Process development for laser-based additive manufacturing of solid oxide fuel cells

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**NANYANG
TECHNOLOGICAL
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SINGAPORE

**PROCESS DEVELOPMENT FOR LASER-BASED
ADDITIVE MANUFACTURING OF SOLID OXIDE
FUEL CELLS**

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School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University in partial fulfilment of the
requirements for the degree of Master of Science

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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This thesis contains material from 1 paper(s) published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

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The contributions of the co-authors are as follows:

- A/Prof Su, Dr Sun and Dr Wei provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Lee and Dr Baek.
- I designed the study and performed all the laboratory work at the School of Mechanical and Aerospace Engineering. I also analyzed the data.
- All microscopy, including sample preparation, was conducted by me.

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Abstract

Solid oxide fuel cells (SOFCs) are electrochemical conversion devices which directly convert chemical energy of the fuel into electrical energy with high efficiency. SOFC comprises of an anode, electrolyte and cathode layer that are fabricated individually upon each other, usually one at a time. Additive manufacturing (AM) is a new fabrication technique that utilizes a layer by layer fabrication technique, which can potentially be suitable for use in SOFC, since it is also building different materials in a layer-wise manner. Furthermore, the use of laser-based AM techniques can eliminate the issue of long sintering hours by directly densifying the materials using laser as the heat source. In addition, SOFCs possessing newer designs can be fabricated with ease using this technique, gradient-structure electrodes can also be created either by design or varying the laser parameter and material composition. Therefore, this thesis aims to develop a process as well as study the feasibility for fabricating SOFC using laser-based AM techniques.

First, a step-by-step process was conducted to identify significant factors affecting the building of Nickel metal support structures using Selective Laser Melting (SLM) process. Laser power, scanning speed and hatch spacing were found to be the dominant factors affecting the printability of the parts. Next, a porous structure was designed and printed which acted as a metal support for SOFC. A functional cell was further built upon the metal support and the electrochemical performance was investigated. Although a low open circuit voltage (OCV) of 0.53 V was obtained with a maximum power density of 11.0 mW/cm² from the cell, it demonstrated potential of this technique as a new fabrication process.

In order to realize the fabrication of the entire SOFC by laser-based AM, the influence of laser on SOFC materials were conducted. The effect of two different laser sources, Nd:YAG fibre laser and CO₂ laser was studied on NiO-YSZ anodic material, which showed that CO₂

laser was better absorbed by the oxide material. In addition, dendrite features were formed on the surface, which were influenced by the rapid solidification process and could be modified by adjusting laser processing parameters. Although the laser-modified SOFC did not perform as well as the conventional one, it was found that significant improvement was made on the charge transfer kinetics. Lastly, the influence of laser on YSZ electrolyte surface showed that the polarization resistance of the cell was reduced due to better oxygen adsorption/dissociation process. These experiments demonstrated that laser-based AM is a viable fabrication tool for SOFC.

1. Introduction

1.1. Solid Oxide Fuel Cells (SOFCs)

Fuel cells are electrochemical devices that are well-known for its high energy conversion efficiency among the many different types of energy sources as illustrated in Figure 1-1. Currently, there are many types of fuel cells available in the market, including proton exchange membrane (PEMFC), molten carbonate (MCFC), solid oxide (SOFC) and phosphoric acid (PAFC). Among them, SOFCs offers the additional advantage of having a solid electrolyte which avoids corrosive liquid environments during usage, having good long-term stability and allowing a wider range of fuels to be used due to its higher operating temperatures [1].

Figure 1-1. Efficiency of fuel cell compared to other energy sources [2]

In addition to the previously mentioned benefits, SOFCs can potentially replace conventional combustion engines and be the energy conversion system of the future due to the higher efficiency that can be achieved. SOFCs can directly convert chemical energy from the fuel gas into electrical energy using a one-step conversion process

instead of the two-step process used by conventional combustion engines, first into heat energy then into electrical energy. In addition, carbon pollution is reduced due to the lower CO₂ emissions during the process, which results in significant environmental advantages [3].

In SOFCs, electrical energy is produced during the reaction of fuel with an oxidant via the diffusion of oxide ions across an ion-conducting electrolyte layer. It is primarily composed of a dense electrolyte layer that is sandwiched between the porous anode and the cathode layer. Electrons that are generated through fuel oxidation are accepted by the cathode for oxygen reduction, while the oxide ion released passes through the electrolyte layer and complete the electrical circuit. Figure 1-2 demonstrates the process by which electricity is generated.

Figure 1-2. Basic SOFC structure and the corresponding reactions at the electrodes

Although SOFCs are composed of 3 different components, the fabrication of SOFCs are usually conducted with each component being fabricated individually before the

next component is added. Current fabrication techniques can be further differentiated into 2 categories, one for traditional and thicker SOFCs while the other for thin film SOFCs. For thicker SOFCs, the fabrication methods tend to be more traditional ceramic processing techniques such as dry pressing [4] and tape-casting [5]. However, with the ongoing trend to reduce overall SOFC and electrolyte thickness, in order to achieve higher power density to weight ratio and reduce ohmic resistance respectively, thin film fabrication techniques were also developed such as spin-coating [6-9], pulsed laser deposition [10-13], atomic layer deposition [14-16] and micromachining techniques [17-19].

1.2. Additive Manufacturing

Additive manufacturing or 3D printing is a manufacturing technique that allows the user to create customized parts using a layer upon layer fabrication method. As compared to conventional subtractive manufacturing technologies such as milling, drilling or computer numerical control (CNC) systems, this technique allows parts with higher complexity to be build, providing a greater degree of freedom for product designers. The customized parts are designed using computer-aided design (CAD) software, whereby it can be easily modified to suit different needs, instead of creating a new mould each time [20]. The file is then sliced into multiple layers using the machine's software to obtain information such as the cross-sectional area of each individual sliced layer. This information will then be used by the machine to print out the relevant parts.

According to ASTM F2792, AM can be classified into 7 different categories based on its process technology as shown in Table 1-1 [21]. Different process technologies are

suitable for manufacturing different materials and many of the current machines in the market use one or more of these processes to fabricate parts. For example, Selective Laser Melting (SLM) or Electron Beam Melting (EBM) combines directed energy deposition and powder bed fusion processes to manufacture metallic components by melting a thin layer of powder at each layer. Stereolithography Apparatus (SLA) on the other hand, selectively cures a vat of photo-polymer resin to form polymeric parts.

Table 1-1: Classification of AM process technology based on ASTM F2792 [21]

Process	Explanation	Machines
Binder Jetting	A liquid bonding agent is selectively deposited to join powder materials	3D Printing (3DP)
Directed Energy Deposition	A focused thermal energy is used to fuse materials by melting as they are being deposited	Laser Engineered Net Shaping (LENS)
Material Extrusion	The material is selectively dispensed through a nozzle or orifice	Fused Deposition Modelling (FDM)
Material Jetting	Droplets of build material are selectively deposited	<u>Polyjet</u>
Powder Bed Fusion	Thermal energy selectively fuses regions of a powder bed	Selective Laser Melting (SLM) Selective Laser Sintering (SLS) Electron Beam Melting (EBM)
Sheet Lamination	Sheets of material are bonded to form an object	Laminated Object Manufacturing (LOM)
Vat Photo-polymerization	Liquid photo-polymer in a vat is selectively cured by light-activated polymerization	<u>Stereolithography Apparatus (SLA)</u>

Designers have utilized this new technology to come up with a new range of ideas ranging from aerospace to food products. General Electric (GE) Aviation had successfully printed functional fuel nozzles for its LEAP engines that were not only 5 times more durable than previous model but also reduced the number of brazes and welds required from 25 to 5 [22]. NASA had also demonstrated the future of AM by printing a ratchet wrench on-board the International Space Station, with the design file

being transmitted from ground to space [23]. In the food industry, Barilla, a pasta company, had recently announced its intention to create new pasta designs by 3D printing that will allow for a whole new eating experience [24].

Current research trends in AM include using it for aerospace [25] and biomedical applications [26], construction [27] and also for topology optimization [28]. Prosthetic or implants can be easily customized based on individual patient's requirement, while topology optimization of products optimizes material layout within a given space and can be easily printed by AM which would otherwise be subjected to manufacturing constraints. The research interest within AM is continuously growing to include different kinds of applications. With increasing research of AM into different fields of applications, more will be able to benefit from the advantages that this technology can provide.

With the rise in popularity of AM and to increase the applications of AM, it would be interesting to study and develop a process that is able to utilize the advantage of this new technique in the fabrication of SOFCs especially since it is also a layer building process with many different components.

1.3. Research Motivation

Presently, most conventional methods of fabricating SOFCs can only result in homogeneous samples being fabricated within a single step. However, gradient-structured electrodes or bilayer electrodes which incorporates an additional functional layer, had been shown to enhance the performance of SOFCs by Holtappels *et al.* [29] and Gross *et al.* [30] respectively, which require each layer of the anode to be fabricated

separately and are usually manually intensive or repetitive and involving a time-consuming sintering process.

