Mastering MOXIE
Perovskite Anode Supported Cells and Gas flow Analysis for the Development of a Martian Solid Oxide Electrolysis Based Propellant Plant

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Abstract

As human civilization prepares to expand towards space, it seems evident that the use of local resources to support the missions is crucial for sustainable and cost-effective space exploration. MOXIE is the first off-world demonstration of such in-situ resource utilization, producing $O_2$ using atmospheric $CO_2$. In this thesis possible optimizations for a Martian propellant plant is investigated. Using MOXIE’s solid oxide cell technology as a starting point, this study focuses on developing more capable and enduring electrodes in solid oxide cells. Furthermore, inside MOXIE, a crossover flow between the cathode and the anode was detected, in order to maintain high output purity, analysis of the leak was performed. This work seeks to improve longevity and performance of the electrodes by testing performance after infiltrating with solution at various pH values. The performance are tested on pre-fabricated perovskite anode supported cells, the performance has been investigated with electrochemical impedance spectroscopy and morphological characterization by scanning electron microscopy. The polarization resistance of samples were lower at higher alkalinity. Using morphological characterization it is suggested the low resistance stems from sets of small particles, even though bigger particles also were present. The MOXIE system include multiple manifolds near inlets and exhausts, and some crossover flow are to be expected. To maintain high $O_2$ purity, anode overpressure is suggested. Further a model to describe diffusive flow in the region of pressure equilibrium between anode and cathode is presented.
Acknowledgements

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<td>Two-Phase-Boundary</td>
</tr>
<tr>
<td>3PB</td>
<td>Three-phase-boundary</td>
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<tr>
<td>AC</td>
<td>Alternating current</td>
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<tr>
<td>aq.</td>
<td>Aqueous</td>
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<tr>
<td>ASR</td>
<td>Area Specific Resistance</td>
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<td>BSE</td>
<td>Backscattered electrons</td>
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<tr>
<td>CGO</td>
<td>Gd doped-ceria</td>
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<tr>
<td>CTE</td>
<td>Coefficient of thermal expansion</td>
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<td>DTU</td>
<td>Technical University of Denmark</td>
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<td>EDS</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
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<td>EtOH</td>
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<td>HEPA</td>
<td>High efficiency particulate air</td>
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<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
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<td>ISRU</td>
<td>In Situ Resource Utilization</td>
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<tr>
<td>LaB6</td>
<td>Lanthanum hexaboride</td>
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<td>LFSNT</td>
<td>$La_{0.4}Sr_{0.4}Fe_{0.03}Ni_{0.03}Ti_{0.94}O_3$</td>
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<td>LST</td>
<td>La-doped SrTiO$_3$</td>
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<td>MAV</td>
<td>Mars Ascent Vehicle</td>
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<td>MIEC</td>
<td>Mixed ionic and electronic conductor cells</td>
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<td>Mars OXygen ISRU Experiment</td>
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<td>NASA</td>
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<td>Rp</td>
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<td>YSZ</td>
<td>Yttria Stabilized Zirconia</td>
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1 Introduction

With Earth’s uncertain future due to climate change, wars, global pandemics and natural disasters, an off-world human settlement would be an effective safeguard against the loss of technological advancement or in worst case scenario the extinction of humanity caused by planet-wide catastrophe. The obvious target for an off-world human settlement would be Mars[1–3]. Mars is both close to Earth and of similar size, compared to other celestial bodies in our solar system, Mars has the most Earth-like temperature. Mars holds resources necessary for sustained human presence such as carbon in the atmosphere and water that can be processed from underground ice [1, 2, 4]. Further, the scientific value that is possible on Mars is immense: A primary goal for NASA’s Mars missions has long been to search for extraterrestrial life and this also applies to Mars 2020 mission[5]. Giovanni’s observation of Martian canals were both inaccurate and translated incorrectly[6], however it did spark an interest in both the public and the scientific community about Mars and the possibility of extraterrestrial life[7]. Since Giovanni’s time our methods of observation have been refined tremendously, with this our expectations of life have been equally lowered. Furthermore, our knowledge of the building blocks of life has also been improved significantly since then. Today the prevailing view amongst scientists seem to be that life forms rather easily if the right conditions are met[1]. On Earth recent simulations suggest life formed 4.5 billion years ago, only 40 million years after the formation of Earth[8], which is a relatively short time period when compared to the life cycle of planets. This further supports the view that life forms easily at the right conditions.

The early years after formation Mars had oceans and rivers[9], just like Earth at this time, but it seems clear that Mars is not abundant with life today such as Earth. If Mars was ever full of life, the evidence should show as Martian investigations continue. Whether such evidence is found or not, it will bring answers that undoubtedly will bring us clues about the mystery of life itself.

Bringing samples back from Mars is pivotal in this search for evidence of life. While the Mars rovers have been increasingly advanced with more equipment and possibilities for investigation, the weight and volumetric restrictions imposed on these missions make it clear that a full scale terrestrial laboratory will be a massive advantage for understanding Mars better. For this reason the National Aeronautics and Space Administration (NASA) of the United States and the European Space Agency (ESA) have come together to bring home samples collected by NASA’s Perseverance rover[10, 11]. Whether bringing a human crew or a robot back from Mars, a return mission is among the biggest technological challenges humanity has ever faced. A return mission from Mars will need a Mars Ascent Vehicle (MAV) to leave Mars orbit, and a Return Earth Vehicle waiting in Mars orbit to bring the cargo and/or crew to Earth. However, bringing anything from the Martian surface to orbit is no easy task, a major challenge is how to provide the large mass of cryogenic propellant needed to power the MAV[10, 12]. Transporting propellant, from Earth to Mars to power
the MAV, requires hundreds of launches. A MAV carrying a crew of 4 would require 24MT of oxygen to reach Mars orbit while a crew of 6 would require 36MT\[1\]. Even though the cost of launching to space has been reduced drastically since NASA started using private companies for launching, the cost is still vast to not explore alternatives\[13\]. Producing basic essentials by In Situ Resource Utilization (ISRU) could save many trips and reduce the cost of Mars exploration massively. The oxidizer in a $C H_4$ and $O_2$ propellant system takes up to 78\% of the total propellant mass\[1\], therefore the production of $O_2$ on Mars could save the cost of transporting up to 19MT of $O_2$ for a 4-crew mission. There are multiple suggested methods to produce $O_2$ on Mars. One possibility is to extract water from ice on Mars and convert this into rocket propellant, yet this would need prospecting, mining and refining. A more practical first step is to produce oxygen directly from the $C O_2$ rich Martian atmosphere\[1\]. The dominant mission suggestion to carry humans to Mars would consist of a two step plan with a 26 months interval. The first step would establish infrastructure, this could include an ISRU plant along with the MAV, the power system and the Mars habitat\[12\]. Producing the propellant over a 14 month period would give sufficient time to fill the MAV tanks before commencing step 2: the launch of the human crew. The amount of propellant and time to produce would determine the ISRU plant size and production rate. To investigate the possibilities and validate its feasibility the Mars OXygen ISRU Experiment (MOXIE) has been developed.

The primary goals of the MOXIE project are "to verify and validate the technology of Mars ISRU as a springboard for the future, and to establish achievable performance requirements and design approaches that will lead to a full-scale ISRU system based on MOXIE technology"\[12\]. To do this three requirements must be fulfilled by MOXIE. MOXIE must produce at least 6g/h of $O_2$ with the mass, volume and power allocated to this purpose, MOXIE must produce $O_2$ with > 98\% purity and it must meet the two prior requirements for at least 10 operational cycles\[12\].

Some design compromise had to be made because MOXIE was fitted inside the Perseverance rover. MOXIE is expected to run at least 10 times in the primary mission in one Martian year (687 Earth days), this necessitates that MOXIE is capable of thermal cycling to its 800\degree C operating temperature at least 10 times in addition to several test cycles on Earth during testing. A full scale ISRU plant is expected to run continually, thermal cycling is thus not expected to the same extent. The operating time of MOXIE is expected to be a few tens of hours while a ISRU plant is expected to run for >10000 hours, any method whose life time intrinsically is lower than the necessary operating period was discouraged. The mass, volume and power constraints cause a significant challenge. Key aspects of MOXIE include mechanical acquisition of Martian air with a scroll compressor, conversion of $C O_2$ to $O_2$ using Solid Oxide Electrolysis Cells (SOEC), a power supply delivering up to 4A and several sensors for control and telemetry. The key parameters to assess are: flow rate, oxygen production rate, oxygen purity and voltage–current relationship of the SOEC\[14\]. A box diagram illustrating
the basic elements of MOXIE is shown in figure 1. A more optimal prototype would not have been mounted inside the rover, in order to make it substantially larger with a more capable power source[12].

Figure 1: Box diagram illustrating MOXIE elements, inspired by [14]. CO$_2$ is acquired from a scroll compressor, when the gas is compressed it is sent to the SOEC which splits it to CO and O$^{2-}$, the CO is vented out with the excess CO$_2$, the oxygen ions, pass through the SOEC and forms O$_2$ from where it is measured and then exhausted back to the martian atmosphere.

This thesis seeks to understand the issues MOXIE face and investigate possible solutions. In parallel with the thesis work I was trained as ‘payload downlink lead’ (PDL) for MOXIE with responsibility to fetch data and report any anomalies to mission lead. In total I have done 200 hours of PDL. On April 20th 2021, the 60th sol (Martian day) after Perseverance had landed on Mars, I had the honour of fetching the data for MOXIE’s first oxygen run, which was the first demonstration of ISRU on another planet and the first major step toward a sustainable human presence in space[15].

The extreme conditions which space inherently offers, gives opportunity to address issues on Earth too. SOC technology is not only advantageous for space exploration, but also for terrestrial needs. With the recent IPCC report of 2021 there is no doubt that human influence has warmed the atmosphere, ocean and land[16]. Energy production is by far the largest part of global greenhouse gas emission with more than 70%. This is showcased in Figure 2[17]. In 2016 the total energy supply of the world was 13761 million tons of oil equivalent which corresponds to 18.3 terrawatt years (TWy), additionally the global energy demand is only expected to grow[17, 18].

The top priority in energy research and development is therefore investigating environmentally friendly alternatives to fossil fuels, this can be renewable energy sources such as wind and solar energy. However, these particular technologies are often criticized for not providing the necessary supply reliability,
which generates a need to store large amounts of energy for times where less energy is being produced\cite{19}. A promising method for this is to convert surplus electricity into accessible chemical energy such as hydrogen or ammonia, the energy is then easily stored and transported, comparable to petrol. The process is shown in Figure 3. In countries like Denmark and Germany, where a large percentage of the energy production comes from wind and solar sources, there is a need for cheap energy storage to make up for the fluctuating energy production\cite{20}. Solid Oxide electrolysis and fuel cell (SOC) technology is a promising solution to this issue. SOC technology offers energy conversion between electrical and chemical energy at high efficiency\cite{21}. 

Figure 2: **Global greenhouse gas emissions by sector.** The largest slice is by far is from the energy sector with 73.2% of all greenhouse gasses emitted. The transport sector is behind about 1/6 of the total energy consumption. 

*Figure created by 'OurWorldInData.org'*
Figure 3: Storage of excess green off-peak electricity. By using excess green off-peak electricity to produce hydrogen or synfuels through electrolysis, the output can be stored or transported to be converted back to electricity when and where needed.

