Fast large-scale current oscillations in SOFCs with intermediate fuel utilisation

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Abstract. In the push towards renewable energy technology fuel cells are set to replace many conventional means of power generation. Their efficiency and cleanliness compared to internal combustion engines is undisputed, however widespread adoption has yet to occur on a global scale. Two of the key issues affecting their mass adoption are their cost and their long-term stability. Whilst long-term testing has proven fuel cells a worthy competitor in the energy market, there are still reports in the literature of degradation caused by a number of different phenomena. In particular, most long-term testing focuses on intermediate fuel utilisation whereas many applications require high fuel utilisations. It is known that at high fuel utilisations several degradation mechanisms may come into play, sometimes resulting in agglomeration, cracking, decreased power output, and electrical oscillations. In this paper, current oscillations are reported in a solid oxide fuel cell under intermediate fuel utilisation which places it firmly in the applicable region for standard operation. Thus it is incumbent on fuel cell researchers to understand and control this unwanted behaviour in order to ensure long-term stability of a fuel cell stack. A prototype model is used here to explore potential causes using first principles.

Keywords - solid oxide fuel cells, fuel utilisation, instabilities, oscillations, nonlinear dynamics

1. Introduction
The continued industrialisation of an ever-increasing number of societies around the globe brings both opportunity, as well as new existential threats. Through the choice of technology, coupled with a deep scientific understanding, we aim to enhance the opportunities and mitigate the threats that new technology brings. In particular, it is noted that the expansion of industry, economic growth, energy production, and road transport is strongly correlated with increasing air pollution [1]. There exist many strategies to mitigate air pollution caused by industry through the removal of contaminants or traffic management (see for example [2,3]), however it is noted that the most beneficial impact comes from the introduction of cleaner, more efficient technologies [4].

Solid oxide fuel cells (SOFC) are not only capable of operation that produces water as the only emission, but have been demonstrated to give high efficiencies in terms of energy production and storage [5,6]. Furthermore, stacks on the order of kilowatts have been tested for long-term stability, one of which was able to reach 40,000 h of continuous operation, far exceeding the target for mobile applications of 10,000 h, and also meeting the requirements for decentralised energy conversion [7–9].

The correct management of fuel utilisation is critical to the long-term durability of a fuel cell stack, and it is well known that under high fuel utilisation, degradation leading to multiple steady states, autonomous oscillations in electrical output, and cell failure may occur [9–19].
Resolving these issues will help to lower the barrier to market and allow fuel cells to contribute towards technological development whilst simultaneously improving the quality of our air.

In [9] it is recommended to keep fuel utilisation below 85% using their particular SOFC configuration in order to avoid detrimental nickel oxidation at the anode. Additionally, small fluctuations and full oscillations can be seen in their galvanostatic tests at 80% and 90% fuel utilisations respectively. In order to operate with such high fuel utilisations we must fully understand the mechanisms occurring within the fuel cell under such conditions to enable better design of SOFCs that can tolerate such a load. High fuel utilisations were simulated in [13] for a single cell and a basic mathematical model was used to explore the potential origins of the observed steady state multiplicity. A more detailed analysis of the results presented in [13] that also explores the origins of autonomous oscillations will be presented in a forthcoming paper.

The scope of this paper is to present experimental results on fast, large-scale, autonomous current oscillations observed in an SOFC that was not operated under high fuel utilisation, placing it firmly in the practical operating range, and to explore potential causes using a first principles approach. Usually this kind of undesirable behaviour is observed under high fuel utilisations and attributed to a number of mechanisms in the literature. Observing unstable output at intermediate fuel utilisation is significant as it indicates that there is more to consider than simply reactant starvation. Oscillations at intermediate fuel utilisations have been observed before in [7] and [8], however the exact mechanism requires further clarification. A post-analysis of the cells in the stack showed several degradation mechanisms including mechanical damage, sealant issues, and nickel oxidation. Clearly a detailed understanding of the causes of the degradation will allow for more effective SOFC configurations and operating conditions to be designed.

The following section will provide details on experiments using tubular SOFCs under intermediate fuel utilisation. The occurrence of autonomous oscillations will be discussed in conjunction with steady state multiplicity in the results section, followed by a modelling approach used in [13] and [20] which allows for the exploration of potential mechanisms giving rise to this behaviour.