The use of AM in the field of SOFCs can potentially help improve and expand the designs of current SOFCs. In addition, gradient-structured electrodes can be easily manufactured through this process by varying either its design, material composition or processing parameters at each layer. In particular, the application of laser-based additive manufacturing such as SLM and SLS on SOFC would greatly reduce the fabrication time and simplify fabrication process. This technique utilizes a high energy density laser beam that is able to locally melt or sinter powdered materials together forming the desired shape in a relative short amount of time replacing long hours of sintering. Furthermore, the excessive powder can be removed and recycled after each process, reducing the amount of wastage, making AM a complementary fabrication technique for SOFC which is also known for being a green technology. Design of the structures can also be easily controlled and modified through CAD software and no moulds are required for each new design as compared to conventional methods. In addition, due to the rapid solidification process experienced by the materials during melting or sintering by laser, new crystallized microstructures might be achieved that were not attainable during normal sintering process, introducing a new area of interest to understand the link between these microstructures with SOFC's performance.

1.4. Research Objectives

The use of direct laser-based AM methods to fabricate SOFCs is a relatively new research area. Although the printing of a wide range of materials had been studied by other researchers, few studies were conducted on materials that are suitable or are being used as SOFC materials. The influence of laser melting on these materials are currently unknown, especially the effect it has on the overall performance of the cell.

The purpose of this research is to study the feasibility of fabricating SOFCs using laser-based AM techniques and the effect of laser on overall fuel cell performance. As this topic is still at its infancy stage and with the difficulty of directly building a full cell at this current stage, we will first focus on the fabrication of metal support structures using AM, and the full cell will be further built on it and tested. Next, the effect of laser scanning on anodic and electrolyte materials were studied.

For the first objective, the research scope covers:

1. Identifying and optimization of a conductive material as metal supports for SOFC by SLM
2. Fabrication of a fully functional fuel cell on the metal support
3. Studying the electrochemical performance of a metal supported SOFC

For the second objective, the research scope covers:

1. Studying the effects of different laser types on ceramic materials
2. Effects of laser-modification on anode surface
3. Effects of laser-modification on electrolyte surface

2. Literature Review

2.1. Principles of SOFCs

SOFCs are solid state devices that utilize an ion conducting ceramic material as the electrolyte. In order to obtain reasonably high performance, the typical operating temperature for SOFCs range from 800 to 1000 °C, whereby ions are able to move efficiently across the electrolyte. SOFCs are composed of primarily 3 components: anode and cathode with the electrolyte positioned in between. Electrodes are responsible for catalysing the fuel or oxidant while ions are conducted across the electrolyte. Figure 1-2 shows the basic operation of a SOFC, with hydrogen being delivered as the fuel to the porous anode and oxidized. The electrons released are forced through the external circuit, before arriving at the cathode side and reacting with oxygen.

During the reaction, oxygen reduction reaction (ORR) occurs at the cathode-electrolyte interface whereby oxygen molecules combine with the electrons from cathode and are reduced into oxygen ions.

These oxygen ions will then migrate through the solid electrolyte layer and arrive at the anode side whereby hydrogen oxidation reaction (HOR) occurs, forming water and releasing electrons as shown in Equation (2)

As the electrons travel from the anode to the cathode side through an external circuit, electricity is generated, and the by-product of this process is only pure water and heat, which are green products that do not contribute to the pollution of the environment.

Combining Equation 1 and 2, the overall SOFC reaction is:

2.1.1. Performance of SOFCs

The performance of a fuel cell can be characterized by its current-voltage relationship, or “I-V curve”, which measures the voltage output for a given current. The theoretical maximum voltage (E) given out by a fuel cell or open circuit voltage (OCV), is defined by the Nernst potential as shown:

$$E = E^0 - \frac{RT}{2F} \ln \left(\frac{\rho_{H_2O}}{\rho_{H_2} \cdot \rho_{O_2}^{\frac{1}{2}}} \right) \quad (4)$$

whereby E^0 is the standard-state reversible voltage, R is the ideal gas constant, T is the fuel cell operating temperature, F is the Faraday’s constant and ρ is the partial pressure of the respective gases.

The standard-state reversible voltage can be further obtained through:

$$E^0 = -\frac{\Delta g_{rxn}^0}{nF} \quad (5)$$

whereby Δg_{rxn}^0 is the standard-state Gibbs free energy change for reaction and n is the number of moles of electrons. For a typical hydrogen-oxygen fuel cell, this equates E^0 to be 1.23V under standard-state condition.

However, the actual cell voltage obtained is always lower than its theoretical value due to irreversible losses occurring during fuel cell operation. The losses can be classified into three major types such as:

1. Activation losses (η_{act}): due to the electrochemical reaction at the electrode/electrolyte interface.
2. Ohmic losses (η_{ohmic}): due to ionic conduction of charge carriers through the electrolyte.
3. Concentration losses (η_{conc}): due to mass transport limitations

Therefore, the actual voltage of a fuel cell can be expressed as:

$$V = E - \eta_{act} - \eta_{ohmic} - \eta_{conc} \quad (6)$$

Figure 2-1 shows a typical I-V curve with the shape of the curve being a resultant of the three different types of losses. Activation losses usually happen at the low current region, while ohmic losses becomes more dominant during the middle current regime. Lastly, under high current density, concentration losses are the most prominent.

Figure 2-1. Schematic of a typical I-V curve [31]

2.2. SOFC Anodes

Anodes are negative electrodes in SOFCs whereby electrons are discharged from the cells. In order to facilitate the flow of fuel and to act as reaction sites for oxidation, the anode requires a porous structure to function efficiently. Its primary function is to promote electrochemical oxidation of the fuels. The electrochemical processes often take place at the interfacial sites or triple-phase boundary (TPB) sites, where anode, electrolyte and gaseous fuel meet. Thus, the anode's performance can be improved by increasing TPB distances leading to more catalytic reactions.

The general requirements of SOFC anodic materials include good chemical and thermal stability, high electronic conductivity under fuel cell operating conditions, excellent catalytic activity towards oxidation of fuels and having matching coefficient of thermal expansion (CTE) with the electrolyte to prevent delamination [32]. Conventionally,

metals which include platinum (Pt), iron (Fe), cobalt (Co) and nickel (Ni) were used as anodes.

Nickel was a common anodic material due to its high electrochemical activity for hydrogen oxidation reaction and lower cost with the electrical conductivity of Ni reaching 2×10^5 S/cm. When comparing the polarization resistance of Pt electrodes with Ni-patterned electrodes, it was found to be higher, which showed that Pt is electrochemically less active than Ni, which prompted more research into this material [33]. However, the use of pure Ni as anode was hindered by the agglomeration of particles at high operating temperature that restricted the flow of fuel and greatly reduced the number of reaction sites available [34]. This issue was first resolved by Spacil, who mixed fine yttria-stabilized zirconia (YSZ) electrolyte material with Ni to inhibit aggregation of Ni particles [35]. These Ni cermet anodes also helped to enhance SOFC performance by providing oxide ion conductivity in addition to the electronic conductivity of the metal and extend TPB [36].

Following the addition of YSZ into Ni, Nickel oxide - yttria stabilized zirconia (NiO-YSZ) became one of the most commonly used anode material due to its lower cost, being chemically stable in reducing environment at high operating temperatures and having similar CTE with YSZ electrolyte [37]. Conventional NiO-YSZ powder were fabricated through mechanical mixing and milling of NiO and YSZ powder in the desired ratio to obtain a homogenous blend of the required powder. Since its conception to overcome issues regarding pure Ni coarsening effect and CTE mismatch, tremendous progress had been achieved for NiO-YSZ. The conductivity of the material depended on the composition, microstructure, distribution of Ni and YSZ phases as well as the amount of porosity present, and these factors were further influenced by the sintering

temperature and heat treatment experienced by the material. Although the ratio of Ni could be increased to improve electrical conductivity, it was more ideal to balance it such that both ohmic and activation polarization were minimized.

In addition to ceramic-based anodes, studies were also conducted on using metal supported SOFCs. As ceramic anodes are more brittle, metal-supported SOFC help provide the mechanical backbone for the operation at a lower cost, while still meeting the requirements of an anode. Furthermore, instead of a homogeneous anode structure, a gradient-structured anode was also helpful in improving the performance of SOFCs by enhancing different properties of the anode at different heights to achieve optimal effect.

2.2.1. Metal Supported SOFC

As electrolyte thickness is reduced to minimize ohmic resistance [38], electrodes needed to be thicker to provide sufficient mechanical support for the fuel cell. However, as these electrodes are commonly made up of brittle ceramic or cermet materials, the mechanical robustness it provided is limited. By replacing the thick anode with a porous metal backbone coupled with a thin layer of functional anode layer, the mechanical robustness of the system can be greatly enhanced, making it easier for implementation into portable applications whereby the cells are likely to experience shock, vibration or mechanical loading [39], while the functional layer allows catalytic activities to take place at the interface.