SOC technology supports electric vehicles, but can also be used for cars powered directly by SOFC technology. Toyota is producing $H_2$ powered SOFC cars as Japan works towards a hydrogen powered society[22]. Larger SOC systems can also be used at remote locations outside of established powergrids to power remote settlements or produce syngas for synfuels at remote power plants such as offshore wind farms, the latter is a core part in achieving emission reductions before 2030 in Denmark[23]. The production of energy neutral synfuels is a promising approach for the green transition, synfuels can be used in existing internal combustion engines that the large majority of all transport vehicles are using today. Additionally SOC technology can synergize with carbon capture, since one of the main challenges is developing sinks in which the $CO_2$ can be stored. SOEC can use the captured $CO_2$ for syngas production[24].
SOC technology has reached commercialization, but there is still areas that can be optimized. Key challenges include lowering the cost of materials, production and operation and increasing the life-time[25]. SOCs require high operation temperatures for the electrochemical reactions and molecular movement to occur, typically in the range of 700-1000°C. Lowering this temperature would reduce the operational costs and increase the longevity[26]. Life extension of SOCs can also be achieved by removing sources of degradation and ensuring mechanical stability.
2 Theory

2.1 Solid Oxide Cells

The basic principle of SOC technology is simple, but materials, atmospheric content and temperature offer great variability that can be tailored for specific needs.

The fundamental elements of SOCs are a dense ion-conducting electrolyte sandwiched in between a porous anode and cathode. The process of SOCs depends on whether they are used as SOEC or SOFC\cite{12, 21, 27}.

Fuel mode

For SOFC mode, a fuel is applied to the anode, and an oxidant is applied to the cathode. A current is made to flow through the electrical load that needs electricity and continues into the cathode filled with oxygen. Every two electrons generate an oxygen ion (\(O^{2-}\)) which can then travel through the electrolyte. As it arrives at the anode it will react with the fuel and release the two electrons which again flows to the electrical load, thus closing the circuit\cite{21}. The process is shown in Figure 4.

![Solid Oxide Fuel Cell using \(H_2\). Oxygen is ionized at the cathode and pass through the electrolyte, as the ions reach the anode they will react with the \(H_2\) and reduce to \(H_2O\), the leftover electrons can pass back through an electrical load and back to the cathode, thus a constant current can be maintained.](image)

The most common fuel used for SOFC is \(H_2\)\cite{28}, the reaction at the cathode is

\[
O_2 + 4e^- \rightarrow 2O^{2-} \tag{1}
\]
As the negative oxygen ions arrive at the anode a second reaction happens:

\[ 2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^- \]  

(2)

The \( H_2O \) will be released and the electrons will flow through the electrical load and back to the cathode.

**Electrolysis mode**

Electrolysis mode uses the same basic components but in a different manner. Electrolysis is used to manufacture molecular products utilizing electricity, it is the reverse operation compared to fuel mode. A heated gas is applied to the cathode side, which is split to form oxygen ions, the ions will move through the electrolyte. The outcome will be the molecular constituents separated. A common gas to separate is steam in order to produce clean \( H_2 \) and \( O_2 \)[29].

**Steam Electrolysis**

Regular steam electrolysis splits gaseous \( H_2O \) to \( H_2 \) and \( O_2 \)[29], the net reaction is:

\[ 2H_2O \rightarrow 2H_2 + O_2 \]  

(3)

This is done by applying steam to a high temperature porous cathode, inside the cathode the steam will react at the active sites:

\[ 2H_2O + 4e^- \rightarrow 2H_2 + 2O^{2-} \]  

(4)

The charged oxygen ions are pushed through the ion-conducting electrolyte by an applied voltage. As the ions reach the anode they will oxidize to form \( O_2 \) and release excess electrons as expressed here:

\[ 2O^{2-} \rightarrow O_2 + 4e^- \]  

(5)

This process is illustrated in Figure 5.
Figure 5: **Steam electrolysis applied for production of hydrogen.** Steam is fed to the cathode side where the \( H_2O \) molecules will split at activation sites. The charged oxygen ions are pushed through the ion-conducting electrolyte, on the anode site this will form \( O_2 \) and release the excess electrons.

**MOXIE Electrolysis**

MOXIE produces \( O_2 \) by high temperature dry \( CO_2 \) electrolysis, the net chemical reaction is:

\[
2CO_2 \rightarrow 2CO + O_2 \tag{6}
\]

This is similar to the reaction for steam electrolysis as shown in eq. 3. The reaction happens in two parts. The reaction take place inside the SOEC of MOXIE, where a gas of \( CO_2 \) is applied to the cathode side, see Figure 6. Inside the porous cathode structure, activation sites will catalyze the first reaction:\[30\]:

\[
2CO_2 + 4e^- \rightarrow 2CO + 2O^{2-} \tag{7}
\]

An applied potential pushes the negatively charged \( O_2^{2-} \) through the ion-conducting electrolyte. The second reaction happens as the \( O_2^{2-} \) arrives to the anode, here it will oxidize to form \( O_2 \) in the same manner as steam electrolysis as shown in eq. 5.
Figure 6: **MOXIE dry electrolysis**: CO₂ as applied to the cathode side, inside the cathode the CO₂ is split to CO and O²⁻, the O²⁻ is pushed through the ion conducting electrolyte while the CO is pushed out along with excess CO₂. The oxygen ions form O₂ by oxidization.

Another more common method is H₂O / CO₂ co-electrolysis for the production of syngas. Here both CO₂ and H₂O are applied to the cathode, the two prior electrolysis reactions, as shown in eq. 4 and 7, happen simultaneously. Additionally, the reverse water gas shift chemical reaction occurs:

\[
CO₂ + H₂ \leftrightarrow CO + H₂O
\]  

This reaction increases the performance of CO₂ electrolysis substantially, while still maintaining a similar performance for H₂O electrolysis. The oxygen ions travel through the electrolyte, while H₂ and CO remain at the cathode side and can be gathered. The syngas of mixed H₂ and CO can be used to produce synthetic fuel. The addition of steam is highly beneficial for pure CO₂ electrolysis, but was not added for MOXIE as it could interfere with measurements of the other instruments on the Perseverance rover.

**Nernst potential**

The electrolysis reaction is favorable when the voltage is above the Nernst potential \(V_N\). For MOXIE the potential is:

\[
V_N(O₂) = V_{rev} + \frac{RT}{4F} \ln \left( \frac{p_{CO²}p_{O₂}}{p_{CO₂}²} \right)
\]  

10
where $R$ is ideal gas constant, $T$ is temperature and $F$ is Faraday’s constant. $p_{CO}$ and $p_{CO_2}$ are the partial pressures for the respective gasses at the cathode side of the cell, $p_{O_2}$ is partial pressure of oxygen on the anode side. $V_{rev}$ is the voltage which the reaction can happen in the reverse direction[31].

For safe operation the SOEC voltage is constrained to stay below the threshold for carbon production via the Boudouard reaction:

$$2CO \rightarrow 2C + O_2$$

(10)

The Nernst potential for this reaction is given by:

$$V_N(C) = V_{rev} + \frac{RT}{4F} \ln \left( \frac{p_{O_2}}{p_{CO_2}} \right)$$

(11)

These limits create a window in which the $O_2$ production occurs without carbon production. The voltage window as a function of CO mole fraction was modelled by Hecht et al.[12] as shown in Figure 7. When the CO mole fraction is small, the safe operation window is large, but decreases as CO mole fraction increases.

Figure 7: Safe Voltage Zone by Hecht et al.[12]. Nernst potential of CO and and $CO_2$ is plotted against CO mole fraction at atmospheric pressure at the MOXIE testing facility, the model assumes anode and cathode is at the same pressure. The safe operation voltage windows decreases if either temperature decreases or if the CO mole fraction increases.
The reason why carbon production at the cathode of MOXIE is highly unwanted is because it causes degradation. The electrocatalyst used on MOXIE is Ni, which is a commonly used electrocatalyst, due to its excellent electrocatalytic effect that greatly improves the overall performance of the cell. Yet, Ni is also a very capable carbon deposition catalyst. Carbon deposition is highly unwanted because it covers the electrochemically active sites which in time will lead to lower electrolysis yield and in long term the total failure of the cell\cite{32, 33}.

### 2.2 Electrode Materials

#### State-of-the-art electrode material

The state of the art electrode has long been Ni and Yttria Stabilized Zirconia (YSZ) cermet, written as Ni:YSZ, this is used for its excellent electrocatalytic activity combined with high ionic conductance. For Ni-YSZ the electrochemical reaction happens at the three-phase-boundaries (3PB), at which ion conducting YSZ, electronic conducting Ni and gas reactants are in simultaneous contact\cite{25}.

The Ni-YSZ provide high reaction rates for $\text{H}_2\text{O}/\text{CO}_2$ reduction and $\text{H}_2/\text{CO}$ oxidation reactions but can be a considerable cause of long-term degradation if acceptable conditions are not met notably the Nernst potential as described in the previous section\cite{34}.

The Ni-based electron conducting backbones can be destroyed by Ni/NiO redox reaction if the right conditions are not met, this could happen during a system shutdown or an interruption of fuel supply. This leads to permanent performance degradation\cite{35}, therefore other cell types have been thoroughly investigated for the past decades, some examples are Mixed ionic and electronic conductor (MIEC) cells, metal supported cells (MSC) and perovskite type cells, in particular La-doped SrTiO$_3$ (LST) \cite{29, 36–38}.

Mogensen et al.\cite{39} listed requirements for a material to be efficient as both an electrode and current collector: First the ionic conductivity should be at least $\sigma_i \geq 0.1 \text{ S/cm}$ and the electronic conductivity $\sigma_e \geq 100 \text{ S/cm}$ at operating conditions. The material must have mechanical (dimensional) and thermodynamic stability over a wide range of temperatures and oxygen partial pressures. The materials coefficient of thermal expansion (CTE) must match that of the electrolyte. The materials must have chemical compatibility with the electrolyte both during operation and fabrication. Additionally, the material should have high electrocatalytic activity for oxygen reduction at the cathode or fuel oxidation at the anode.

A material can be infiltrated with nanoparticles to achieve a desired effect. A MIEC material can be doped with Ni to increase the electrocatalytic ability, while a Ni:YSZ cell can be doped with an MIEC such as Gd doped-Ceria (CGO) to increase the active area of the cell. Applying both Ni and an MIEC nanoparticles to any electron conducting material can make into a high performing electrode\cite{38, 40}.

In this work the effect of infiltrating both Ni and CGO on three cells of different materials will be investigated. The first cell is an anode supported cell
made of the MIEC CGO, the second is also an anode supported cell made of the electron conducting perovskite $La_{0.4}Sr_{0.4}Fe_{0.03}Ni_{0.03}Ti_{0.94}O_3$ (LSFNT). The last cell is LSFNT on a metal support. The metal support provides excellent stability and high electron conductance.

**MIEC**

MIEC cells have for a long time been seen as a promising material for SOCs [39] since there are various upsides using an electrode of composite electron/ion conducting material. Ceria is known to have pronounced catalytic properties, good ion-conduction through doping, and desirable stability at 500-700°C[39]. The MIEC nature of ceria under reducing conditions extends the reaction zone from a 3PB to a two-phase boundary (2PB) since the gas now can react at any point of the electrode[26]. The improved ion conductance compared to Ni-YSZ results in more active reaction sites that help extend the utilization length of the electrode[25].

Pure ceria based material will expand and contract during reduction and oxidation, respectively, this will lead to cracking at the electrode/electrolyte interface which ultimately results in detachment[41]. Various doped-ceria has therefore been investigated through the years. The most promising of which is Gd doped-ceria (CGO) which has shown superior performance and stability compared to pure ceria[26, 39, 42].

Ceria has also been favored for electrolysis involving carbon, as it has shown excellent carbon-deposition suppression properties, additionally CGO has shown to increase sulphur tolerance which is a common trace gas in industrial operation[26, 43]. Gd doped-ceria infiltrated with metal nanoparticles such as Ni and Cu has shown superior electrochemical performance to that of Ni-YSZ [25, 44].