2. Experimental

An anode-supported tubular cell with the standard Ni/YSZ/LSCF configuration (dimensions are given in [13]), was ramped up to the operating temperature of 973 K at a rate of 10°/min in pure hydrogen in order to reverse any oxidation that may have occurred in the anode during storage. After maintaining a stable open circuit voltage (OCV) fuel mixtures of hydrogen and nitrogen were fed to the cell, simulating intermediate fuel utilisations. The cathode was exposed to ambient air. The cell voltage was held at a constant value using a potentiostat for at least 20 minutes while the current was recorded, after which, the cell voltage was reduced in steps of 0.1 V and the process repeated. Plots of the current against time were generated and the data were used to calculate the average current at each fixed voltage. These values were plotted in the IV-plane for each fuel composition and fitted with cubic splines in order to generate the characteristic curves. All fuel compositions are given as $H_2/N_2$ ml/min.

3. Results & Discussion

Using a 60/80 fuel composition provided a steady current output at 0.7 V, as can be seen in Fig. 1a. Upon dropping the cell voltage to 0.6 V some minor fluctuations began to appear alongside the expected increase in current density. The fluctuations continued to grow until distinct, large-scale oscillations were observed at 0.25 V. The limitations of the potentiostat meant that the current could not be recorded at voltages below 0.25 V since the changes in the cell output were too abrupt for the Chroma 6312 Modular DC Electronic Load to handle. A key feature of Fig. 1a is that the average current at each voltage level does not monotonically increase as
the voltage decreases, which is in contrast to the usual behaviour seen in polarisation curves for fuel cells. Considering the average current over a given region as a fixed point in a dynamical system, this behaviour corresponds with steady state multiplicity similar to that observed in [13].

Figure 1: Potentiostatic tests performed at simulated intermediate fuel utilisations: (a) Voltage range 0.25 V - 0.7 V fuel composition 60/80 ml/min (b) Voltage range 0.3 V - 0.7 V fuel composition 50/90 ml/min.

In Fig. 1b the current output of the cell was measured over the range 0.3 V - 0.7 V for a fuel composition of 50/90. Fluctuations were seen immediately at 0.7 V which steadily grew to large-scale oscillations as the cell voltage was decreased. Compared with the 60/80 composition, the amplitude of the oscillations at each voltage was larger for the 50/90 composition. Again, due to the potentiostat limitations, measurements were unobtainable below 0.3 V. Similarly to the other fuel composition, steady state multiplicity can be seen when taking the average current densities for each fixed voltage. Fig. 2 plots these values for both compositions along with tentative cubic spline interpolants. In fact, the exact shape of the polarisation curves under these conditions remains to be seen as the number of possible steady states has been hypothesised to be between one and five [16]. More detailed measurements are needed to fully determine the exact nature of the polarisation curves, however, first a study is required to determine the appropriate scan rates for various operating conditions since the dynamic response of a fuel cell can occur on both extremely long and extremely short time scales. For example, oscillations have been observed experimentally in SOFCs with periods on the order of seconds [14], minutes [12] and even hours [11]. It’s certainly possible for oscillations due to different phenomena to occur simultaneously, resulting in mixed-mode oscillations. Therefore it is important to determine scan rates that truly reveal the character of the cells dynamic response.

 Origins of Oscillatory Behaviour
Most oscillatory behaviour (particularly short time scale oscillations) in SOFCs has been observed under reaction depletion. In other words, when the fuel cell is operated under high fuel utilisation, local nickel oxidation takes place which changes the anode microstructure and causes electrical oscillations by various mechanisms. Due to the operating conditions imposed on the
cell to induce these oscillations, quite often the average current output is quite low. However in the present experiments the short time scale oscillations occurred for intermediate fuel utilisation compositions and resulted in large oscillations around relatively high current densities that lie in the range of most practical applications.

It is therefore important to try to understand why these oscillations occurred in these experiments but not in others. It is repeatedly demonstrable that high fuel utilisation inevitably leads to oscillations, although the full mechanisms are yet to be elucidated. On the other hand, such large, short time scale oscillations as observed here are more rare and appear to many fuel cell engineers to occur randomly. Of course the perception that they occur randomly stems from a lack of understanding of their cause. It is the purpose of this section to explore potential mechanisms and eliminate possibilities in the hope that future work in this area will be able to further clarify the situation.

In what follows, similar notation and generic equations to those in [13] are used, with the signs of the differential terms for various operating conditions given in Table 2 of [13].