Metal-supported SOFCs have been prepared using a variety of materials including Ni, FeNi and ferritic stainless steel. Porous Ni tubes that functioned as both support and anode had been fabricated by Mineshige *et al.* [40]. Even though CTE of Ni was higher

than YSZ, thermal stresses were mitigated by having a small tube diameter. During operation, coarsening of Ni particles was usually the issue in SOFC anodes, but Cho *et al.* still managed to obtain reasonable power density of 470 mWcm^{-2} at 800°C [41]. Iron had also been added to Nickel to form Ni-Fe alloys that are strong and relatively easy to produce. Although it helped to lower the CTE mismatch and material cost of pure Ni, it became more susceptible to sulphur and coking.

Ferritic stainless steel was another favourable material choice among developers due to its low cost, good oxidation resistance and low CTE. However, when operating at high temperature and coupled with Ni-YSZ as the anode layer, inter-diffusion between Ni and Iron or Chromium would occur, reducing oxidation resistance and increasing CTE of the steel support. Researches were done to reduce this phenomenon by using fabrication processes that required relatively low temperature sintering such as electrophoretic deposition (EPD) [42], pulsed laser deposition (PLD) [43] and plasma spray [44]. However, these require high cost equipment with complicated procedures and were not suitable for cells of different shapes or having a large surface area.

As thickness of anodes increases, concentration and activation resistance would increase as well. In order to overcome this increased resistance experienced by the anode, gradient anode structures which would provide better performance was conceived.

2.2.2. Gradient Anodes

Anodes fabricated with a variation in porosity or material composition within its structure can be identified as a functionally gradient anode. For a gradient anode, smaller pore sizes near the electrode/electrolyte interface provide for larger surface area

per unit volume or longer TPB distance which helped increase catalytic activities, while larger pores at the electrode/air interface helped to facilitate efficient gas diffusion for the cells [29]. Besides altering the porosity, varying the material composition would also be beneficial for SOFC performance by having a “conduction layer” made of more conductive materials for electrical conduction, while the “functional layer” comprised of materials with higher catalytic activities and have thermal expansion coefficient that matched the electrolyte, preventing warpage and delamination. For example, Aruna *et al.* showed that the addition of YSZ to Ni helped reduce the thermal coefficient of anode from $13.3 \times 10^{-6} \text{ K}^{-1}$ to $10.4 \times 10^{-6} \text{ K}^{-1}$, making it thermally more compatible with the YSZ electrolyte and preventing delamination [45].

Muller *et al.* took it further by envisioning both an anode structure that possess gradient particle size and Ni content in his multilayer anode [46]. Figure 2-2 shows three homogeneous layers, with the first layer consisting of smaller particles of Ni and YSZ in order to achieve smaller porosity and longer TPB distance. Higher YSZ content was also used to ensure that CTE matched with that of the electrolyte. Good electrical contact with the interconnector and efficient gas diffusion was realized using higher Ni content of larger particle sizes at the electrode/air interface.

Figure 2-2. Multilayer anode with gradient composition and porosity [46]

Many researchers had taken advantage of the benefit that gradient anodes provided and improved their anodes by constructing a thin “functional layer” paired with a separate “conduction layer” made with different material compositions. Gross *et al.* demonstrated that this method led to excellent performance of the SOFC reaching a maximum power density of 208 mW/cm² at 700 °C [30]. In addition to the increase in performance, this method allowed different aspects of the anode to be treated individually, allowing greater design flexibility. Several techniques had since been developed to create a gradient anode structure which included multilayer dry pressing [29], multilayer screen printing [47], multilayer tape casting [48], freeze tape casting [49, 50] and phase inversion process [51].

In multilayer dry pressing, the composites were compacted together to form a circular pellet, using different concentrations of graphite as pore formers to vary the porosity within NiO-YSZ. In order to obtain the gradient structure, this process had to be repeated with each varying concentration of graphite at different layers before sintering together [29]. For the multi-layer screen printing method, different sizes of pore formers were added to NiO-YSZ paste in order to vary the porosity obtained before joining the different layers together by screen printing, creating the gradient structure [47]. In multilayer tape casting, the films were fabricated with porosity controlled by the concentration of carbon black added before being laminated together to form the anode [48]. Although these methods had managed in successfully fabricating a gradient anode, the fabrication process tend to be tedious and manually repetitive with each individual layer being fabricated separately, as each layer created are homogeneous in nature with random pores.

Freeze-tape-casting process was a novel process that combines tape casting and freeze casting concepts to tailor continuously graded pore structures [49, 50]. This process involved tape casting of the solvent mixture, followed by dry freezing to create ice crystals within the mixture and lastly to undergo sublimation to remove the ice crystals. Porous structures were created when the ice crystals were changed into gas. Size and density of the ice crystals could be further controlled by varying the solids loading and freezing temperature. Due to the growth direction of ice crystals, pores formed were aligned and showed a gradual decrease in size at the opposite surface. Lastly, the graphite-assisted phase inversion process was a process that required repeated immersion of the anode tube in various solvents for phase inversion reaction to occur, creating various porosity [51]. However, this process required continual and repeated dip-coating of the anode tube to obtain the desired porosity with no control of the uniformity of the pores created.

Although these fabrication methods had shown to be able to fabricate a functionally gradient anode, the common problem was that these processes were still largely repetitive in steps, requiring different layers to be manufactured separately before assembling together. In addition, the porosity and microstructures obtained were largely random with little or no control over the positioning and structure, which would result in ineffectiveness towards gas diffusion and catalytic reactions. This would ultimately reduce the optimized performance that could be achieved by the anode. A new manufacturing technique known as additive manufacturing could potentially be used to overcome these previously mentioned issues by having more precise control over where the pores are positioned.

2.3. SOFC Electrolytes

Electrolytes are dense layer within the SOFC that allows oxygen ions to pass through while preventing cross flowing of fuels in SOFCs. Fuel cell performance can be affected by the electrolyte as it contributes largely to the ohmic resistance of the system. General properties that an electrolyte must possess include having a dense structure, high ionic conductivity, negligible electronic conductivity and stability in oxidizing and reducing environments. Although most electrolytes used ion-conducting materials, there are some research that focus on using proton-conducting material as electrolyte with promising results [52].

Some electrolyte materials that are widely investigated for SOFCs are Ytria Stabilized Zirconia (YSZ), Lanthanum Strontium Gallium Magnesium (LSGM), and Gadolinium or Samarium Doped Ceria (CGO or CSO). The operating temperature of the fuel cell is largely dependent on the ionic conductivity of these material at the given temperature. YSZ is able to fulfill the electrical requirements at high temperature and has good mechanical properties. It is also the most widely used electrolyte material. LSGM has higher ionic conductivity than YSZ, however it is less compatible with LSGM-NiO anodes because of the reactivity of NiO, than the corresponding composite NiO-YSZ anodes are with YSZ. Ceria doped with rare earth materials has received considerable attention recently due to its high conductivity at lower temperature and is suitable for low temperature SOFC operations.

Ytria is doped into zirconia to stabilize the cubic fluorite phase, as well as to increase the oxygen vacancies within the structure. In addition, although the ionic conductivity in YSZ is dependent on the concentration of oxygen vacancies present within the

material, however, the threshold of adding yttria was 8 mole% [53]. Higher yttria content would lead to a decrease in ionic conductivity. Another factor that would affect the ionic conductivity was the transportation of oxygen ion through the electrolyte layer, which is affected by the grain boundary densities.

2.4. SOFC Cathodes

Similar to anode, cathodes must have a porous structure to allow oxygen molecules to flow, where they are reduced into oxygen ions at the interface. For an efficient SOFC operation, the cathode must possess high electronic conductivity, stability in an oxidizing atmosphere, good chemical compatibility, sufficient porosity and high catalytic activity during oxygen reduction reaction.

Perovskite materials which have been widely used as cathode materials in SOFCs, possess the general formula of ABO_3 , in which A and B are cations with a total charge of +6 as shown in *Figure 2-3*. The lower valence A-site cation is composed of a mixture of rare and alkaline earths such as La, Sr, Ca or Ba and coordinated to 12 oxygen anions, while the B-site cation which occupy much smaller space and consists of reducible transition metal such as Mn, Fe, Co or Ni are coordinated to 6 oxygen anions [54]. Therefore, the redox catalytic reaction is usually provided by the B-site cations. By choosing suitable A and B-site cations, overall valence will be less than 6 and a large and stable number of oxygen ions vacancies can be introduced, facilitating bulk ionic oxygen transport [55].