**Anode supported perovskite cells**

Modified ceramic perovskite materials have been investigated because of its inherent stability and high theoretical electronic conductivity ($> 100Scm^{-1}$) in both SOFC and SOEC conditions[45].

Perovskite based oxide ($ABO_3$) is a typical complex oxide catalyst which is known to have several desired properties such as excellent thermal and mechanical stability, physical compatibility with typical electrolyte material, flexibility and low production costs[46]. Among these, SrTiO$_3$ has been getting a lot of attention due to fine electronic conductivity, tolerance to impurities and mechanical stability during redox conditions[47]. A-site doped SrTiO$_3$ materials have shown high electronic conductivity ($> 100Scm^{-1}$ at 850°C), A-site doped SrTiO$_3$ such as (La,Sr)TiO$_3$ have been studied extensively [38, 47, 48]. Doping both A and B-site can assist in tailoring for optimal performance. Sudireddy & Agersted found small amounts of A-site doping in already Nb-doped SrTiO$_3$ increased electronic conductivity with nearly 100%[48]. Furthermore, Nielsen et al.[38] produced $La_{0.4}Sr_{0.4}Fe_{0.03}Ni_{0.03}Ti_{0.94}O_3$, here La is doped on the A-site.
of Sr, both Fe and Ni are doped to B-sites of Ti. This electrode was infiltrated by $Ce_{0.8}Gd_{0.2}$ (CGO20), here they found the performance to be among the best for redox stable and corrosion resistant electrodes.

**Metal supported cells**

Lowering the operation temperature (500-800°C) of SOCs offers improved stability, increased material durability and robustness and a wider choice of component materials can be used, including metals\[49\]. Placing the cell on a metal support offers higher thermal conductivity which can both improve thermal shock resistance and internal thermal gradient stability, this means that MSCs are more tolerant to rapid thermal cycling compared to ceramics and cermet\[27, 50\]. Additionally, the cost of metal will typically be lower compared to the traditional use of ceramics and cermet. MSCs allow for excellent redox tolerance as the metal support should constrain volume expansion and offer increased resistance against mechanical stress making it optimal for mobile usages\[29, 38, 51\]. Functional cells have been produced in a trilayer by co-sintering a Ni-support/Ni-YSZ anode/YSZ electrolyte, with a reasonable power density of 470mW cm$^{-2}$, but with significant coarsening which is a major cause of degradation.\[52\] Adding Fe to the support reduces the cost, and the CTE of Ni-Fe is a better match to YSZ, however the susceptibility to coking, sulfur poisoning and redox intolerance is still a major issue for the longevity of these cells due to the Ni \[35\]. Stainless steel alloy can be tailored to have a CTE matching the electrolytes while achieving excellent corrosion resistance \[37\].

The state-of-the-art cermet electrodes Ni-YSZ on metal supports pose serious challenges during processing, the culprit has been found to be the high sintering temperature of 1200°C that causes corrosion in oxidizing atmosphere\[49\]. This can be eluded through alternative fabricating methods such as atmospheric plasma spray and pulsed laser deposition\[53, 54\]. Another common method is to use perovskite type electrode and tailor properties through doping and infiltration\[38, 48\]. Nielsen et al. \[38\] produced metal supported LSFNT infiltrated with Ni and CGO nanoparticles that had good performance, were redox stable, corrosion resistant, had good processing properties and sufficient electronic conductivity\[38\].

**MOXIE Electrode Material and optimization possibilities**

Since the issue with Ni in carbon-rich atmosphere was well known when MOXIE was developed, alternative Ni-free electrodes were researched. A possible candidate was Pt-YSZ, but the electrolysis performance was deemed to low \[4, 12, 31\]. As MOXIE had strict volume and mass constraints, a high performance was needed to meet the oxygen production requirements of 6g/hr. This lead to Ni:Ceria being chosen as the cathode, ceria being an MIEC has great electronic and ionic conduction, while the Ni acts as electrocatalyst\[31\].
In this thesis I will investigate the possibility to make improved electrodes through infiltration of Ni and CGO, sequentially. Since smaller particles result in larger surface-to-volume ratio, the smaller size should increase electrocatalytic effect of Ni\[^{55}\]. It has been suggested that pH can alter the size of metal particles\[^{56}\]. To evaluate the effect of pH on particle size, Ni solutions were made at pH of 2, 7 and 12. The Ni solutions were sequentially infiltrated together with neutral solutions of CGO. Additionally, complementary solutions was made using ethanol (EtOH) as solvent. EtOH has a higher viscosity than water and should therefore spread out the infiltrate more easily. The performance will be investigated with Electrochemical Impedance Spectroscopy (EIS), and morphological characterization will be done with Scanning Electron Microscopy (SEM).

2.3 Gas flow inside Mars oxygen ISRU experiment

The atmospheric pressure of the Perseverance landings site, the Jezero crater, varies from 6 mbar during Martian summer to 8 mbar during winter. The crater is at higher elevation than any likely human landing site, thus CO\(_2\) acquisition here should be more difficult in the crater. Thus reliable acquisition here implies the same for possible landing sites where an ISRU plant could be needed\[^{12}\]. Mars’ atmosphere contains about 95.5\% CO\(_2\), 2.8\% N\(_2\), 2\% Ar\[^{57}\]. MOXIE acquires CO\(_2\) from the Martian atmosphere through a high efficiency particulate air (HEPA) filter using a scroll pump. Figure 8 shows the gas flow through the MOXIE system. The pump compresses the intake gas from about 6 mbar to 1000 mbar. On the other side of the pump is a small plenum for the gas to stabilize and help shelter the SOEC from pressure spikes as a result of the rotating pump. The gas is injected through a flowmeter into the SOEC on the cathode side of all the cells, here it is split to CO and O\(_2\). The CO is guided to an exhaust vent with excess CO\(_2\). A sensor, ‘P4’ measures the pressure at the CO and CO\(_2\) exhaust before it is released back into the atmosphere. The Ar and N\(_2\) from the atmosphere will also pass to the exhaust with the CO and CO\(_2\) and will not react with the cathode.

The pure oxygen that has passed to the anode side is collected in a separate outlet stream. Before the O\(_2\) is released, composition sensors characterize the outlet, these verify mass flow of oxygen, and the purity of oxygen is found by measuring O\(_2\) and CO\(_2\) partial pressures. There is no CO-sensor since it would oxidize instantly in the oxygen stream. Before the SOEC product is released the pressure is measured by the pressure sensor ‘P5’. The ratio between compressor speed and SOEC current is critical to produce maximum amount of oxygen while avoiding carbon formation.
Figure 8: Gas flow through full MOXIE system: Martian atmospheric gas enters through a HEPA filter to the compressor inlet, where it is pressurized to 500-1000mbar. A small plenum stabilizes the air before it proceeds into the SOEC, the CO$_2$ is split into CO and O$_2$ at the cathode, the CO and unreacted gas will continue out the SOEC, the pressure sensor ‘P4’ will measure it before it is released. The O$_2$ that is produced at the anode side will leave the SOEC independently, where a O$_2$ and a CO$_2$ sensor will measure the composition of the SOEC product, the pressure sensor ‘P5’ will measure the gas before it is released.

On sol 15, a cold compressor sweep was instigated during an instrument health check. A compressor sweep involves turning on the compressor at varying speeds while the SOEC is off at room temperature (RT). When the SOEC is off, the pressure at the O$_2$ exhaust (P5) should be at Mars ambient (0.01bar). The pressure at the excess gas vent (P4) should be the only sensor that measures a change as compressor RPM is change.
Figure 9: **Crossover flow detected during a health check on sol 15.** The red line is the measured pressure at anode exhaust (P5), the yellow line represents the measured pressure at the cathode exhaust (P4). The purple line represents the dynamic model, this shows the expected pressure of P5. The blue is the sum of measured P4 and P5.

Figure 9 shows that P4 increases in steps defined by the compressor speed, since the SOEC is not on, all the inlet gas is expected to pass through the cathode exhaust. The dynamic model of P4 shows that the expected pressure at P4 is supposed to be greater than measured. P5 is seen to increase slightly in similar manner to P4, and by adding P4 and P5 a similar pressure is reached. The combined P4 and P5 is in fact very similar to the expected outcome from the dynamic model. A crossover flow between the cathode side and anode side is suspected. This is not uncommon for a system with numerous seals and joints in a system that swings between RT and 800°C, and was observed in both the Flight model (on Mars) and the engineering model (on Earth).

In this thesis the crossover flow was investigated in order to provide information on how to keep purity at above the recommended level of 99.6% while having a maximum O2 production outcome.

### 2.4 Theory of analysis methods

**Electrochemical impedance spectroscopy**

The electrical resistance of Ohm’s law is the ability of a circuit element to resist the flow of an electrical current, the resistance of Ohm’s law can only be applied to an ideal resistor, which must have the some inhibiting properties: 1. The resistor must follow Ohm’s law at all current and voltage levels, 2. The Resistance must be independent of frequency, and 3. For AC circuits, the current and voltage signals must be in phase[58]. In real world appliance, circuit elements most often exhibit much more complex behavior, therefore the concept of impedance is introduced. Much like resistance, impedance is the measure of an element’s ability to impede the flow of current, but without the simplifying
properties. By applying a sinusoidal voltage signal \( V(t) = V_0 \cdot \sin(\omega t) \) to excite an AC current response: \( I(t) = I_0 \cdot \sin(\omega t + \phi) \) the impedance can be measured using the radial frequency \( \omega \) and phase shift \( \phi \)[59].

\[
Z = \frac{V(t)}{I(t)} = \frac{V_0 \cdot \sin(\omega t)}{I_0 \cdot \sin(\omega t + \phi)} = Z_0 \cdot \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \tag{12}
\]

The impedance can be expressed as magnitude \( Z_0 \) and a phase shift from the time dependent potential and current: The potential is given as:

\[
V(t) = V_0 \cdot e^{i\omega t} \tag{13}
\]

and the current:

\[
I(t) = I_0 \cdot e^{i(\omega t - \phi)} \tag{14}
\]

Using Euler’s formula, impedance can be represented by a complex function:

\[
Z = \frac{V(t)}{I(t)} = Z_0 e^{i\phi} = Z_0 (\cos \phi + i \sin \phi) \tag{15}
\]

Which can be split to a real (\( Z_{\text{real}} \)) and an imaginary part (\( Z_{\text{Im}} \)).

Plotting \( Z_{\text{real}} \) against \( Z_{\text{Im}} \) at all measured voltage frequencies results in a Nyquist plot, this can be can be seen in Figure 10a, due to the nature of the plot it is not possible to see what frequencies corresponds to which point, this however can be seen on the Bode plot associated with the Nyquist plot, as shown in Figure 10b. Generally a cell of good performance will have a low impedance both on the real and imaginary axis.

![EIS example spectrum for a symmetrical cell, plot on the left is a Nyquist plot which is the real impedance (\( Z_{\text{real}} \)) plotted against the negative imaginary impedance (\(-Z_{\text{Im}}\)). On the right is a Bode plot, here the log of voltage frequency is plotted also against the negative imaginary impedance. Both resistances have been multiplied by the area of the cell and divided by 2. On the Nyquist the characteristic resistances are noted, Polarization resistance \( R_p \) is found by the length of the curves, series resistance \( R_s \) is the length from zero to the first point of the curve, area specific resistance (ASR) is the total sum of \( R_s \) and \( R_p \). Arcs denote electrochemical processes. On the Nyquist plot the frequency of which these processes occur can be seen.](image)
On the $Z_{\text{real}}$ axis the range from 0 up until the start of the curve is series resistance, also called ohmic resistance, this resistance is generally due to the electrolyte and the electrolyte-electrode interface.

