion to useful electrical energy can be achieved using a variety of technologies, however solid oxide electrolysis cells (SOEC) and solid oxide fuel cells (SOFC) in particular have been shown to be extremely efficient [1,2].

Whilst many of the processes which govern SOFC behaviour are reasonably well understood, there exists a gap in the knowledge with regard to nonlinear dynamics. As pointed out by Hanke-Rauschenbach et al. [3] in their review of nonlinear dynamics of fuel cells, most nonlinear behaviour has been experimentally observed in proton exchange membrane fuel cells (PEMFC), with many potential mechanisms discussed with regard to the specific cell composition and operating conditions. For SOFCs, on the other hand, there exist a relatively small number of experimental results in the literature on oscillations [4–13], and mostly only theoretical studies on steady state multiplicity (SSM) [14–16]. Bessler et al. [17] have observed local negative differential resistance (NDR) which results in multiple steady states using a segmented SOFC setup, however the global iU curves show no such

behaviour. They point out the importance of understanding the origins of this behaviour since part of a cell or stack may be operating under critical conditions whilst the global behaviour gives no such indication. Furthermore, the only experimental results on global SSM in SOFCs that the authors are aware of is a lab-on-a-chip type application which uses *n*-butane as the fuel in conjunction with a micro-reformer and micro-SOFC in the planar configuration [18]. They observe that the NDR and resulting SSM are consistently repeatable, and referencing the prototype model of Hanke-Rauschenbach et al. [3] tentatively suggest that competitive adsorption may be the driving mechanism, however a detailed analysis was not presented.

In the PEMFC literature there are a number of reports of SSM with various mechanisms proposed (see for example [19–24]). The noteworthy paper by Kulikovskiy et al. [19] shows local NDR at the cathode side using a segmented fuel cell setup. The behaviour is attributed to diffusion losses and a simple model which considers the limiting diffusion current and the current that would be generated in the absence of diffusion losses is developed. The model is able to qualitatively demonstrate how local oxygen starvation can lead to the observed NDR. In addition, several potential mechanisms are identified in [3] which may give rise to this behaviour. Although the model in [3] is best suited to the analysis of PEMFCs, a similar situation can be expected in SOFCs regarding various potential mechanisms. In this work, an adaptation of

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Table 1
Tubular SOFC dimensions.

Dimension	Value
Anode thickness	560 μm
Electrolyte thickness	10 μm
Cathode thickness	30 μm
Cell length	5 cm
Active cell area	7.95 cm^2
Internal diameter	5.5 mm

the prototype model in [3] is used to analyse the present experimental results obtained on SSM in hydrogen-fuelled SOFCs under high fuel utilisation. The model has been adapted such that the relevant physicochemical phenomena for SOFCs under the operating conditions used in the experiments are included specifically.

The experimental approach used here was to simulate a nitrogen-rich reformate gas since most interesting nonlinear dynamics tend to occur at high fuel utilisations. Additionally these fuel compositions are likely to be reached further downstream of a fuel cell stack, where the stack may exhibit normal global behaviour whilst the cells towards the end are operating in a critical regime. A post-analysis of the anode using scanning electron microscopy (SEM) was conducted and used to aid in the development of the prototype model.

2. Experimental

2.1. Materials & equipment

Anode-supported tubular SOFCs composed of an inner Ni/YSZ anode, YSZ electrolyte and outer LSCF cathode were obtained from Adelan Ltd. with dimensions given in Table 1. Gas inlet/outlet manifolds were machined from ceramics and bonded using both ceramic and silver pastes in order to minimise leakage, with high purity hydrogen (99.995%) and nitrogen (99.99%) obtained from Praxair Co. Ltd. The cathode was exposed to ambient air.

Gas flow was controlled using mass flow controllers from Omega Engineering Inc ($\pm 1\%$ accuracy) with standard 1/4" fittings and Swagelok valves. All electrochemical measurements were conducted using a Chroma 6312 Modular DC Electronic Load and scanning electron microscopy with a FEI Nova Nano Scanning Electron Microscope 450.