Figure 2-3. Unit Cell of the ABO_3 perovskite structure [56]

2.5. Laser-Based Additive Manufacturing

Laser-based AM is a combination of directed energy deposition and powder bed fusion process. This technique utilizes a high energy laser beam to selectively scan the powder bed thereby transferring enough heat energy to melt or sinter the powdered material, bonding them together. SLM and SLS are two examples of the most commonly used laser-based AM processes. Both of these processes typically vary in their laser systems due to the different materials it focused on with SLM resulting in melting while SLS resulting in sintering of the powdered material.

The interactions between laser and material can be very complex, or in other cases, be simply seen as a heat source. A laser emits electromagnetic radiation through simulated emission and is classified based on the lasing medium used such as Gas laser (CO_2 , excimer), Liquid laser (organic liquid dye), Solid State laser (Nd-YAG, Ti: sapphire, fibre laser), Semiconductor laser (quantum cascade lasers, diode laser) and Free Electron laser [57]. In addition, a laser can further radiate in either continuous wave or pulsed mode, resulting in different energy profiles emitted and the exact wavelength that it is emitted depends on the laser medium as shown in *Table 2-1*.

Table 2-1. Wavelengths for selected laser types [58]

Lasing medium	Laser type	Wavelength
Solid-state	Ruby	694 nm
	Nd:YAG	1,064 nm
	Ti:Sapphire	650–1,100 nm
Gas	CO ₂	10.4 μ m
	Excimer	193 nm (Ar-F)
		248 nm (Kr-F)
		308 nm (Xe-Cl)
		351 nm (Xe-F)
Semiconductor	GaN	0.4 μ m
	Quantum cascade	mid-far IR
Free electron		far IR to vacuum UV

Due to the difference in absorptivity between materials at different wavelength, this led to the development of SLM machines equipped with fiber laser which focused on metallic materials, while SLS machines equipped with CO₂ laser concentrated on polymeric materials. The difference absorptance level between different materials such as metals, carbides, oxides and polymers were studied by Tolochko *et al.*, whereby it was found that metal and carbides experienced higher absorptance level with a lower wavelength of 1.06 μ m, while oxide and polymers showed the opposite effect, having higher absorptance level at 10.6 μ m [59]. Other than the material type affecting absorptivity, factors that will affect the amount of laser energy absorbed by the material included the condition of scanned materials and operating temperature. Powdered materials had shown to possess higher absorptivity compared to bulk material due to internal reflection that increased absorption rate of the laser [60]. As for the temperature dependence of laser absorptance, Zhang *et al.* studied the absorptance of several ceramic materials using Nd:YAG and CO₂ laser and found that the shift in reflection band of the material at elevated temperatures, led to a change in absorptivity of laser at that wavelength [61].

2.5.1. Laser-Based AM of Metallic Materials

The fabrication of metallic parts with AM required the use of a high energy source to join powdered materials together forming the desired parts, due to its high melting point. SLS is a direct energy deposition technique which utilized a laser beam to selectively scan and sinter particles together. When low melting metals or when higher energy was used such that densification occurred due to melting instead, the term selective laser melting (SLM) is often interchangeably used. Currently, due to the trend of directly manufacturing dense metallic components, SLS is primarily used for lower energy processes such as the processing of polymers while SLM is majorly used for achieving fully dense metallic pieces.

As interest in SLM technology among the fields of aerospace, automotive and medicine grew, material research for SLM had also expanded from Steel [62] and Titanium [63] in the early years to include more materials such as Aluminum [64], Copper [65], Inconel [66], Cobalt-Chromium alloy [67] and Gold [68].

Most research on metals had focused on achieving dense metallic parts and also on the mechanical properties in relation to their applications. Several researchers such as Mumtaz *et al.* [69] and Murr *et al.* [70] had shown that parts manufactured using SLM were capable of reaching near 100% density. Mumtaz *et al.* optimized and fabricated high density Waspaloy, while Murr *et al.* studied on microstructural and mechanical behavior of Ti-6Al-4V. During fabrication, materials would undergo complex thermal history including directional heat extraction, repeated melting and rapid solidification unlike conventional methods. These factors would affect the microstructural evolution and thus the eventual properties of that material. Alcisto *et al.* compared the mechanical

properties of Ti-6Al-4V under conventional and laser free form fabrication process. It was found that although both methods produced specimens of comparable mechanical strength, laser processed Ti-6Al-4V showed consistently lower elongation [71]. In general, similar results had been obtained for other SLM-fabricated materials showing comparable mechanical properties but lower elongation [70]. Studies had also been done to control the microstructural growth by varying parameters. This was shown by Bormann *et al.* who built NiTi specimens using different process parameters and obtained different phase transformation temperature due to the formation of different Ti-rich phases as more Ni evaporated at higher energy densities [72].

Porous Structures

Using this new technology, interesting and complex metallic structure could also be achieved. Studies had thus branched out into the design and fabrication of porous light-weight structures for aerospace or medical applications. Well-aligned structures with varying porosities could be pre-design using CAD model and easily fabricated using SLM after optimizing scanning parameters. Yadroitsev *et al.* showed by using stainless steel material that the smallest controlled width between two thin walls obtainable using SLM was about 200 μm , below which the walls will be connected [73]. This was due to the laser spot size and minimum melt width that could be achieved with each scan line. Wang *et al.* further formulated design rules for porous structures fabricated by SLM [74]. Some of the factors that would determine a successful structure included process parameters, inclined angle and geometric features. Optimization of processing parameters allow consistent mechanical strength over the porous structure. When building structures with overhanging features, it should not be smaller than 40° as it will accumulate large residual stress and resulting in warpage of the part. Lastly, any

porous structure designed should consider the printing resolution which was affected by the powder particle size and morphology, laser spot size and heat affected zone.

In addition to well-designed porous structures, more complex and random porous structures were demonstrated by Pattanayak *et al.* using chemical treatment after printing [75]. A bone structure was mimicked by printing a porous titanium structure with pore sizes ranging from 400 to 800 μm , then chemical etching was done on the material to achieve fine networks of titanium oxide with smaller feature sizes. Other methods of fabricating smaller pores included Wang *et al.* who managed to reduce the pore sizes achieved to between 2 and 5 μm by adding small additives into the powder mixture that would sublime when heated, leaving behind smaller random pores [76].

Therefore, SLM had been shown to be an effective new technique for manufacturing dense and porous structures. In addition, with the success of printing metallic materials, there has also been an increasing demand for its use on ceramic materials.

2.5.2. Laser-Based AM of Ceramic Materials

There had been an increasing demand for ceramics with higher complexity and structure such as for medical implants whereby mass customization is required. However, processing of ceramics with high complexity had traditionally been difficult to produce. Methods such as forging, casting, extrusion and machining were capable of only forming parts with simple geometries. AM provided a cheaper alternative for mass customization of ceramic parts with more complex features, thereby expanding the scope of its applications. There had been multiple studies done with regards to the fabrication of ceramic materials, and they can be categorized according to their process technologies. Early works such as ink-jet printing and SLA focused on adding a

sacrificial binder phase within the ceramic materials to bind them together. The binder material will be subsequently burned out after which an additional sintering step was required to densify the specimens. More recent works aimed to sinter or melt ceramics directly using a laser source which eliminates the need for an additional sintering process.

The use of laser-based AM techniques such as SLS and SLM had been studied, either by directly sintering the ceramic particles together, or by an indirect method whereby a sacrificial binder phase was sintered together during the process before being burned out during post heat treatment and densification of the part. Furthermore, in order to produce parts with higher density, there had been studies that utilized slurries instead of powder as the starting material that helped increase the powder bed density and thus the density of parts produced.

Direct Manufacturing via Laser-based AM

In direct manufacturing, a laser beam was used as a localized heat source that partially or fully melted the particles, fusing them together. First, powder was spread evenly onto the platform by the recoater. Next, the laser would selectively scan the cross-sectional area of the part. The first layer is melted directly onto the substrate to allow for better heat conduction during the building process and to prevent delamination of the printed parts. Subsequent layers of powder were deposited by the recoater with the same layer thickness after laser scanning of the previous layer and the process is repeated until the part had completed.

Limited studies had been done with regards to direct laser-based manufacturing of ceramics. However, most of the studies were conducted on alumina and zirconia

materials as they are widely utilized in high end engineering disciplines due to their excellent mechanical strength and resistance to thermal and wear. Bertrand *et al.* first showed that YSZ ceramic parts could be successfully fabricated by direct laser sintering process reaching a density of 56% without any additional binders involved [77]. It was also found that density of the part produced was proportional to powder bed density, which was in turn a function of powder size and shape. Juste *et al.* tried to increase the density of alumina obtained by adding graphite additive into the powder mixture to improve absorptivity of the material and succeeded in obtaining parts of 90% density [78]. Near 100% density zirconia-alumina was further obtained by Wilkes *et al.* via preheating the powder bed to at least 1600 °C, which lowered the thermal gradient and produced crack-free specimens [79].