The area under the curve is the interesting part for this study as this is the impedance due to the electrode. This means the smaller the integral, the better the anode performance. The real part of this integral is the polarization resistance $R_p$. Specific electrochemical and transport processes of the cells are activated at different frequencies, some processes will behave differently in changing atmospheres or at various temperatures. The variation of these are used to identify the nature of the specific of the process. The processes are also dependant on electrode material and structure.

**Scanning electron microscopy**

Scanning electron microscopy (SEM) is a powerful tool for obtaining surface information on surface topography, chemical composition and crystalline structure of the top microns of a specimen [60]. By using electrons instead of light, the SEM achieves extremely high resolution, allowing magnification up to 1,000,000x compared to an optical microscope which can magnify around 1000x[60]. Furthermore, several different signals are produced when electrons interact with the specimen, which can be used in various investigations[61].

The resolution of visible-light microscopy is traditionally given by the classic Rayleigh criterion, as the smallest distance that can be resolved[61, 62]

$$\delta = \frac{0.61 \lambda}{\mu \sin(\beta)} \quad (16)$$

As it can be seen from equation 16, that the resolution is directly dependent on the wavelength of the radiation, $\lambda$, and inversely dependent on the refractive index, $\mu$, and the collection semi-angle, $\beta$[62]. Optical microscopy is thereby limited by the wavelength of light (400nm-700nm). However, the wavelength of electrons is given by the de Broglie equation: $\lambda = \frac{h}{mv}$, which further depends on the velocity of the accelerated electrons, $v = \sqrt{\frac{2eV}{m}}$, resulting in

$$\lambda = \frac{h}{\sqrt{2meV}} \quad (17)$$

If the acceleration voltage is assumed to be 10 keV, the theoretical resolution is 0.12 Å using the classic Rayleigh criterion. Yet, this resolution is not realistic for electron microscopes due to aberrations and defects in the lenses[62], resulting in a practical resolution around 1 nm[60].

The SEMs used in this work have a lanthanum hexaboride ($\text{LaB}_6$) electron gun and a field emission gun (FEG), respectively. The $\text{LaB}_6$ gun is a thermionic source meaning that electrons are emitted when the source is heated[62]. The FEG is a sharp tip of tungsten emitting electrons if a large electric potential is applied across it and an anode. This source has a smaller probe size, due to the
tip having a radius of \(< 0.1 \, \mu m\), which often results in more monochromatic electrons\cite{62}. Furthermore, comparing the two mentioned electron sources, the FEG would in general provide a higher brightness, higher resolution and longer life time than the \(LaB_6\) source\cite{62}. High vacuum \(10^{-6} \, \text{torr}\) is typically present to protect and avoid contamination of the \(LaB_6\) filament\cite{60} and to limit the electrons from colliding with gas molecules. However, the use of a FEG requires ultra high vacuum (\(10^{-11} \, \text{torr}\)), due to the need of the source surface to be pristine\cite{62}. The electrons from the source are accelerated through a column where they are affected by different electromagnetic lenses\cite{62}. The lenses consist of copper coils producing magnetic fields as current is lead through. The force acting on the electrons is given by the Lorentz’ force and the strength of the lens depends on the current\cite{62}. Two types of lens systems are normally found in SEMs being condenser and objective lens. The condenser lens system converge the electron beam focusing the beam onto the specimen thereby controlling the spot size of the probe\cite{60}. The objective lens focuses the probe onto the specimen\cite{62}. The de-magnified electron probe is scanned across the specimen in discrete locations in the selected area by scanning coils\cite{60}. The electrons penetrate the surface of the specimen in a tear drop shaped volume\cite{61}. Here different signals are generated, the three used in this work being secondary electrons, backscattered electrons and x-rays\cite{60}. These signals are collected by different detectors above the specimen stage. The secondary electrons (SE) are electrons that are knocked out of their orbit by an incoming electron. These electrons carry high resolution topographical information of the surface of the sample, as only the electrons in orbit close to the surface can escape\cite{60}. 

20
Backscattered electrons (BSE) are electrons from the incident beam being scattered elastically on atomic nuclei[61]. These electrons have high energy meaning that they are not absorbed by the sample to the same extent as secondary electrons, lowering the lateral resolution[61]. However, the backscattered electrons possess compositional and topographical information[61]. The compositional information is a Z-dependence, as the electrons interact with the nuclei of the atoms in the specimen. The FE-SEM used a novel approach to filter out the topographical information from the SE to focus purely on compositional data[63], this means both clear high contrast topography and pure compositional data can be obtained simultaneously and mixed if needed, see Figure 11. Additionally, X-rays are generated as the electrons interact with the specimen volume[64]. The incident electron eject an electron from a core shell in an atom in the specimen, leaving the atom in an excited state. The atom will then relax into a lower energy state by having an electron from an outer shell fill the empty
position in the core shell.\textsuperscript{61} This relaxation emits a characteristic X-ray, which can be used for energy dispersive X-ray analysis (EDS)\textsuperscript{64}. These carry chemical information of high sensitivity and high spatial resolution\textsuperscript{64}.

For SOFC electrode studies, SEM is often used to get a view of microstructure and infiltrate deposition\textsuperscript{38, 48, 65}. The performance of the cell is dependant on the surface-to-volume ratio of the infiltrated particles, since smaller particles intrinsically have higher surface to volume area, this will be the focus of the SEM investigation. The size and size distribution will be measured using ImageJ software \textsuperscript{66}. The particles measured will be from selected areas that are deemed representative for the sample. Energy-selective backscattered electron detector can help differentiate the different infiltrate particles by filtering out undesirable topography signal\textsuperscript{67}.
3 Experimental

3.1 Sample electrode preparation

Samples

For the investigation, three samples were obtained, they were all produced as part of earlier projects at the Technical University of Denmark (DTU). Of the three samples, two are half-cells and one is symmetrical, a half-cell is an electrode and an electrolyte. A symmetrical cell is two electrodes of the same material sandwiching an electrolyte. One of the half-cells is an MIEC anode supported cell, the anode is CGO and the electrolyte is YSZ. The other half-cell is a metal supported cell, here the anode is LSFNT, the electrolyte is also YSZ. The symmetrical cell is an anode supported cell with LSFNT as both anode and cathode, the electrolyte is YSZ. To use EIS on a cell there must be both an anode and a cathode, that means the CGO sample and the metal supported sample need a reference cathode in order to test anode performance, the reference cathode and the impedance resulting from this must be known and subtracted to obtain the performance characteristics of the anode alone. For symmetrical samples, both electrodes can be infiltrated simultaneously and then afterwards tested with EIS, this is an advantage when testing electrode performance because the impedance due to the anode is equal to that of the cathode, and is thus very easy to subtract, which is simply done by halving the resulting impedance. The CGO samples were fractured by hand into semi-square pieces into \(1\text{cm}^2\), the MSCs had to be cut with a precision diamond saw, these were cut to 0.8cm x 0.8cm pieces. For the symmetrical cells, the electrolyte was laser-cut and the LSFNT electrode were spray-coated on afterward to form 0.6cm x 0.6cm electrode area.

Preparation of infiltrate solutions

In this work, the influence of pH value of infiltrate solutions is investigated, additionally the effect of using EtOH as solvent compared to water is also investigated. In order to wet-infiltrate sequentially the Ni-solution and CGO-solution were made separately, and in total seven solutions were made, these are shown in Table 1. The two CGO solutions were made using water and EtOH as solvent. The Ni-solutions were made at different pH-values, for the acidic solution, nitric acid was used to get a pH value of 2. For the alkaline solution, ammonia was used to get a pH value of 12. Since the pH scale is only defined in water, a workaround was needed for the EtOH based solutions. EtOH based solution with pH 2 were not produced since EtOH and nitric acid is potentially explosive. In all solutions, 5wt% P123 was added as surfactant.

CGO solutions

For these experiments CGO20 was produced, here the 20 indicates a 20% Gd to Ce ratio, which is written as: Ce\(_{0.8}\)Gd\(_{0.2}\)O\(_{1.9}\). To produce this, Ce(III) nitrate
Table 1: The produced solutions made for this work. The acidic solution in EtOH was not made since nitric acid with EtOH is potentially explosive.

hexahydrate and Gd(III) nitrate hexahydrate were used. To calculate the weight needed to produce a 2M CGO solution in 25mL, I combine the molar mass of the nitrate as shown in equation 18 using the molar mass from Table 2.

\[ M_{\text{Ce\_nitrato}} = M_{\text{Ce}} + (M_N + 3 \cdot M_O) \cdot 3 + 6 \cdot (M_H + 2 \cdot M_O) = 434.217 \text{g/mol} \] (18)

With a fraction of 0.8 in a 2M CGO solution in 25mL, the total grams of Ce nitrate needed is:

\[ M_{\text{Ce}} \cdot \frac{0.8 \cdot 2}{40} = 17.37 \text{g} \] (19)

The same method is used to calculate the for gadolinium nitrate

\[ M_{\text{Gd\_nitrato}} = [M_{\text{Gd}} + (M_N + 3 \cdot M_O) \cdot 3 + 6 \cdot (M_H + 2 \cdot M_O)] \cdot \frac{0.2 \cdot 2}{40} = 4.51 \text{g} \] (20)

Since 25mL is the final volume, the H\(_2\)O from the nitrates must be subtracted, since both nitrates have the same amount of H\(_2\)O, it is simply done by:

\[ V_{\text{add\_H\_2O}} = 25 \text{mL} - M_{\text{H\_2O}} \cdot \frac{2}{40} = 19.59 \text{mL} \] (21)

Table 2: Elements, their corresponding molar mass and fraction for producing wet-infiltration solutions.

To summarize: The aqueous CGO solution of Ce\(_{0.8}\)Gd\(_{0.2}\)O\(_{1.9}\) was made by adding 17.37g Ce nitrate, 4.51g Gd nitrate and 19.59g of H\(_2\)O.

For the 2M CGO solution in EtOH, the lower density of EtOH has to taken into account when measuring by weight. The density of EtOH \(\rho_{\text{EtOH}} = 0.789 \text{g/mL}\).

\[ m_{\text{add\_EtOH}} = V_{\text{add\_H\_2O}} \cdot \rho_{\text{EtOH}} = 15.46 \text{g} \] (22)
Neutral Ni solutions

The 0.15M aqueous Ni solution with pH value of 7 was made using the same method but as a 0.15M in 100mL.

\[
M_{Ni_{\text{nitrate}}}=\left[M_{Ni}+(M_{N}+3\cdot M_{O})\cdot 2+6\cdot (M_{H}+2\cdot M_{O})\right] \cdot \frac{0.15}{10} = 1.29g \tag{23}
\]

Again the H₂O from the nitrate is subtracted:

\[
V_{\text{add}_\text{H}_2\text{O}}=100mL - M_{H_2O} \cdot \frac{0.15}{10} = 99.52mL \tag{24}
\]

Thus to produce aqueous 0.15M 100mL Ni solution 1.29g of Ni nitrate and 99.52mL of water. When using EtOH as solvent, the 99.52mL

\[
m_{\text{add}_\text{EtOH}}=V_{\text{add}_\text{H}_2\text{O}} \cdot \rho_{\text{EtOH}} = 78.52g \tag{25}
\]

The 0.15M Ni in 100mL EtOH is made by adding 78.25g EtOH to 1.29g of Ni nitrate.