**Chemical Origins**

Given 2 chemical species in a fuel cell system, $Z_1$ and $Z_2$, a planar dynamical system can describe the chemical kinetics as,

$$\frac{dZ_1}{dt} = f_1(Z_1, Z_2), \quad \frac{dZ_2}{dt} = f_2(Z_1, Z_2),$$

(1)

where the functions on the right hand sides represent reaction-diffusion equations. For oscillations to occur we examine the conditions under which a Hopf bifurcation may take place. According to the Hopf bifurcation theorem [21], we can expect to see oscillations when the eigenvalues of the linearised system about an equilibrium point form a complex conjugate pair with zero real part along with some other quite generic conditions. The eigenvalues of the above system are given by,
\[
\frac{1}{2} \left\{ \left( \frac{\partial f_2}{\partial Z_2} + \frac{\partial f_1}{\partial Z_1} \right) \pm \sqrt{\left( \frac{\partial f_1}{\partial Z_1} \right)^2 - 2 \frac{\partial f_1}{\partial Z_1} \frac{\partial f_2}{\partial Z_2} + 4 \frac{\partial f_1}{\partial Z_2} \frac{\partial f_2}{\partial Z_1}} \right\},
\]

which requires that the 2 terms in the first line (non-radical terms) be of opposite sign in order for a Hopf bifurcation to take place. According to [13] for a purely chemical system the reactants would have both \(\frac{\partial f_1}{\partial Z_1} < 0\) and \(\frac{\partial f_2}{\partial Z_2} < 0\) meaning that oscillations would not be expected to occur. However if the chemical system is autocatalytic then one of the reactants can be the product of the other one meaning that the sign of one of the derivatives would reverse. Under such conditions we would expect a Hopf bifurcation and therefore the onset of oscillations arising from nonlinear chemical dynamics. Such a behaviour was observed for a methane reforming SOFC in [14].

**Electrochemical Origins**  Given a chemical species in a fuel cell system, \(Z\), and an overpotential, \(\eta\), a planar dynamical system can model the cell dynamics as follows:

\[
\frac{dZ}{dt} = f(Z, \eta), \quad \frac{d\eta}{dt} = \frac{1}{C_{dl}} (i - j_Z(Z, \eta)).
\]

The first equation represents the chemical kinetics and the second equation represents charge conservation (\(i\) is cell current density, \(j_Z\) is the Faradaic current). Examining the eigenvalues of the above system and with \(\frac{\partial f_1}{\partial Z} < 0\) we then require \(\frac{\partial j}{\partial \eta} - \frac{\partial j_Z}{\partial \eta} > 0\). However, Kirchoff’s law requires that \(U = U_0 - \eta - r_e\) where \(U\) is the cell voltage, \(U_0\) is the OCV, and \(r_e\) is the electrolyte resistance. Also Faraday’s law states that \(j_Z = nFR_Z\) where \(n\) is the valency number, \(F\) is Faraday’s constant and \(R_Z\) represents the reaction terms determined by mass action. This gives \(\frac{\partial n}{\partial \eta} < 0\) and \(\frac{\partial j_Z}{\partial \eta} > 0\) meaning that a Hopf bifurcation will not arise under these conditions. However, if the first equation represents a surface reaction then it’s possible that \(\frac{\partial f_1}{\partial Z} > 0\), and if the discriminant of the eigenvalues is negative, a Hopf bifurcation can occur. It can be shown using the conditions in [13] that the discriminant can never be negative and we thus rule out the possibility of oscillations occurring as a result of the interactions between basic mass action kinetics and charge conservation dynamics.

**Temperature-Related Origins**  Given a chemical species in a fuel cell system, \(Z\), and variable temperature, \(T\), a planar dynamical system can model the cell dynamics as follows:

\[
\frac{dZ}{dt} = f(Z, T), \quad \frac{dT}{dt} = h(Z, T).
\]

The second equation now represents heat transfer within the fuel cell and to the surroundings. Following the same method of analysis, the eigenvalues reveal that a Hopf bifurcation is indeed possible if either the reaction rate constant or the electrolyte resistance has a strong dependence on the temperature (enough to cancel out the negative term in the non-radical part of the eigenvalues). Consistent with these findings, the occurrence of nonlinear dynamics related to temperature fluctuations has been theoretically investigated before and found to occur depending on the electrolyte properties [16]. Furthermore, if the first equation represented a surface reaction rather than the usual chemical reaction, then a Hopf bifurcation becomes possible under reaction depletion.
Origins from Nickel Redox Cycling

Given a chemical species in a fuel cell system, \( Z \), and changing nickel content of the anode, \( X \), a planar dynamical system can model the cell dynamics as follows:

\[
\frac{dZ}{dt} = f(Z, X), \quad \frac{dX}{dt} = g(Z, X). \tag{5}
\]