Slurry-based AM

Slurry-based AM could be seen as a branch from direct manufacturing, whereby ceramic slurries were used instead of powder. This technique helped to increase the powder bed density, thereby allowing ceramic parts of higher density to be built. During the fabrication process, solvent vaporized upon heating by the laser, leaving behind the sintered parts. Finished products were then removed by washing away the remaining slurry surrounding the part.

Tang demonstrated this process by mixing silica powder with an inorganic binder to form a green layer [80]. Other experiments included that of Gahler *et al.* [81] and Klocke *et al.* [82] which did not require the use of a binder phase. Instead, the slurries were formed using only powder and water. Gahler *et al.* had further managed to achieve a density up to 92% of the theoretical density after laser sintering of alumina-silica [81].

Similarly, Tang *et al.* had developed a method by mixing silica sol together with silica particles to form the slurry [83]. This method was named Selective Laser Gelling (SLG) due to the “gelling effect” of colloidal particles or sol. In this process, the sol having nanoparticles would help form networks bridging the distance between larger particles, forming a dense and crack-free green part after laser beam scanning. In addition, by achieving an optimal viscosity of the slurry, internal structure [84] or a multi-channel part with interconnected pores [85] can be fabricated without the use of support.

Indirect Manufacturing via Laser-based AM

Ceramics are materials that have high melting point as well as having low thermal shock resistance. Hence parts produced by the direct method tend to have cracks caused by the thermal stresses. Indirect SLS is a way to obtain ceramic parts with a higher density without the appearance of cracks.

The binders were important in ensuring the quality of the parts produced. It could be classified either as organic or inorganic binders. Organic binders were burned off during the heat treatment process, while inorganic binder could not be removed by thermal treatment and would remain as part of the ceramic. Inorganic binders were typically metal phosphates, metal silicates and metal borides. Lee used boron oxide powder, an inorganic binder, together with alumina powder for laser sintering [86]. Whisker-like aluminum borate grains were observed growing on the surface of the alumina particles as a secondary phase after the heat treatment process, modifying the particles’ microstructure.

Various types of organic binders had already been studied, including stearic acid [87], phenolic [88], poly methyl methacrylate (PMMA) [89] and polyamide (PA) [90]. Due

to low powder bed density, sintered density was limited. In order to further increase the density of final product, Deckers *et al.* used cold isostatic pressing on sintered PA mixed with alumina powders [91]. Isostatic pressing of the samples managed to double the green density of the specimen. However, this method could only work on simple geometry and if internal or intricate parts were concerned, it would not be feasible. Another way to increase the density which was by infiltration was tried by Shahzad *et al.* [92]. Polypropylene (PP) – alumina composite powder which was prepared by a thermally induced phase separation process was used in this experiment. Green SLS part with only a density of 29% to 34%, increased to 64% after infiltrating with alumina suspension, and upon further warm isostatic pressing, a final density of 89% could be obtained.

Although indirect manufacturing methods were able to achieve higher density, it required lots of post processing steps such as burning out of binder, infiltration in some cases and further post sintering. These greatly increased the fabrication time compared to direct manufacturing, whereby no post processing is required.

2.6. Additive Manufacturing of Fuel Cells

Additive manufacturing had been perceived as a cost-effective way of developing fuel cells, with reduced material wastage and higher design flexibility. Various AM technologies had been researched on regarding their use in fuel cells. FDM had been utilized in the fabrication of a miniature PEMFC stack by Chen *et al.* [93]. A reduction in fabrication time during initial development phase was achieved while being able to deliver reliable performance with peak power densities of 99 mWcm⁻² at 0.425 V when connected in parallel and 92 mWcm⁻² at 4.25 V when in series under natural convection.

Graphite PEMFC bipolar plates which were previously difficult to machine due to its brittleness were redesigned and manufactured with three new types of flow field design using SLS by mixing graphite with phenolic as the binder [94].

For the use of additive manufacturing in SOFC, the most commonly used technique would be inkjet printing, which provided a cheaper and faster alternative. Tomov *et al.* demonstrated that with the use of inkjet printing, dense YSZ electrolyte layers of 6 μm thickness could be easily fabricated and were of the same quality as those of conventional method [95]. Similarly, Wang *et al.* had used the sol-gel method combined with inkjet printing technology to create a dense gadolinium-doped ceria (GDC) electrolyte coating which only required a sintering temperature of 1100 °C [96]. In addition, inkjet printing also allowed the printing of a dense electrolyte on an unconventional electrode support structure such as a honeycomb shaped cathode [97]. Beside the fabrication of electrolyte layers using inkjet printing, gradient anode structure with varying material concentration and porosity had been easily fabricated by adding different percentage of graphite as pore formers [98].

Adding on to the research done on printing single component of SOFC, some researchers had managed to build a fully functional SOFC using AM. Sukeshini *et al.* fabricated an anode supported SOFC using inkjet printing showing an OCV of 1.1 V and maximum power density ranging from 0.43 to 0.46 W/cm² at 850 °C [99]. Other than inkjet printing, Manogharan *et al.* had successfully fabricated a fully functional SOFC using the binder jetting technique [100]. In the process of binder jetting, binders are selectively applied to powdered material layer by layer, which will then be burned off during the sintering process, thus achieving the part. As densification of the

electrolyte was an issue with this technique, dilution of the fuel gas was required, and an OCV of only 450 mV was achieved for the cell.

These researches had shown the capability of using AM in manufacturing of fuel cells and the corresponding performances were compiled in *Table 2-2*. However, the use for SOFCs is still limited and these were usually indirect methods of fabrication as it required lots of post processing steps after fabrication. A laser-based AM technique such as SLS or SLM will greatly help to reduce fabrication time, by directly sintering or melting the particles together. In addition, a gradient structured SOFC could be easily fabricated by either changing the material composition or processing parameters during manufacturing.

Table 2-2. Performance of 3D printed fuel cells

Fabrication method	Component printed	Performance	Reference
FDM	PEMFC stack	Operating at 70 °C, Free Convection: 99 mWcm ⁻² at 0.425 V (parallel) 92 mWcm ⁻² at 4.25 V (series) Forced convection: 123 mWcm ⁻² at 0.425 V (parallel) 105 mWcm ⁻² at 5.25 V (series)	Chen <i>et al.</i> [80]
SLS	PEMFC bipolar plates	Single Path Serpentine Flow Field: 0.246 Acm ⁻² at 0.7 V Triple Path Serpentine Flow Field : 0.385 Acm ⁻² at 0.7 V Interdigitated Flow Field: 0.396 Acm ⁻² at 0.7 V	Chen S. [81]
Inkjet printing	SOFC YSZ electrolyte layer	Cell A at 800 °C: OCV - 1.01 V, mWcm ⁻² Cell B at 800 °C: OCV - 1.02 V, 150 mWcm ⁻²	Tomov <i>et al.</i> [82]
Inkjet Printing	SOFC cell: NiO-YSZ/ YSZ/ LSM- YSZ /LSM	OCV: 1.1 V 0.43 - 0.46 Wcm ⁻² at 850 °C	Sukeshini <i>et al.</i> [86]
Binder Jetting	SOFC cell: Ni-YSZ/ YSZ/LSM	OCV: 450 mV (leakage)	Manogharan <i>et al.</i> [87]

Based on the literature review on different fabrication technologies of key components of SOFC and the review of different laser-based AM techniques, it was found that there was a lack of study on the use of direct laser-based AM for the fabrication of SOFCs. In addition, little research was done on the influence of laser processing on SOFC materials. In order to bridge the gap, this research will explore the use of laser-based AM methods to directly fabricate a SOFC and also this research will study the effect of laser scanning on SOFC anode and electrolyte materials as well as the effect on fuel cell performance.

3. Experimental Details

3.1. Additive Manufacturing of Metal Supports for SOFC

3.1.1. Material Selection

Nickel was chosen as the material choice for the metal support. Many metal-supported SOFCs use stainless steel as the material choice due to its low cost, good oxidation resistance and low CTE. However, when operating at high temperature with Ni-YSZ as the anode layer, inter-diffusion between Ni and Fe or Cr would occur, reducing oxidation resistance and increasing CTE of the steel support. Furthermore, when Fe or Cr diffused into the Ni containing anode, insulating oxides could be formed that would weaken catalytic activities at the functional layer [101]. Therefore, Ni is a suitable material choice for the metal support as it does not poison the anode and can eliminate previously mentioned issues. Ni is also strong enough for handling and enduring thermal cycling due to its mechanical strength and ductility [41]. Furthermore, current research on pure Ni using SLM is only limited to one study involving balling behavior of Ni powder with the SLM process [102]. On the other hand, Ni-based alloys such as Inconel [103, 104] and Hastelloy X [105] had been extensively studied, which showed that Ni is a suitable material candidate for SLM usage.