Acidic Ni solutions

For the acidic Ni solution (pH=2) fuming nitric acid (HNO₃) was used, this had to be diluted before being used as solvent. These dilution calculation are based on standard pH calculations: Since each molecule of HNO₃ provides 1 H⁺.

\[
pH = -log_{10}(M_{H\text{NO}_3}) = -log_{10}(H^+) = 2 \tag{26}
\]

Solving the equation yield the number of moles needed for a solution with a pH value of 2.

\[
- log_{10}(M_{H\text{NO}_3}) = 2 \Rightarrow M_{H\text{NO}_3} = 0.01M \tag{27}
\]

1mL of \(m_{H\text{NO}_3} = 1.4g\) and \(M_{H\text{NO}_3} = 63g/mol\):

\[
m_{H\text{NO}_3}/M_{H\text{NO}_3} = 0.0222mol \tag{28}
\]

Thus the amount of solvent needed to make a solution with a pH value of 2 with 1mL of \(H\text{NO}_3\) is:

\[
0.0222mol/0.01mol = 2.22L \tag{29}
\]

1mL \(H\text{NO}_3\) must be diluted to 2.22L with water solvent for a pH of 2. The density is 1 g/mL. This was used to make the aqueous Ni solution with the same method as the prior Ni solutions: 1.29g of Ni nitrate and 99.52mL of the \(H\text{NO}_3\) solution to make a 0.15M Ni solution in 100mL with a pH value of 2. The acidic nickel solution in ethanol was not made because nitric acid with ethanol causes an exothermic reaction that is potentially explosive.
Alkaline Ni Solutions

For the aqueous alkaline Ni solution, I first needed to dilute a 28% ammonia water down to achieve a pH value of 12 some calculations are presented.

\[ pH + pOH = 14 \Rightarrow pOH = 2 \] (30)

\[ pOH = 2 = -\log_{10}(\left[OH^-\right]) \Rightarrow \left[OH^-\right] = 0.01 \] (31)

The reaction between NH\(_3\) and H\(_2\)O is:

\[ NH_3 + H_2O \rightarrow NH_4^+ + OH^- \] (32)

This means every one mole of ammonia that ionizes produces 1 mole of ammonium cations and 1 mole of hydroxide anions. The dilution formula is used to find the amount of H\(_2\)O needed to dilute 1g of 28\% NH\(_3\), with \( M_1 = 14.8M \) and \( V_1 = 0.983 \) For 1g of 28\% NH\(_3\) \[ 68 \] and \( M_2 = 2M \).

\[ M_1V_1 = M_2V_2 \Rightarrow \frac{M_1V_1}{M_2} = 6.66mL \] (33)

That means 1g of 28\% NH\(_3\) needs to be diluted with 6.66g of water to have a solution with a pH value of 12, which equals a 3.7\% NH\(_3\). When the solutions were made, the ammonia was diluted with 7g of water resulting in a 3.5\% NH\(_3\) with a pH value of 11.78, molarity: 2.02M and a density of 0.987g/L. For 1.29g of Ni nitrate with 98.2mL of water to produce 100ml of basic 0.15M Ni nitrate solution, keeping in mind the 0.52g of H\(_2\)O from the Ni nitrate. The change in pH should not be significant for the conclusions of the experiments.

For basic Ni in EtOH a 2M ammonia solution in ethanol was used \[ 69 \], since the pH scale cannot be used for non-aqueous solutions the same molarity was used to keep it comparable. The density \( \rho = 0.785g/mL \) means a for 100mL 0.15M Ni nitrate solution the same 1.29g of Ni nitrate and 77.9mL of the ammonia ethanol solution.

Infiltration

The cells were sequentially infiltrated first by CGO and then by Ni. This was done by adding a drop of the infiltrate on the anode side, then it was let sit for 40 seconds, and the leftover infiltrate was gently removed with a lab tissue. The symmetrical cells were flipped and infiltrated on both sides before getting heat treated. The heat treatment was done by inserting the cells in furnace at 350°C for 30 minutes, then taken out and let cool for a couple of minutes. Then next step was to infiltrate with Ni and treat thermally again also at 350°C. Since the solutions were only 0.15M, Ni had to be infiltrated four times for every one time CGO was infiltrated in order to get a 1:10 weight ratio of Ni to CGO. All cells underwent 5 infiltration cycles for a total of 25 calcination run of 30 minutes per cell. When the MSC was heat treated, flakes appeared on the surface, see Figure 12, this was suspected to be due to the infiltration ‘boiling’ rapidly in the cell.
 pushing much of the infiltrate out. This was suspected since only the metallic cells had this issue, and metals has a quite high thermal conductivity. Instead of having a constant temperature of 350°C the oven was cooled to 150°C and then heated back to 350°C, this was done in order heat up the MSC slower and thus suppress the rapid expansion of the infiltrate that is suspected to cause this. With the new thermal profile there were no more issues.

Figure 12: Flakes of infiltrate. Left: MSC, Right: LSFNT, 'flakes' of infiltrate seem to have bubbled up and solidified, therefore a new thermal profile for the thermal treatment.

Since ethanol has a boiling point of 78°C a lower temperature would also be needed to evaporate it from the porous cells. Therefore a new thermal profile was used to heat treat the cells when infiltrated with ethanol solutions. Therefore the oven was started at room temperature (RT) and heated to 100°C for 15 minutes, then let cool and start from RT and heat up to 100°C. Once per cycle the cells were heated from RT to 350°C, i.e after one CGO infiltration and four Ni infiltrations.

In total 15 types of infiltrated cells were produced, these are showcased in Table 3.

<table>
<thead>
<tr>
<th>pH</th>
<th>CGO</th>
<th>LSFNT</th>
<th>MSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>aq.</td>
<td>aq.</td>
<td>aq.</td>
</tr>
<tr>
<td>7</td>
<td>aq. &amp; EtOH</td>
<td>aq. &amp; EtOH</td>
<td>aq. &amp; EtOH</td>
</tr>
<tr>
<td>12</td>
<td>aq. &amp; EtOH</td>
<td>aq. &amp; EtOH</td>
<td>aq. &amp; EtOH</td>
</tr>
</tbody>
</table>
3.2 Electrochemical characterization

CGO and MSC samples

Due to time limitations the CGO and MSC were not fitted with a reference cathode, for this reason, these were not prepared with platinum paste. The symmetrical LSFNT samples were prioritized since they already had a cathode fitted and could be investigated with EIS.

Contact layer application

To prepare for the EIS measurements, platinum paste was applied to the electrodes on both sides of the symmetrical cells to get a better electrical conductivity to the connectors of the rig. After the Pt paste was applied with a brush, the cells were put in an alumina sample holder standing to allow a more even heat treatment, see Figure 13. The furnace was set to 600°C for 5 hours with a ramprate of 120°C.

![Figure 13: LSFNT cells with Pt paste before going in the furnace. The cells arranged such they stand up for the electrodes to get a more even heat treatment.](image)

3.3 Electrochemical impedance spectroscopy

The cells were carefully inserted in the four sample holders and the weights were dropped to hold the cells in place. The rig was inserted in an alumina tube that was fixed in the oven, with a control box protruding, this was all fixed with steel bolts. Gas inlets were fastened with nuts, and wiring were connected to a data
acquisition system. The rig setup is illustrated in Figure 14.

Figure 14: Cross section illustration of the anode testing rig. The illustration was made by T. Ramos et al. for a safety analysis document concerning the anode rig.
A program was developed to run the experiments. First the temperature was set to 650°C and the furnace was flushed with N₂. The gas composition was set to 5% H₂O/H₂ and real and imaginary impedance were measured at voltage of frequencies between 10⁻¹ to 10⁵HZ for each cell. The temperature was then increased to 700°C and measurements were taken again, then again for 750°C and at last back to 650°C. Thereafter, the composition was set to 20% H₂O/H₂ and measurements were made again at the 4 step temperature range, finally the steam content was increased to 50% and the measurements were again taken at 650, 700, 750 and x650 (650 second time), the temperature profile is shown in Figure 15.

Figure 15: Temperature profile from the EIS measurements. The temperatures are off increased by +40°C because the sensors need calibration, thus the actual temperature in the furnace are lower than the plot shows. The program was adjusted accordingly. Measurements were taken at the plateaus of 650°C, 700°C, and 750°C and again back at 650°C. The first steps correspond to 5% H₂O/H₂, the middle steps: 20% H₂O/H₂ and the last steps 50% H₂O/H₂.

3.4 Microstructual characterization

In order to get a fresh surface, the cells were fractured. The two ceramic type cells (CGO and LFSNT) were simply broken by using two sets of tweezers. The MSCs were cut halfway with a diamond saw, then the other half was ripped apart to create a half fresh surface. The ceramic cells were carbon coated to improve the imaging because the conductive layer of carbon inhibits charging and improves the secondary electron signal. To carbon coat, carbon thread was mounted in a vacuum chamber between high-current electrical terminals, after
degassing the thread was heated by applying 7V to create a continuous stream of carbon that coats the sample in a fine layer of few nanometers of carbon. The samples were attached to the samples holders with double sided carbon tape, and placed at a 90° angle, so that the fractured surface pointed straight up, this is seen in figure 16a. A piece of carbon tape connected the fractured surface and the sample holder to lead extra charging away from the surface. The set up can be seen in Figure 16b.

Figure 16: SEM set up. (a) TV image of a CGO sample standing up, using carbon tape, an additional piece of tape connects the fracture surface to the sample holder to diminish charging which distorts electron microscopy. (b) Overview SEM image of an LFSNT backbone showing. On the left, carbon tape is attached to the the rectangular LFSNT backbone.
4 Results - Electrode investigation

In SOC analysis it is customary for Nyquist plots to have equal tick size on the X and Y axis, this makes it easier to compare the results to similar studies. In this work this was not done, because of very large ASRs. Plotting on equal axes would result in very small arcs that are illegible.

4.1 Results - Electrochemical impedance spectroscopy

EIS - Aqueous pH 2

To determine the impedance it is necessary to multiply $Z_{\text{real}}$ and $Z_{\text{Im}}$ with the active electrode area, but this sample fractured as seen in Figure 17. The low resistance at 650°C compared to x650°C in Figure 18 suggests the sample fractured between the measurement of these points. Therefore information extracted from the EIS measurements was limited, however the EIS of this sample can still be evaluated as function of measuring temperature and atmosphere composition. From Figure 18 and Table 4. As the first 650°C measurements can be disregarded, it can be seen the ohmic resistance decreases significantly as temperature rises. Their seem to be one major process that happening near $10^3$Hz. With the composition range in Figure 19 it is clear that the process shifts to higher frequencies as steam content increases.

Figure 17: Broken pH 2 aq. sample, it is believed it broke during mounting, thus the effective area of the cell resistances cannot be determined. The electrode seem to be still 80-90% intact, and there is small bits of electrode scattered around.
Figure 18: **Temperature range for the aq. sample with pH 2.** The measurements were taken at 650°C, 700°C, 750°C and again at 650°C (x650).

Figure 18 shows measurements of the aq. pH 2 sample at various temperatures, on the left the Nyquist plot shows a large decrease in series resistance but the polarization resistance is similar for all the temperatures. The two measurements at 650°C have different series resistance, this suggests something happened with the electrolyte or with electrolyte/electrode interface during the temperature cycle. There seems to only be one peak for both plots, suggesting only one process is occurring. On the right is the bode plot, here the peak can be seen near $10^3$Hz which decreases as temperature increases. The two measurements at 650°C follow the same trends as on the Bode plot. The resistances of the temperature range are showcased in Table 4.