The second equation now represents the rate of change of the nickel content of the anode. Similarly to the other 3 cases the eigenvalues of the above system can easily be determined. The non-radical part of the eigenvalues requires that \( \frac{\partial f}{\partial Z} \) and \( \frac{\partial g}{\partial X} \) be of opposite signs. From the typical forms of the rate equations associated with the changing nickel content it can be shown that \( \frac{\partial g}{\partial X} < 0 \). This means that unless we consider surface reactions a Hopf bifurcation will not result from the above system. Considering a surface reaction, the condition that the discriminant be negative is only satisfied if the surface coverage of the reactant is very low. Under these conditions nickel oxidation will occur and oscillations become possible via a Hopf bifurcation.

4. Conclusions

Fast, large-scale current oscillations were observed in a tubular SOFC where reaction depletion was not an issue. A common explanation for instabilities is that reaction depletion causes nickel oxidation and via one mechanism or another gives rise to the oscillations. For these experiments this was clearly not the case and so a brief analysis was conducted to investigate other potential causes. From the cases considered above, it seems most likely that the observed oscillations could be attributed to either an autocatalytic surface reaction scheme involving some intermediate species (since the only reactant supplied to the anode was hydrogen), or to nonlinearities arising from a strong temperature dependence of the reaction rate constant or electrolyte conductivity. Further work is required to determine the unique attributes of oscillations caused by each of these phenomena, some of which will be presented in a forthcoming paper.

References

[1] Roy R 2014 The Cost of Air Pollution: Health Impacts of Road Transport (OECD Publishing) http://dx.doi.org/10.1787/9789264210448-en
[2] Schnelle K B, Dunn R F and Ternes M E 2016 Air Pollution Control Technology Handbook (Second Edition) (Boca Raton: CRC Press)
[3] Keuken M, Sanderson E, van Aalst R, Borken J and Schneider J 2005 Contribution of traffic to levels of ambient air pollution in Europe Health Effects of Transport-Related Air Pollution ed Krzyzanowski M et al (Denmark: World Health Organization) chapter 2 pp 53-84
[4] Fenger J 1999 Atmos. Environ. 33 4877-4900
[5] Jensen J H, Larsen P H and Mogensen M 2007 Int. J. Hydrog. Energy 32 3253-57
[6] Braun R, Klein S A and Reindl D T 2006 J. Power Sources 158 1290-1305
[7] Blum L, Packbier U, Vinke I C and de Haart L G J 2013 Fuel Cells 13 646-653
[8] Groß-Barsnick S M, Fang Q, Batfalsky P, Niewolak L, Blum L and Quadakkers W J 2019 Fuel Cells 19 84-95
[9] Fang Q, Blum L, Peters R, Peksen M, Batfalsky P and Stolten D 2015 Int. J. Hydrog. Energy 40 1128-36
[10] Yoshizumi T, Taniguchi S, Shiratori Y and Sasaki K 2012 J Electrochem. Soc. 159 F693-F701
[11] Marina O A, Pederson L R, Coyle C A, Thomsen E C and Edwards D J 2011 J. Electrochem. Soc. 158 B36-B43
[12] Wang Z, Wei Z, Wei B, Chen K, Huang X, Pan W and Su W 2011 Electrochim. Acta 56 6688-95
[13] Sands D J and Wongyao N 2018 J. Electroanal.Chem. 812 59-67
[14] Sands D J, Uddin J and Needham D J 2016 J. Electrochem. Soc. 163 F856-62
[15] Park K, Lee S, Bae G and Bae J 2015 Renew. Energy 83 483-490
[16] Mangold M, Krasnyk M and Sundmacher K 2006 J. Appl. Electrochem. 36 265-275
[17] Huang T J, Huang M C, Chen W J and Chou C L 2009 Chem. Eng. J. 153 164-9
[18] Parackal B 2017 *An investigation of low temperature direct propane fuel cells* (University of Ottawa: Master’s thesis)

[19] Kawasaki T, Matsuda J, Tachikawa Y, Lyth SM, Shiratori Y, Taniguchi S and Sasaki K 2019 *Int. J. Hydrog. Energy* **44** 9386-99

[20] Hanke-Rauschenbach R, Mangold M and Sundmacher K 2011 *Rev. Chem. Eng.* **27** 23-52

[21] Wu J and Zhou K 1995 *New numerical methods for high dimensional hopf bifurcation problems* *Bifurcation and Chaos: Theory and Applications* ed Awrejcewicz J (Berlin: Springer-Verlag) pp 47-69