In this experiment, gas atomized spherical nickel powder (TLS Technik GmbH & Co.) with size a size of D90 45 μm or smaller was used in the experiment as shown in Figure 3-1. The powder size had to adhere to a range of 20 to 63 μm as prescribed by the machine, as smaller particle sizes, would lead to uneven spreading of the layer, while larger particle size would clog the recoater.

Figure 3-1. Powder morphology of Nickel used for SLM

3.1.2. SLM Fabrication Process

The machine used for fabrication was SLM 250 HL (SLM Solutions GmbH). The machine is equipped with a fiber laser having a wavelength of 1.06 μm , maximum power of 400 W and a laser spot size of 80 μm . A reduced platform of 100 by 100 mm was used for the print. Steel was chosen as the base plate material due to its low cost, availability as well as having a melting point of around 1370 $^{\circ}\text{C}$ which is slightly lower than nickel's melting point of 1455 $^{\circ}\text{C}$, thus ensuring that good bonding could be achieved between the first few layers and the base plate, which is important for the success of subsequent layers. As SLM is an additive process, an error at the earlier stages will be accumulated to cause failure in the final print job.

Optimization of the material's parameter was conducted by first performing single line scans over a larger parameter setting and narrowing it down further. Single lines with varying power and scanning speed were drawn by the laser to determine suitable parameters as described by Table 3-1. The process was repeated 20 times with each

layer thickness being 50 μm to produce a thin wall structure with a height of 1 mm for easier observation.

Table 3-1. Variation of single lines parameters

Layer Thickness		Laser Power (W)			
50 μm		350	300	250	200
Scanning Speed (mm/s)	200	SL _{A1}	SL _{B1}	SL _{C1}	SL _{D1}
	250	SL _{A2}	SL _{B2}	SL _{C2}	SL _{D2}
	300	SL _{A3}	SL _{B3}	SL _{C3}	SL _{D3}
	350	SL _{A4}	SL _{B4}	SL _{C4}	SL _{D4}
	400	SL _{A5}	SL _{B5}	SL _{C5}	SL _{D5}
	450	SL _{A6}	SL _{B6}	SL _{C6}	SL _{D6}
	500	SL _{A7}	SL _{B7}	SL _{C7}	SL _{D7}
	550	SL _{A8}	SL _{B8}	SL _{C8}	SL _{D8}
	600	SL _{A9}	SL _{B9}	SL _{C9}	SL _{D9}
	650	SL _{A10}	SL _{B10}	SL _{C10}	SL _{D10}
	700	SL _{A11}	SL _{B11}	SL _{C11}	SL _{D11}
	750	SL _{A12}	SL _{B12}	SL _{C12}	SL _{D12}
	800	SL _{A13}	SL _{B13}	SL _{C13}	SL _{D13}
	850	SL _{A14}	SL _{B14}	SL _{C14}	SL _{D14}
	900	SL _{A15}	SL _{B15}	SL _{C15}	SL _{D15}
	950	SL _{A16}	SL _{B16}	SL _{C16}	SL _{D16}
	1000	SL _{A17}	SL _{B17}	SL _{C17}	SL _{D17}

Next, a 2^4 -factorial test was conducted to determine the significance of four different factors by comparing with the resulting relative density of the SLM fabricated part. The four parameters varied were laser power, scanning speed, hatch spacing and distance from center as shown in Table 3-2. The printed blocks are placed in a circular pattern away from the center.

Table 3-2. Factorial test to determine significant factors for SLM of nickel parts

Factors		Values	
		Low (-)	High (+)
Laser Power (W)	A	200	350
Scanning Speed (mm/s)	B	200	500
Hatch Spacing (mm)	C	0.1	0.2
Distance from <u>centre</u> (mm)	D	20	40

After that, a structure possessing thin wall features with increasing spacing in-between each wall was designed as shown in Figure 3-2. The laser processing parameters were also shown in Table 3-3. The thin walls were drawn with a thickness of 0.001 mm, which was below the printing capability of the machine to simulate a thin wall structure and determine the smallest feature size achievable. The spacing in between each thin wall was increased by 0.1 mm after each wall from 0.1 mm to 0.9 mm. This was used to understand the smallest spacing available for distinct individual thin walls to occur and to incorporate these values into future designs.

Figure 3-2. Thin wall structure with increasing space in-between (a) CAD file and (b) printed part

Table 3-3. Processing parameters of thin wall structure

		Scanning Speed (mm/s)				
		100	200	300	400	500
Laser Power (W)	150	A1	B1	C1	D1	E1
	200	A2	B2	C2	D2	E2
	250	A3	B3	C3	D3	E3
	300	A4	B4	C4	D4	E4
	350	A5	B5	C5	D5	E5

Lastly, porous block structures were fabricated by keeping the power constant while varying the hatch spacing, scanning speed and scanning orientation angle as described in Table 3-4. The scanning orientation angle is the angle at which the scanning angle is increased with each layer as demonstrated in *Figure 3-3*. This allowed for different porous structures to be created easily, by manipulating the scanning patterns. After the experiment, the blocks were weighed using a balance with reference to a dense block and the porosity of the blocks could be inferred from these results.

Figure 3-3. Visualisation of scanning line at different layers with different scanning angle such as (a) 90 ° and (b) 45 °

Table 3-4. Scanning parameters for (a) 90°, (b) 30° and (c) 45° scanning angles

(a)		Angle 90°	Scanning Speed (mm/s)				
			100	200	300	400	500
Hatch Spacing (mm)	0.2	T1 _{A1}	T1 _{B1}	T1 _{C1}	T1 _{D1}	T1 _{E1}	
	0.3	T1 _{A2}	T1 _{B2}	T1 _{C2}	T1 _{D2}	T1 _{E2}	
	0.4	T1 _{A3}	T1 _{B3}	T1 _{C3}	T1 _{D3}	T1 _{E3}	
	0.5	T1 _{A4}	T1 _{B4}	T1 _{C4}	T1 _{D4}	T1 _{E4}	
	0.6	T1 _{A5}	T1 _{B5}	T1 _{C5}	T1 _{D5}	T1 _{E5}	
	0.7	T1 _{A6}	T1 _{B6}	T1 _{C6}	T1 _{D6}	T1 _{E6}	
	0.8	T1 _{A7}	T1 _{B7}	T1 _{C7}	T1 _{D7}	T1 _{E7}	

(b)		Angle 30°	Scanning Speed (mm/s)				
			100	200	300	400	500
Hatch Spacing (mm)	0.4	T2 _{A1}	T2 _{B1}	T2 _{C1}	T2 _{D1}	T2 _{E1}	
	0.5	T2 _{A2}	T2 _{B2}	T2 _{C2}	T2 _{D2}	T2 _{E2}	
	0.6	T1 _{A5}	T2 _{B3}	T2 _{C3}	T2 _{D3}	T2 _{E3}	
	0.7	T1 _{A6}	T2 _{B4}	T2 _{C4}	T2 _{D4}	T2 _{E4}	
	0.8	T1 _{A7}	T2 _{B5}	T2 _{C5}	T2 _{D5}	T2 _{E5}	

(c)		Angle 45°	Scanning Speed (mm/s)				
			100	200	300	400	500
Hatch Spacing (mm)	0.4	T3 _{A1}	T3 _{B1}	T3 _{C1}	T3 _{D1}	T3 _{E1}	
	0.5	T3 _{A2}	T3 _{B2}	T3 _{C2}	T3 _{D2}	T3 _{E2}	
	0.6	T3 _{A5}	T3 _{B3}	T3 _{C3}	T3 _{D3}	T3 _{E3}	
	0.7	T3 _{A6}	T3 _{B4}	T3 _{C4}	T3 _{D4}	T3 _{E4}	
	0.8	T3 _{A7}	T3 _{B5}	T3 _{C5}	T3 _{D5}	T3 _{E5}	

3.1.3. Fuel Cell Fabrication

The detailed procedures for fabrication of a complete fuel cell are illustrated in Figure 3-4. First, the SLM-fabricated Ni metal support was first heated in air to 1400 °C for 2 h, whereby the surface of the structure was oxidized into NiO. This step is to lower the difference in CTE mismatch between the metal support and the anode layer, which

would cause warping when sintering together. Next, NiO-YSZ slurry (Fuel Cell Materials) was coated on top of the structure and dried at 300 °C before a second layer was coated to achieve a flat and even surface. Subsequently, the green anode support was sintered at 1400 °C.

The YSZ electrolyte suspension was prepared by mixing YSZ powder, ethanol solvent, polyvinyl alcohol (PVA) binder, polyethylene glycol (PEG) and dibutyl phthalate (DBP) plasticizer and fish oil dispersant together and ball milling the mixture overnight to obtain a dispersive and stable suspension. The weight ratio of PVA: PEG: DBP: fish oil is 1:1:1:1 at 1 wt% to ethanol solvent in total, while the YSZ powder was at 5 wt% to the ethanol solvent. Desirable electrolyte thickness was achieved by repeatedly spray coating the surface and waiting for the solvent in previously deposited layer to evaporate. After the spraying process, the green half-cell was sintered at 1500 °C for 5h to densify the electrolyte.