Table 4: **Resistances - Temperature range of aq. pH 2 at 20% steam**

<table>
<thead>
<tr>
<th>pH 2 aq.</th>
<th>650°C</th>
<th>700°C</th>
<th>750°C</th>
<th>x650°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p[\Omega \cdot \text{cm}^2]$</td>
<td>0.124</td>
<td>0.914</td>
<td>0.594</td>
<td>1.067</td>
</tr>
<tr>
<td>$R_s[\Omega \cdot \text{cm}^2]$</td>
<td>4.446</td>
<td>32.103</td>
<td>21.566</td>
<td>41.274</td>
</tr>
<tr>
<td>ASR[\Omega \cdot \text{cm}^2]</td>
<td>4.5702</td>
<td>32.917</td>
<td>22.160</td>
<td>42.341</td>
</tr>
</tbody>
</table>

On the left side of Figure 19, the Nyquist plot shows the 20% steam has the smallest integral while the 50% is only slightly larger. The 5% has a much larger ohmic resistance and largest integral of the three, it has a slightly different shape than the other two. Right: Th bode plot shows a relaxation near 100Hz as steam content increases, and is hard to spot at 20% steam. A second peak rises near $10^3$Hz as steam content increases, while it also shifts slightly to the right. From Table 5, where these resistances are showcased, it can be seen that the far lowest $R_p$ is at 20% steam content.
4 RESULTS - ELECTRODE INVESTIGATION

Figure 19: Composition range of pH 2 aq. sample at 700°C. The measurements were taken at steam ratio of 5%, 20% and 50% H₂O/H₂.

Table 5: Resistances - Composition range of aq. pH 2 at 700°C

<table>
<thead>
<tr>
<th>pH 2 aq.</th>
<th>5% H₂O/H₂</th>
<th>20% H₂O/H₂</th>
<th>50% H₂O/H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p$[Ωcm²]</td>
<td>1.205</td>
<td>0.806</td>
<td>1.105</td>
</tr>
<tr>
<td>$R_s$[Ωcm²]</td>
<td>45.484</td>
<td>32.103</td>
<td>33.345</td>
</tr>
<tr>
<td>ASR[Ωcm²]</td>
<td>46.689</td>
<td>32.909</td>
<td>34.450</td>
</tr>
</tbody>
</table>

EIS - Aqueous pH 7

For the sample infiltrated with the aq. pH 7 solution it can be seen from figure 20 that the integral decreases on the Nyquist plot as temperature increases. Each curve has a major and a minor peak which indicates two processes are happening in the electrode. At 650°C the minor peak seem almost quenched. At the Bode plot there is one major peak at $10^3$Hz and one minor near 10Hz. The minor peak does not change with temperature but the major decreases as temperature is increased. By looking very carefully a very small shift to the right can also be seen as well. The resistance values of the temperature range plot are showcased in Table 6.

Figure 20: Temperature range for aq. sample with pH 7 at 20% steam. The measurements were taken at 650°C, 700°C, 750°C and again at 650°C (x650).
4 RESULTS - ELECTRODE INVESTIGATION

Table 6: Resistances - Temperature range of aq. pH 7 at 20% steam

<table>
<thead>
<tr>
<th>pH 7 aq.</th>
<th>650°C</th>
<th>700°C</th>
<th>750°C</th>
<th>x650°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p$ [$\Omega cm^2$]</td>
<td>0.074</td>
<td>0.052</td>
<td>0.041</td>
<td>0.082</td>
</tr>
<tr>
<td>$R_s$ [$\Omega cm^2$]</td>
<td>0.827</td>
<td>0.576</td>
<td>0.429</td>
<td>0.824</td>
</tr>
<tr>
<td>ASR [$\Omega cm^2$]</td>
<td>0.901</td>
<td>0.628</td>
<td>0.470</td>
<td>0.906</td>
</tr>
</tbody>
</table>

In the Bode plot on the left side of figure 21 it is shown that the smallest integral is at 50% steam, $R_p$ at 20% is slightly larger than that of 50%, while that of 5% is significantly larger, $R_s$ and ASR is also significantly larger compared to the two others. There are clearly 2 peaks, the minor peak for 20 and 50% are major at 5%. The Bode plot shows a clear peak near 10 Hz for 5% which diminishes as steam is increased, meanwhile the peak at $10^3$Hz increases slightly and is shifting to the right. The resistances from the plot has been tabulated, this is shown in Table 7.

![Bode plots](image)

Figure 21: Composition range for aq. sample with pH 7 at 700°C. The measurements were taken at steam ratio of 5%, 20% and 50% H$_2$O/H$_2$.

Table 7: Resistances - Composition range of aq. pH 7 at 700°C

<table>
<thead>
<tr>
<th>pH 7 aq.</th>
<th>5% H$_2$O/H$_2$</th>
<th>20% H$_2$O/H$_2$</th>
<th>50% H$_2$O/H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p$ [$\Omega cm^2$]</td>
<td>0.100</td>
<td>0.052</td>
<td>0.046</td>
</tr>
<tr>
<td>$R_s$ [$\Omega cm^2$]</td>
<td>0.714</td>
<td>0.576</td>
<td>0.597</td>
</tr>
<tr>
<td>ASR [$\Omega cm^2$]</td>
<td>0.814</td>
<td>0.628</td>
<td>0.643</td>
</tr>
</tbody>
</table>

The best performance for this sample was measured at 750°C with a steam content of 50%, here the $Z_{Im}$ ranges between 0 and 0.02 $\Omega cm^{-2}$. The $Z_{Real}$ ranges between 0.435 and 0.470 which results in a electrode resistance of 0.035$\Omega cm^{-2}$, this is showcased in Figure 22.
EIS - Aqueous pH 12

The sample infiltrated at pH 12 in aq. solution show a relative lower impedance compared to the other samples. In Figure 23 the plots look similar to the aq. pH 7 sample. At the Nyquist plot a major and a minor peak can be seen. The major peak is decreasing as temperature is increased. Th Bode plot specifies at which frequency these processes take place. Near $10^3$Hz a large peak is seen decreasing as temperature increases, there seem to be no shift to either side. There is no observable change for the peak at 10Hz during the temperature variations. The tail at the beginning of 650°C x650°C at the Nyquist plot and their corresponding points at the end of the Bode plot are due to electromagnetic induction from wiring connecting to the sample holders and are not relevant for electrode performance. The tails can therefore be disregarded, the tails of the measurements at 700°C and 750°C are negative and can be seen in the appendix. The resistance values from the temperature range is showcased in Table 8.

![Figure 22: Composition range for aq. sample with pH 7 at 750°C. The figure is cropped to showcase the low ASR especially at 50%.](image)

![Figure 23: Temperature range for aq. sample with pH 12. The measurements were taken at 650°C, 700°C, 750°C and again at 650°C (x650).](image)
4 RESULTS - ELECTRODE INVESTIGATION

Table 8: Resistances - Temperature range of aq. pH 12 at 20% steam

<table>
<thead>
<tr>
<th>pH 12 aq.</th>
<th>650°C</th>
<th>700°C</th>
<th>750°C</th>
<th>850°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p [\Omega \text{cm}^2]$</td>
<td>0.065</td>
<td>0.047</td>
<td>0.038</td>
<td>0.072</td>
</tr>
<tr>
<td>$R_s [\Omega \text{cm}^2]$</td>
<td>0.606</td>
<td>0.389</td>
<td>0.265</td>
<td>0.608</td>
</tr>
<tr>
<td>ASR [\Omega \text{cm}^2]</td>
<td>0.671</td>
<td>0.436</td>
<td>0.303</td>
<td>0.680</td>
</tr>
</tbody>
</table>

In Figure 24 the steam to hydrogen ratio is varied. The Nyquist plot on the left shows the integral-values are smallest for 50% $H_2O/H_2$-ratio, closely followed by 20%. The 5% looks noteworthy different. This can be further explored by looking at the Bode plot on the right. The peak between 10 and 100Hz are remarkably larger for 5% $H_2O$ an is significantly decreased for the higher steam content and shifted to the right, the change between 20% and 50% is small. The peak at $10^3$Hz decreases in amplitude while also shifting to the right for higher steam percentage. The resistances are showcased in Table 9 A similar behavior is observed on the Bode plot, the peak at 10Hz is small for 20% and 50% but large for 5%. The other peak $10^3$Hz does not change amplitude but shifts slightly to the right with increasing steam content.

Figure 24: Composition range for aq. sample with pH 12. The measurements were taken at steam ratio of 5%, 20% and 50% $H_2O/H_2$.

Table 9: Resistances - Composition range of aq. pH 12 at 700°C

<table>
<thead>
<tr>
<th>pH 12 aq.</th>
<th>5% $H_2O/H_2$</th>
<th>20% $H_2O/H_2$</th>
<th>50% $H_2O/H_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p [\Omega \text{cm}^2]$</td>
<td>0.103</td>
<td>0.039</td>
<td>0.048</td>
</tr>
<tr>
<td>$R_s [\Omega \text{cm}^2]$</td>
<td>0.457</td>
<td>0.408</td>
<td>0.388</td>
</tr>
<tr>
<td>ASR [\Omega \text{cm}^2]</td>
<td>0.560</td>
<td>0.447</td>
<td>0.436</td>
</tr>
</tbody>
</table>

The best performance of all the samples were pH 12 at 750°C with a steam content of 50%, $Z_{Im}$ ranges between 0 and 0.017 $\Omega \text{cm}^2$. The $Z_{Real}$ ranges between 0.282 and 0.312 which results in a electrode resistance of 0.030 $\Omega \text{cm}^2$, this is showcased in Figure 25.
RESULTS - ELECTRODE INVESTIGATION

Figure 25: The best performance of all the cells were infiltrated with aq. pH 12 solution, plotted in a temperature range.

EIS - EtOH pH 7

The samples infiltrated with ethanol solutions were found to have generally poor performance, from the Nyquist plot in Figure 26 a clear trend can be seen: when the temperature increases the electrode resistance decreases. There is only a single peak dominating at all temperatures with a slight shift to the right, on the Bode plot it can be seen this process happens near $10^3$ Hz, the resistances are tabulated in Table 10.

Figure 26: Temperature range for EtOH pH 7 at 20% steam content. The measurements were taken at 650°C, 700°C, 750°C and again at 650°C (x650).

Table 10: Resistances - Temperature range of EtOH, pH 7 at 20% steam

<table>
<thead>
<tr>
<th>pH 7 EtOH</th>
<th>650°C</th>
<th>700°C</th>
<th>750°C</th>
<th>x650°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p$ [Ω cm²]</td>
<td>6.407</td>
<td>3.278</td>
<td>1.660</td>
<td>5.988</td>
</tr>
<tr>
<td>$R_s$ [Ω cm²]</td>
<td>0.924</td>
<td>0.629</td>
<td>0.454</td>
<td>0.924</td>
</tr>
<tr>
<td>ASR [Ω cm²]</td>
<td>7.331</td>
<td>3.907</td>
<td>2.114</td>
<td>6.912</td>
</tr>
</tbody>
</table>

The composition range in Figure 27 shows similar behavior as the temperature range. The decrease in impedance due to increasing steam percentage is not quite as significant as with temperature variations, however the shift of the single peak to the right is significant, the resistances are showcased in Table 7.
4 RESULTS - ELECTRODE INVESTIGATION

Figure 27: Composition Range for EtOH pH 7 at 700°C. The measurements were taken at steam ratio of 5%, 20% and 50% H₂O/H₂.

Table 11: Resistances - Composition range of EtOH pH 7 at 700°C

<table>
<thead>
<tr>
<th>pH 7 EtOH</th>
<th>5% H₂O/H₂</th>
<th>20% H₂O/H₂</th>
<th>50% H₂O/H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rp [Ω cm²]</td>
<td>3.892</td>
<td>3.282</td>
<td>2.771</td>
</tr>
<tr>
<td>Rs [Ω cm²]</td>
<td>0.689</td>
<td>0.629</td>
<td>0.629</td>
</tr>
<tr>
<td>ASR [Ω cm²]</td>
<td>4.581</td>
<td>3.911</td>
<td>3.400</td>
</tr>
</tbody>
</table>

EtOH pH 12 electrochemical impedance spectroscopy

Like the neutral EtOH infiltrated sample the resistance was very high for the EtOH pH 12 sample. Since this sample was also broken, as seen Figure 28, the resistances are considered uncalibrated. From the trend some information can still be extracted. On the Nyquist plot of Figure 29 a single peak stands, that is decreases as temperature rises. On the Bode plot the peak is found near 10¹ⁱ Hz. The resistances are showcased in Table 12.