2.2. Procedure

Pure hydrogen was passed through the anode chamber during warm-up to ensure the cell was in a reduced state. The temperature was ramped up to 973 K at a rate of 10° per minute then held at open circuit voltage for a further 40 min. The gas line was then switched to a mixed feed of various compositions of hydrogen and nitrogen.

For each gas composition tested the flow rates were adjusted and the cell allowed to stabilise for 10 min. Tests were performed with both a constant flow rate under variable compositions, as well as variable flow rate conditions in order to more finely tune the fuel ratio. It was seen that a 50:50 $\text{H}_2:\text{N}_2$ ratio repeatably gave the same performance with a total flow rate of both 200 ml/min and 100 ml/min (not shown in this manuscript) which justifies this procedure in the range of flow rates used in the experiments. Cell polarisation curves were recorded with a potentiostat using a scan rate of 50 mV/s.

After testing, the cells were cooled down in a purely inert atmosphere in order to preserve the state of the cell as it was when operated under high fuel utilisation. Samples of the anode were taken from the same parts of the cell and compared with the cells as received using SEM.

3. Results & discussion

3.1. Fixed flow rate

Characteristic iU curves were obtained for a fixed fuel stream flow rate of 240 ml/min at different gas compositions, with each composition tested 3 times. Fig. 1a–d shows typical polarisation behaviour, with the current drawn at each cell potential decreasing as the hydrogen in the fuel channel decreases. After the concentration of hydrogen supplied to the fuel channel drops below a critical value, a branch of NDR (where differential resistance is given by $-dU/di$ with U the cell voltage and i the current density) can be seen over a range of cell voltages. Defining the voltage range where NDR is observed to be $U_L < U < U_H$, Fig. 1e and f shows an increase in both U_L and U_H as the hydrogen in the channel decreases. This indicates that the processes from which this behaviour originates become more sensitive to the applied potential as mass transfer limitations become more significant.

Another interesting feature of Fig. 1 is that at the higher fuel ratios, each experimental run produces the same result with almost zero variance. As the fuel ratio decreases, the cells exhibit the same characteristic curves for each run but the variance is slightly increased. This increase in variance is attributed to inconsistencies in the spatial domain due to microstructural changes in the anode, as will be discussed in Section 3.3.

3.2. Variable flow rate

Preliminary experiments show that changing the inlet flow rate from 200 ml/min to 100 ml/min with pure hydrogen and 50:50 mixtures with nitrogen have negligible impact on the characteristic iU curve. Therefore in order to more finely tune the fuel ratio, experiments were conducted with a fixed amount of hydrogen whilst allowing the amount of nitrogen to vary. Fig. 2 shows the results for fixed hydrogen flow rates of 70, 80 and 90 ml/min.

Similar behaviour can be seen as for the fixed total flow rate. At higher fuel ratios the cell exhibits normal iU characteristics. As the fuel ratio decreases a branch of negative differential resistance begins to form with the onset occurring at higher cell voltages for lower fuel ratios. In all three cases, when the NDR branch initially forms at the lowest cell voltages there are only 2 steady state, however as the fuel ratio decreases further, a third steady state can be seen when the differential resistance returns to positive values.

Comparing Fig. 2a–c it can be seen that higher flow rates of hydrogen in the channel require more dilution before the onset of NDR. This implies that fuel utilisation is key in determining this behaviour and must be considered carefully when designing a stack since the fuel will become depleted further along the stack in the direction of flow. If the fuel ratio drops below a critical value along the stack then the remaining cells may exhibit a NDR branch for a range of cell potentials. The results here show that this problem may be negated by increasing the flow rate in the fuel channel.

3.3. SEM

Samples of the anode were taken from the cells before and after operation under high fuel utilisations and analysed using SEM. Fig. 3a and b shows the anode structure before testing at 5000 and 10,000 times magnification, whilst Fig. 3c and d shows the result after operation at the same magnifications. It can be seen that the anode structure changes significantly after operation under high fuel utilisation, in particular the formation of nickel oxide which is represented by the brighter parts of the image.

The formation of nickel oxide causes local expansion of the anode material which leads to an altered microstructure that is less electrochemically conductive, and also has less surface sites available for the reactions. Cracks are also possible due to volume expansion, leading to

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