Lastly, the cathode layer was painted on the electrolyte surface using a paint brush. Platinum (Pt) ink (Heraeus Materials) was used, with the thickness controlled at 20 µm. A glass slide was used to scrap off excess ink and maintain the thickness across the cathode layer. The cathode was sintered at 1000 °C for 2 h before testing.

Figure 3-4. Flowchart of SOFC fabrication process

3.1.4. Characterization of Electrochemical Performances

Electrochemical characterization was performed using a customized testing station. The fuel cell was sealed to an alumina tube using ceramic sealant on the anode side along with the metal support. A smaller alumina tube was placed inside which supplied the dry hydrogen gas at 50 sccm and a Pt mesh was attached at the end for collecting current on the anode side. The cathode side was exposed to ambient air while Pt mesh was similarly used for current collection. The cell was operated at 800 °C and heated up at a rate of 5 °C/min. I-V and Electrochemical Impedance Spectroscopy (EIS) measurements were characterized by an electrochemical potentiostat (Solartron 1470E, Solartron Analytical, UK). EIS data was measured at open-circuit voltage (OCV) values and scanned from 1 MHz to 0.1 Hz.

3.2. Effect of Laser-modification on SOFC materials

3.2.1. Effect on NiO-YSZ Anode Material

Comparison between laser system on NiO-YSZ

Commercial NiO-YSZ powder (Fuel Cell Materials) was used in the following experiment. Figure 3-5 showed the morphology of powder used with a Brunauer-Emmett-Teller (BET) surface area of 1-4 m²/g. For the comparison between laser sources, SLM 250HL (SLM Solutions GmbH) and HRPS-VII SLS Machine (Wuhan Binhu Mechanical & Electrical Co., Ltd) equipped with fibre laser having 1.06 µm wavelength and CO₂ laser having 10.6 µm wavelength respectively were used in the experiment.

The powder was laid evenly on the platform of both machines and flatten to ensure an even surface during laser scanning. Next a single layer scan was performed on the powder while maintaining the same laser power and scanning speed ratio of 0.4. Due to the difference in capability between the machines, for the fibre laser, a power of 400 W and scanning speed of 1000 mm/s was used, while for the CO₂ laser, the scanning strategy was 100 W power and scanning speed of 250 mm/s was used.

Figure 3-5. SEM image of NiO-YSZ powder used with BET surface area of 1-4m²/g

Effect of laser power on NiO-YSZ

The NiO-YSZ anode substrates were fabricated using NiO-YSZ powder (Fuel Cell Materials) using die-pressing methods. NiO-YSZ powder was dissolved in ethanol solvent while 1 wt% of PVB binder was added into the mixture, before being grinded down using mortar and pestle. Next, 0.3 g of powder was die-pressed using a 10 mm circular mould with a force of 2 tonne. The green anode substrate was subsequently sintered at 1400 °C to achieve a dense structure.

Next, to study the effect of the laser influence on NiO-YSZ, a continuous CO₂ laser system with a wavelength of 10.6 μm (Wuhan Binhu Mechanical and Electrical Co., Ltd, China) was used to scan the surface of the NiO-YSZ substrates. Laser powers were varied between 20 to 80 W to study the microstructural changes, while the scanning speed and the hatch spacing was maintained at 10 mm/s and 0.1 mm respectively.

Electrochemical Testing

After laser modification on the anode surface using a laser power of 20 W, a complete fuel cell was fabricated using the electrolyte and cathode fabrication method as depicted in Figure 3-4 and discussed in chapter 3.1.3 A similar anode-supported cell without laser modification was also fabricated for comparison. Next, electrochemical testing was conducted on the fuel cells using a similar setup as the previous experiment. 50 sccm of dry hydrogen was supplied to the anode side, while the cathode side was exposed to ambient environment. The cells were tested at 800 °C and heated up at a rate of 5 °C/min. I-V and Electrochemical Impedance Spectroscopy (EIS) measurements were characterized by an electrochemical potentiostat (Solartron 1470E, Solartron Analytical, UK). EIS data was measured at 0.7 V values and scanned from 1 MHz to 0.1 Hz.

3.2.2. Effect on YSZ Electrolyte Material

Fabrication of YSZ substrate

Electrolyte substrates were prepared using YSZ powder (Tosoh, Japan). First, 1 g of YSZ powder was die-pressed using a mold with 25 mm diameter at 2 tonne force as shown in Figure 3-6(a) and then sintered at 1500 °C for 5 h to achieve a dense substrate

with a diameter of 18 mm and thickness of approximately 0.8 mm. Next, the YSZ electrolyte substrates were grinded using abrasive paper up to 1200 grit size.

On the cathode side of the YSZ electrolyte, laser scanning using a continuous CO₂ laser system of 10.6 μm wavelength and maximum laser power of 100 W (Wuhan Binhu Mechanical and Electrical Co., Ltd, China) was introduced in Figure 3-6(b). Laser power used was reduced to a range below 30 W to prevent the occurrence of cracks on the scanned surface. The speed of the laser was maintained at 1000 mm/s, while the hatch spacing was fixed at 0.1 mm. Figure 3-6(c) shows the schematic of the fabrication process as described previously. A parameter study was conducted by varying the laser power using 0 W, 10 W, 15W and 20 W and labelled as A, B, C, D respectively as shown in Figure 3-6(d).

Electrochemical Testing

Electrochemical characterization was performed using a customized testing station. A functional SOFC was fabricated by sputtering platinum for 20 mins to create 200 nm thick electrodes on both surfaces which would function as the anode and cathode as shown in Figure 3-6(e). The cells were annealed at 550 °C for 12 h before operating at a temperature of 450 °C, with 50 sccm of dry hydrogen supplied as fuel on the anode side and the cathode side being exposed to ambient air. Gold ring was connected on the anode side as a current collector, while a platinum probe was used on the cathode side. I-V and Electrochemical Impedance Spectroscopy (EIS) measurements were characterized by an electrochemical potentiostat (Solartron 1470E, Solartron Analytical, UK). EIS data was measured at open-circuit voltage (OCV) values and scanned from 1 MHz to 0.1 Hz.

Figure 3-6. Schematics of electrolyte supported SOFC with laser surface modification. (a) Die-pressing of YSZ powder, (b) Laser scanning of YSZ electrolyte surface, (c) Cross-sectional view after laser scanning, (d) YSZ scanned with different laser parameters and (e) a fuel cell configuration for testing

4. Additive Manufacturing of Metal Supported SOFC

The initial study focused on the fabrication of a metal support for SOFC. The metal support structure for SOFC must be able to facilitate efficient diffusion of gas towards the reaction sites, while possessing novel change in structure from the top to the bottom. The first phase of this study will be a parameter study on different printing parameters for Ni in order to achieve the optimized printing parameters and to understand the effect of these parameters. Next part of the study will be on the fabrication of a functional fuel cell that was built on the metal support structure. Lastly, an electrochemical test was conducted to determine the performance of the SOFC and its feasibility.

4.1. Optimization of Processing Parameters

4.1.1. Single Line Track

The first experiment was conducted to narrow down suitable parameters for subsequent experiments by scanning thin lines with varying scanning speed and laser power combinations. The use of a single scan that created thin lines allowed a larger range of laser parameters to be tested on the base plate in a shorter amount of time as the laser only needs to scan a single path.

From the experiment, Ni powder was found to have been successfully melted together on the steel substrate creating a tight bond between the first layers, demonstrating that steel was a suitable substrate material for Ni. If the substrate was incompatible with the material, delamination will occur due to difference in thermal expansion. All combinations of parameter settings were able to achieve visible single melt tracks as observed in Figure 4-1. Although these different parameters successfully produced

single melt tracks, the surface profile of these lines varied according to the parameters used. At higher laser power of 350 W, the scanned lines showed a rougher surface profile as evidenced by the uneven surface observed in Figure 4-1, with the presence of balling observable at some locations. In contrast, as the power was lowered to 200 W, smoother lines were achieved.

Balling which induced high surface roughness on the fabricated part would be harmful for the building process. This can result in the overall printed height being taller than the platform stage, which would damage the recoater during the recoating process, and cause subsequent layers to be unevenly coated, thus failure of the printed part [102]. Balling is formed due to surface tension of the melt and can be formed when insufficient laser energy input result in limited liquid content or splashing of molten pool at high scanning speed [106]. As the nature of balling is random, with no control over the location that it will occur, thus it was important to avoid processing parameter which would lead to balling.

Based on this initial testing, it was shown that steel is a suitable substrate material for this experiment and all parameters tested were able to successfully melt and create a thin structure. Thus, all subsequent experiments would be carried out on the steel substrate. However, a conclusive result for the optimal processing parameter could not be obtained based on the thin lines printed. Therefore, in the next test a more detailed parameter study was conducted to identify significant factors that would affect the outcome of printing Ni components by SLM.