Figure 28: Broken pH 12 EtOH sample. The sample broke into three pieces, since the effective area is no longer 0.36 cm², the impedance per area is considered uncalibrated. It is still possible to extract data using the shape of the curves.
Figure 29: **Temperature range for EtOH pH 12 sample at 20%**. Left: Nyquist plot, the integral values diminish greatly as temperature increases. Right: Bode plot: a slightly asymmetric peak. One process dominates centered near $10^3$ Hz, and increases as temperature rises, but shifts to the left as temperature is decreased.

Table 12: **Resistances - Temperature range of EtOH pH 12 at 20% steam**

<table>
<thead>
<tr>
<th>pH 12 EtOH</th>
<th>650°C</th>
<th>700°C</th>
<th>750°C</th>
<th>850°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$ [Ω cm$^2$]</td>
<td>2.564</td>
<td>2.048</td>
<td>1.630</td>
<td>2.564</td>
</tr>
<tr>
<td>ASR [Ω cm$^2$]</td>
<td>17.399</td>
<td>9.790</td>
<td>5.701</td>
<td>16.791</td>
</tr>
</tbody>
</table>

The composition range of Figure 30 behaves similar to the EtoH pH 7 sample by decreasing impedance as the steam to hydrogen ratio is increased. The resistances from the composition range is showcased in Table 13.

Figure 30: **Composition Range for EtOH pH 12 at 700°C**. Left: In the Nyquist plot it is shown that the impedance decreases as steam content increases, there seem to be only one process happening. Right: The Bode plot show a single peak near $10^3$ Hz that shifts to the right and decreases as steam content increases.
Table 13: Resistances - Composition range of EtOH pH 12 at 700°C

<table>
<thead>
<tr>
<th>pH 12 EtOH</th>
<th>5% H₂O/H₂</th>
<th>20% H₂O/H₂</th>
<th>50% H₂O/H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p[\Omega cm^2]$</td>
<td>9.751</td>
<td>7.532</td>
<td>9.944</td>
</tr>
<tr>
<td>$R_s[\Omega cm^2]$</td>
<td>2.282</td>
<td>2.066</td>
<td>2.066</td>
</tr>
<tr>
<td>$ASR[\Omega cm^2]$</td>
<td>12.033</td>
<td>9.814</td>
<td>9.010</td>
</tr>
</tbody>
</table>

### 4.2 Results - Scanning electron microscopy

An increased performance is expected to stem from high surface-to-volume ratio for best electrocatalytic effect. This will be evaluated by looking into the size and morphology of the infiltrate particles. The size of the particles were measured using imageJ software[66], and the size distribution were estimated from the selected measured particles. The images were taken after EIS testing. The samples were first investigated with a Zeiss Evo 10 which uses a LaB₆ thermionic source, and all samples were screened. Due to the inability to reach sufficient resolution with the Zeiss Evo 10, Zeiss Merlin was used subsequently. The latter mentioned SEM uses a FE source which illuminates a much smaller area and thereby gives better resolution, as described in the theory of SEM. A much higher voltage was used to take the image in Figure 31a which additionally cause the image to be blurred. The image acquired using Merlin show much better resolution as can be seen in Figure 31b.

*Figure 31: Comparison of SEMs.  (a) EVO 10 SEM image of LSFNT backbone infiltrated with EtOH pH 12 solution, the resolution was insufficient. (b) Merlin image of the same sample at a similar electrode/electrolyte interface and at similar magnification, the porous structure of the anode (top) and the dense structure of the electrolyte (bottom) is very clear. Even at this magnification some white spots of infiltrate can be observed if looking closely.*

The infiltrate particles among the porous structure of the anode can be seen clearly in Figure 32.
Figure 32: A SEM micrograph of the porous anode where the infiltrate is seen more clearly as white dots. The infiltrate is seen evenly spread out throughout the porous structure of the anode.

An energy selective backscattered electron detector was used because it receives stronger signal from heavy elements, see Figure 33. This results in heavier elements being brighter and elements of less mass were shown as darker. In this case the dark particles are Ni infiltrate, the mid-grey is the backbone consisting of the dense electrolyte (mainly Zr) and the porous electrode (A composite consisting of La, Sr and Ti). CGO appeared bright, as expected. ESB is a phase contrast method which is very sensitive to topography, smooth surfaces are recommended. The fractured surfaces are not optimal for backscattered imaging, the subsequent description is only a qualitative observation.
SEM micrograph using an energy selective backscatter electron detector, the shade of grey tells of the mass of the element that is detected. Where bright colours of the image represents heavier elements and dark colours represents lighter molecules. In this image the porous anode structure (mid grey) is seen with plenty of CGO (Bright) and Ni (Dark) particles.

LFSNT aq. pH 2
SEM images of LSFNT sample infiltrated with the aq. pH 2 solution are shown in Figure 34, on left side is a high resolution image, where small light particles can be seen on a dark grey electrode. The image on the right shows a larger area of the cell, the infiltrate particles light up the image showcasing the infiltrated particles were spread out through the electrode. The top right corner is darker because the electron beam does not target it, and less electrons are therefore being scattered from there. The LFSNT sample infiltrated with aqueous pH 2 solution had particles evenly spread around the anode structure, see Figure 34. The particles were spherical in shape and selected particles were measured to get a general idea of size distribution, these were selected from multiple areas to get a better estimate. The particles had a relative broad size distribution ranging between 30 to 60nm.
Figure 34: The LSFNT sample infiltrated with the aqueous pH 2 solution: (a) is (b) in higher magnification. (a) show particles spread around the porous anode structure, the particles are spread with some space between. Measuring selected particles from multiple areas to get a rough estimate show diameters ranging between 30 and 60nm. From (b) it can be seen the particles are evenly spread at a larger area, this was seen across other areas as well.

LFSNT aq. pH 7

SEM images of LSFNT sample infiltrated with the aq. pH 7 solution are shown in Figure 35, on left side is a high resolution image, where small light particles can be seen on a dark grey electrode. The image on the right shows a larger area of the cell, the infiltrate particles light up the image showcasing the infiltrated particles were spread out through the electrode.

The aqueous neutral solution showed a fine even layer of infiltrate particles among the entire anode, see Figure 35. The particles seen were spherical and ranged between 30-65nm from a selection of particles measured.

Figure 35: SEM images of the fractured LFSNT pH 7 aq. sample. (a) is enhanced of (b). (a) Small spherical particles are spread evenly among the porous structure, all particles seem to be smaller than 100nm with selected measured diameters ranging from 30 to 60nm. (b) shows evenly spread infiltrate particles among a larger section the porous anode structure.
LFSNT aq. pH 12

SEM images of LSFNT sample infiltrated with the aq. pH 2 solution are shown in Figure 36, on left side is a high resolution image, where small light particles can be seen on a dark grey electrode. The image on the right shows a larger area of the cell, the infiltrate particles light up the image showcasing the infiltrated particles were spread out through the electrode. For the backbone infiltrated with alkaline solution, there was seen two types of infiltrate particles, see Figure 36. Small spherical particles similar to the pH 7 infiltrated anode, these particles size distribution seemed narrow with selected measured diameters between 30 and 40nm.

The other type was slightly elongated spheres, resembling beans, the bean-shaped particles were slightly larger but more homogeneous in size and spread. Measuring them as ellipses, selected minor axis diameters was near 30nm and major axis diameters near 80nm and had a narrow size distribution.

LSFNT EtOH pH 7

SEM images of LSFNT sample infiltrated with the EtOH pH 7 solution are shown in Figure 37, the high resolution image shows where small light particles that can be seen on a dark grey electrode. There seem to be a lot less particles when compared to the SEM images of the electrodes infiltrated with aq. solutions. The particles are seen evenly spread around the porous structure. The shape of the particles are spherical and seem to have a quite broad size distribution. The smaller particles were measured to be near 30nm and the largest were more than 100nm as seen on Figure 37. ESB-SEM was used to confirm the apparent lack of CGO. The ESB highlights compositional information, which means heavy atoms will give more signal, CGO would then be expected to shown as bright spots and Ni as dark spots on the grey backbone. In Figure 38 dark spots of Ni can be seen on the grey backbone, but no bright spots of CGO. It seems to be the CGO that is missing from the the EtOH pH 7 sample.
Ni particles are seen spread out evenly. The size distribution was relatively large with larger grains of Ni measured was greater than 100nm, the smallest was down to 30nm.

Figure 37: SE and ESB-SEM of LSFNT EtoH pH 7. (a) SE image showing particles at the same area as (b). (b) shows dark Ni spots, there is no bright spots and thereby there is no CGO present.

LFSNT EtOH pH 12

EM images of LSFNT sample infiltrated with the EtOH pH 7 solution are shown in Figure 37, the high resolution image shows where small light particles that can be seen on a dark grey electrode. Similar to the prior electrode, this seems to have much fewer particles compared to the electrodes infiltrated with aq. solutions. The particles are seen evenly spread around the porous structure with small particle size and spherical shape, see Figure 39. Selected particle diameters were measured to around 30nm with a narrow size distribution, similar to
the spherical particles of the aqueous pH 12 sample. The lack of particles are possibly the same as for EtOH pH 7., which would mean it is the CGO particles missing.

Figure 39: **LSFNT pH 12 EtOH SEM images.** (a) is enhanced of (b). (a) Particles are spread thinly around the surface, there is no CGO present and therefore no 3PB. It should therefore show poor performance in EIS. The size distribution seem to be large, with the largest around 100nm and smallest roughly at 10nm, the Ni is circular flakes. (b) shows the infiltrate is evenly spread among a larger section of the porous anode structure.
5 Results - MOXIE gas flow

In order to characterize the crossover flow a run was designed by the MOXIE Operation Planning Work Group (OPWG) to test for both cathode underpressure and overpressure. The run was designed to increase P4 with compressor RPM, while keeping a constant SOEC current, this way the same amount of \(O_2\) is being produced, even when more gas is let in. Furthermore the pressure at P4 should rise above P5 to get cathode overpressure which leads to \(CO_2\) streaming into the anode line thus reducing \(O_2\) purity, this is shown in Figure 40.

![Pressure plot from OC13 of P4 and P5](image)

Figure 40: *Pressure plot from OC13 of P4 and P5. CS2 denotes the partial pressure of CO\(_2\) at the anode exhaust vent. As the compressor RPM increase so does the P4 pressure, the CO\(_2\) partial pressure jumps up before P4 P5.*

An interesting observation is that the \(CO_2\) partial pressure increases above ambient even before P4 P5, thus \(CO_2\) is flowing into the anode, even at small anode overpressures. This leads to the assumption that there are two regions of flow, a diffusive flow when P4>P5 and a forced flow when they are not. 'P4' also increases very little as the compressor speed is increased. This can be seen more clearly in Figure 41. The step values for 'P4' were calculated by taking the mean of each step plateau. For 'P4' the small peaks at the beginning of each step were disregarded as the pressure had not stabilized.
Figure 41: **P4 and P5 during OC13 in averaged steps.** The step value is the mean value at each step. P4 increases with equal step sizes until P4 P5, at this kink the step-increase diminishes, this is because CO\textsubscript{2} is heavier than O\textsubscript{2} thus less molecules will be forced through by an equal change in pressure. P5 increases slightly with each step, the step-increase diminishes as P4 P5 in similar manner to P4, but the over all change is much smaller.

**Calculations**

It is clear that the MOXIE O\textsubscript{2} product is of high purity if an anode overpressure of 0.1 bar is maintained, this however comes with the downside that some of the produced oxygen is getting exhausted with the by-products. Constructing an analytical model would be of great help to optimize O\textsubscript{2} output while producing at high purity.

or small leaks the flow is characterized as diffusive, while for large leaks it is characterized as forced flow, in the latter region, diffusive flow becomes negligible. Since the optimal performance is achieved where both flow in both directions are minimal, the model should work for diffusive flow in the region where 'P4' and 'P5' are similar. In the case for diffusive flow, Vandoni et al.\cite{70} made a model to determine back-streaming under the assumption the leakhole is cylindrical. The leak is equal to:

\[
q_{1,\text{diff}} = \eta \frac{p_1}{2\rho L} \left( \frac{p_1}{p_2 m_2} + \frac{p_2}{p_1 m_1} \right) \cdot k T \pi a^2 \tag{34}
\]

here \(q_{1,\text{diff}}\) is the impurity flow (flow of Martian atmospheric gas, \(\eta\) is local impurity concentration, \(p_1\) and \(p_2\) are the pressures at the cathode exhaust and
anode exhaust respectively, \(m_1\) and \(m_2\) is the molecular weight of cathode exhaust gas and anode exhaust gas (\(O_2\)) respectively. The Boltzmann constant is denoted '\(k\)', \(T\) is temperature, \(a\) is the leak diameter, and \(L\) is leak depth, the latter two are both unknown. In the case for \(O_2\) flowing into the cathode (production loss) the impurity flow is \(O_2\) flow and local impurity concentration denotes \(O_2\) concentration at cathode exhaust.

The molecular weight of the cathode exhaust gas is calculated by using a typical run as starting point. In a typical run, the \(O_2\)-production will be 6g/hr, for this 68.9g/hr of atmospheric gas is provided. Thus, 6g/hr goes through the anode exhaust and 62.9g/hr flows through the cathode exhaust. The electrolysis reaction needs \(2CO_2\) to get \(2CO + O_2\), using molar masses the fractional ratio of \(CO\) to \(O_2\) is:

\[
m_{2CO}/m_{O_2} = \frac{56g/mol}{32g/mol} = 1.75
\]

Thus for 1 gram of \(O_2\) produced, 1.75g of \(CO\) is made as by-product, this signifies that for 6g/hr, 10.5g/hr of \(CO\) flows through the cathode exhaust. The fractional relationship between \(CO_2\) and \(CO\) is then

\[
\frac{10.5g/mol}{62.9g/mol} = 0.167
\]

The molar mass of martian atmosphere is 43g/mol, with 95% \(CO_2\), ~ 3% \(N_2\) and 2% \(Ar\). The molar mass of the exhaust is thus: 0.169-28g/mol+0.831-43g/mol = 40.465g/mol

The flow is plotted in both directions as a function of the unknowns and the pressure in figure 42. This will give an idea of how the flow behaves at varying temperatures. The unknowns are \(\eta\), the dimensional factors and the flow itself. For simplicity, \(T\), \(k\) and \(\pi\) is included in this constant since they are all non-variables.

\[
q \cdot C = \frac{p_1}{p_1 + p_2} \left( \frac{p_1}{p_2m_2} + \frac{p_2}{p_1m_1} \right), \quad \text{with} \quad C = \frac{L}{\eta \cdot kT \pi a^2}
\]
Figure 42: **Crossover flow versus cathode pressure at constant anode pressure of 0.65bar.** CO$_2$ flowing into the anode follows a linear path when $P_4\approx P_5$, the O$_2$ flowing into the cathode follows a near linear path with a slight arc pointing downwards. At $P_4=P_5$ the flows are equal in amplitude, however the local impurity concentration $\eta$ is not necessarily equal, and if not the vertex would not be at exactly $P_4=P_5$.

In the case of equal $\eta$’s for Martian atmospheric gas and O$_2$, the flow of CO$_2$ and O$_2$ is non-zero and equal in opposite direction. The flow rate is in still arbitrary units.

This model assumes $P_4 \approx P_5$ and thus is only viable in this vicinity, from Figure 40 it seems this vicinity range about $\sim 0.1$bar from equal cathode and anode pressure.
6 Discussion

6.1 Electrode performance discussion

From the aqueous pH 7 and pH 12 samples, it is clear that two processes are happening. One related to the gas diffusion into the anode between 10 and 100Hz. The other process occurs at 1kHz, this process is clearly temperature dependant and only slightly shifting with changing gas composition. The aq. pH 2 sample did only show a single arc similar to the EtOH samples. This suggests the acidic solvent deactivated one of the processes. The long tails on both Nyquist and Bode plots of Figure 23, are not relevant for the electrode performance as they represent resistance induced from spiralling wiring of the test rig. The peak near 10-100Hz has been denoted, by Primdahl and Mogensen\[71\], as impedance due to gas diffusion, that happens when gas is stagnating on top of the porous anode. This process is mainly dependant on gas composition and porosity of the anode, and not much on the material itself. It is clear from Figure 21 and 24 and their corresponding tables (Table 7 and 9 ) that this is atmosphere composition sensitive. The process occurring near 1kHz is present both for the EtOH and the aq. samples, this suggests it is either a bulk process or related to the Ni electrocatalytic sites. Padinjarethil et al.[72] argue that bulk phenomena are very temperature dependant.

For the aq. pH 2 sample the lowest $R_p$ is at 20% steam in contrast to the aq. pH 7 and pH 12 samples. Either bulk has been changed by the acidity or the sample fractured further near this measurement. Whatever the reason, infiltrating with strong acid evoked too much instability of the cells to be considered for SOC purposes. The ESB image in Figure 38 shows only dark particles that are expected to be Ni. Ceria is a heavy element and would appear bright. If this is the case, there can be little doubt that the poor performance of the EtOH samples was due to lack of CGO. The question regarding the missing CGO need further experimentation to explain, a possible explanation could be the CGO fell to the bottom, there were no clear agglomeration during the time of infiltration however. The Eth samples do however tell of similar particle size as their aqueous counterparts. The particles of the pH 12 samples are estimated to be smaller than those of the neutral solution. However, the aqueous pH 12 sample also had areas of seemingly larger particles, therefore further investigation is needed to understand this.

The $ASR$ and $Ra$ were larger than similar anode supported LSFNT cells infiltrated with Ni:CGO. Nielsen et al.[38] reported $ASR=0.929 \, \Omega cm^2$, and $Ra=0.2 \, \Omega cm^2$ at 650°C and 20% steam. However, these values are mainly dependant on electrolyte and electrolyte/electrode interface, the optimization of these lie in the fabrication of the cells which is outside of the scope for this thesis.

The value of interest regarding electrode performance is the polarization resistance $R_p$, they reported an $R_p=0.8 \, \Omega cm^2$[38]. At similar conditions the aq. pH 7 sample had $R_p=0.074 \, \Omega cm^2$ and for aq. pH 12 $R_p=0.065 \, \Omega cm^2$. The samples in this work thereby showed a remarkable performance increase compared
to similar studies[38]. State-of-the-art SOCs have been reported to have $R_p$ in the vicinity of $0.1 \Omega \text{cm}^2$ at similar conditions[25, 73, 74].

The aq. pH 12 sample had lower $R_p$ and $R_s$ compared to pH 7, suggesting the higher pH value of the wet infiltration increases performances.

Since smaller surface to volume area should exhibit better performance, the SEM micrographs are used to look at morphology and size characteristics. The particle size of the aqueous samples seem similar, but seemingly different size distributions. The morphology of the samples also differs slightly.

The microstructure observations of the aq. pH 12 sample showed particles of two types of morphology: small spherical particles and larger bean-shaped particles. The EtOH and the other aq. samples showed only spherical particles. This could suggest the presence of the bean-shaped particles improve performance. Another possible reason for lower $R_p$ could be narrower particle distribution of the spherical particles. The pH 2 and pH 7 aq. samples both had broader particle distribution, and the narrow particle distribution of the pH 12 aq. sample were centered around smaller particle size. To go further with size comparison a more quantitative method is needed, this could be done by solidifying the Ni solutions and pulverizing it, SEM images could then be used to measure particle size. The CGO and MSC that were infiltrated but had not been tested would be interesting to look further into. EIS could be done by using a reference cathode and exclude the resistance caused by it, subsequently SEM analysis could be performed to investigate morphology.

Applying alkaline infiltrate on perovskite samples did increase performance, and could be a viable tool, however the stability and degradation has to be investigated before it can be considered feasible. The tested samples could be possible candidates for future Martian and terrestrial SOC plants, but testing in CO$_2$ and possible CO$_2$/H$_2$O atmosphere and assessing performance there is needed before it can be considered further.

### 6.2 Gas flow discussion

A crossover flow is a serious concern for O$_2$ purity but can be worked around by operating with anode overpressure. From the data available, an anode overpressure of 0.1 bar is plenty to keep O$_2$ purity at 100%. To produce a model with crossover flow multiple factors must be assessed. To estimate the local impurity concentration $\eta$, the CO$_2$ sensor at the the anode side must be calibrated (CS2), this is still in progress by other members of the MOXIE science team. When CS2 is calibrated, impurity flow can be estimated by using the total and the partial pressure combined using the data from OC13. When this is achieved, a volumetric factor can be calculated, since $\frac{a^2}{T}$ will be the only unknowns of eq. 34.

Fluid dynamics (here in gas kinetics) is a complex topic, where small changes to a model can change the outcome drastically[75] This analysis is based on a cylindrical shaped leak between the anode and the cathode, we have no way to investigate whether this is the case or not. It would be of value to broaden
the crossover analysis to include other models for comparison. An example of this could be Alexander Roth’s method for sealed unit leak detection[76]. For a full scale Martian SOC plant, similar crossover flows are to be expected. The flowrate, pressures and leak volumetric will be different, but this could all be estimated in similar manner as described above to be included in the Vandoni model.
7 Conclusions

Of all the produced cells, only the aq. pH 7 and pH 12 gave satisfying EIS data. Those two samples did show promising results, as the $R_p$ was comparable to state-of-the-art electrodes even at lower temperatures. The pH 12 samples had the lowest $R_p = 0.065\Omega cm^2$, which suggests wet infiltration using alkaline solutions can be used to increase performance. Infiltration of Ni is an effective way of improving the electrocatalytic effect while lowering the amount of Ni used. The LSFNT cell could be a possible upgrade for a full scale MOXIE ISRU plant on Mars, as it comes with high performance and low Ni content, but to be send to Mars the stability of the cell must be tested and affirmed. This demands extensive examination.

Regarding the crossover flow observed in MOXIE, a solution has been proposed. By applying an anode overpressure of more than 0.1bar, $O_2$-purity will be at 100%. A more precise model is in progress in which the overpressure could be lowered to minimize the amount of discarded $O_2$, while maintaining high purity. Crossover flows are likely to happen on a full scale Martian ISRU plant and operating at an anode overpressure is suggested. The Vandoni model when finished could further be used to find a the precise overpressure of acceptable $O_2$ purity.
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Appendices
Appendix A  Analysis

In this appendix, the full scale data sets are shown. These were depicted as crop outs in section 4.
Figure 43: Temperature range for LFSNNT the aq. sample with pH 2.
Figure 44: Composition range of pH 2 aq. sample at 700°C.
Figure 45: Temperature range for aq. sample with pH 7.
Figure 46: Composition range for aq. sample with pH 7 at 700°C.
Figure 47: **Composition range for aq. sample with pH 7 at 750°C.**
Figure 48: *Temperature range for aq. sample with pH 12.*
Figure 49: Composition range for aq. sample with pH 12
Figure 50: The best performance of all the cells were infiltrated with aq. pH 12 solution.
Figure 51: Temperature range for EtOH pH 7 at 20% steam content.
Figure 52: Composition Range for EtOH pH 7 at 700°C.
Figure 53: Temperature range for EtOH pH 12 sample at 20%.
Figure 54: Composition Range for EtOH pH 12 at 700°C.