Figure 4-1. Single track melting of Nickel showing balling on the surface at higher power (red) and a smoother line at lower power (green)

4.1.2. Parameter Study

A 2^4 -factorial experiment was conducted by varying the following parameters: Laser Power (A), Scanning Speed (B), Hatch Spacing (C) and Position on substrate (D). Factorial testing is an efficient way to evaluate the effects of multiple factors in the least number of experiments, by comparing two extreme setting of the same parameter with other parameters. Figure 4-2 showed the positioning of the sample for each run, where the blocks fabricated were randomly positioned. After the Ni blocks were printed, the density of these blocks was measured using Archimedes' principle and compared with 8.9 g/cm^3 as the full density of nickel, Table 4-1 shows the average relative density of fabricated Nickel blocks.

Figure 4-2. 2^4 factorial experiment of SLM fabricated Nickel

Table 4-1. Results of the 2^4 -factorial experiment showing the average relative density of each parameter setting

A	B	C	D	Average Relative Density
-	-	-	-	0.987
+	-	-	-	0.986
-	+	-	-	0.965
+	+	-	-	0.983
-	-	+	-	0.977
+	-	+	-	0.969
-	+	+	-	0.905
+	+	+	-	0.942
-	-	-	+	0.965
+	-	-	+	0.989
-	+	-	+	0.954
+	+	-	+	0.991
-	-	+	+	0.961
+	-	+	+	0.984
-	+	+	+	0.884
+	+	+	+	0.943

Figure 4-3. Analysis of effects: Laser power (A), Scanning speed (B), Hatch spacing (C), Positioning from centre (D)

Figure 4-3 showed the analysis and effect of different parameters on the density of printed parts with factors A, B and C demonstrating a larger effect, while factor D showed little effect on the outcome. This showed that the positioning of the specimen has little influence on the resultant density. Thus, for subsequent print jobs, the entire substrate could be used without impacting the results. From the results obtained, an increase in laser power had a positive effect on the density obtained, while scanning speed and hatch spacing resulted in the opposite. This was because when a higher laser power was used, it ensured that the powder would be fully melted and the liquid would be able to flow and fill the gap between particles, while low laser power could only cause partial melting of the particle and not help to densify the part. As for the scanning speed, at lower speed, more energy was absorbed by the particles which resulted in better melting, while for smaller hatch spacing, the decrease in distance between scan

lines ensured that heat affected region of each melt track would overlap each other, creating a dense structure. Based on the above-mentioned conditions, energy density transferred by the material to the powder bed can be formulated into Equation (7) which states that the energy density supplied by the laser is proportional to the laser power, but inversely proportional to the scanning speed and hatch spacing.

$$\begin{aligned} & \text{Energy Density (J/mm}^3\text{)} \\ &= \frac{\text{Laser Power (W)}}{\text{Scanning Speed (mm/s)} \times \text{Hatch Spacing (mm)} \times \text{Layer Thickness (mm)}} \end{aligned} \quad (7)$$

4.1.3. Porous Structures

As the purpose of this study was to create a metal support structure that is suitable for SOFC, the next study will move on to the fabrication of porous structures. As discussed by Wang *et al.*, when printing porous structure using SLM, the geometric feature of the design is important in determining a successful build [74]. In this case, the feature that is of concern is the melt width of the laser scanning track as this determined the minimum pore size that could be achieved. Figure 4-4 showed the printed structure that was designed with varying width between each thin wall to determine the minimum designed pore size that can be achieved.

Figure 4-4. Printed thin wall structure with varying spacing

Figure 4-5. Melt width of thin wall structure with varying energy densities

As the laser scanned the powder bed, the powder in its path was melted. The melt width is the width of the melted track and was measured using optical microscopy or scanning electron microscopy. Figure 4-5 showed the relationship between average melt width obtained from the thin wall structures with varying energy densities. Based on the fitted curve, it was observed that the melt width increased with increasing energy densities supplied. The increase in melt width with higher energy density supplied, was a result of more particles experiencing melting, thereby expanding the heat affected region and thus the size of the melt width. In addition, due to the high amount of energy density transmitted by the laser, particles in the surrounding region also experienced partial melting and were bonded to the side of the melt track increasing the overall size and

the surface roughness. However, from the fitted curve, there is a limit to the melt width, as higher energy density input would be used to increase the temperature of the melt pool, resulting in vaporization, instead of melting of more particles. Non-continuous melt tracks were also observed at higher energy densities, due to the decrease in melt viscosity and Marangoni effect becoming more dominant [107]. Marangoni effect was the result of a difference in surface tension between 2 melt pools. The liquid would flow from lower surface tension to higher surface tension, resulting in the non-continuous melt track. The difference between the melt tracks obtained was illustrated in Figure 4-6 which showed optical images of two different specimens fabricated with low and high energy densities respectively. Figure 4-6(a) showed clean straight lines printed at lower energy densities, while Figure 4-6(b) showed a large melt width with the presence of many particles sticking to the side of the melt track and making the tracks indistinguishable. On the contrary, there would be a minimum energy density required for melting of the particles to occur.

Figure 4-6. Optical image of melted track at (a) low and (b) high energy densities

Although thin clean straight lines were obtained at lower energy densities, but the size of the melt width was still considered large for meaningful usage in SOFC as this would reduce the surface area available for catalytic activities. This was due to the machine's

limitation in scanning a designed structure. During the scanning process, the machine's laser system was required to scan both the border and the interior of the part, which resulted in multiple scanning being produced, even though the structure was designed according to the melt width that was previously determined.

Thus, a novel method of creating porous structure was created which considered the previously mentioned limitations. For the new printing method, a basic shape such as a cube was created and the hatch spacing was varied at different orientation and distance to create the different porous structures. By increasing the hatch spacing, the gap between each scan line was increased, thereby creating a small pore, while the change in scanning angle helped to create different porosity patterns for the structure. Figure 4-7 showed the structures after printing at various energy densities, while Figure 4-8 showed the top view of the structures at changing scanning angles. It can be observed that as the distance between the spacings were increased, the structure was visually more porous, and by changing scanning angles, different pattern of overlays can be achieved.

Figure 4-7. Porous SLM structures by varying hatch spacing and scanning speed

Figure 4-8. Pore structure of (a) 90°, (b) 30° and (c) 45°

Figure 4-9. Density of blocks vs energy density supplied

Porosity of the fabricated structures was determined by comparing it with the relative density of the blocks, since porosity of the block structures was inversely proportional to the relative density measured. Comparison was conducted between different scanning direction with energy density and the results were shown in Figure 4-9. An exponential curve was fitted for the results. As energy densities supplied to the fabricated part was affected by the hatch spacing, increasing it would decrease the energy density. As expected, at lower energy densities, higher porosity was found in the blocks. This was due to larger hatch spacing which resulted in larger gaps found between each melted track, creating more holes within the structure. However, the energy densities converge to 10 J/mm³ as below that limit, a successful build could not be formed. Interestingly, similar trends were obtained when scanning angle was varied at 30°, 45° and 90°, demonstrating that energy density, which was affected by the hatch

spacing, played a more important role in altering the percentage of porosity present than the overlaying patterns. This could be due to the large hatch spacing involved which decreased the impact of scanning angles on the porosity percentage.

Even though porosity of the structures did not show any significant changes with regards to the scanning angle, however, based on the top view images of the structures in Figure 4-8, smaller orientation angles resulted in more overlapping of the scan lines between layers thus resulting in smaller overall connected pore sizes. This would result in higher contact surface area for catalytic reactions while maintaining high porosity for gas diffusion.

One issue with the increase in hatch spacing was the balling effect that was clearly observed in all three specimens in Figure 4-8. This was due to the lack of support in previous layers to conduct accumulated heat away, resulting in balling of the material. Although the balling phenomenon was frequently avoided in other SLM applications, in the case of a metal support for SOFC, it could be a beneficial occurrence as the balls helped to increase contact surface area especially at the interface.

4.2. Fuel Cell Performances and EIS Characteristics

4.2.1. Fabrication of Metal-supported Fuel Cell

The final design of the metal support was a two-layer porous structure with grid-like pores by alternating scanning angles at 90° for efficient gas diffusion, while the top layers was fabricated by intersecting grids at 90° and 45° in a single layer to form a denser structure as shown in Figure 4-10(a). Due to the layer being a mesh of 2 different structures, it provided higher densification for anode layer to be coated on top.

After the fabrication of the metal support, the next step was to incorporate the metal structure with a functional SOFC. The anode, electrolyte and cathode layers were subsequently fabricated on top of the structure using more traditional methods. The main issue during the fabrication was the mismatch of CTE as well as the difference in shrinkage rate between different materials.

Due to the difference in CTE experienced between Ni and NiO-YSZ, warpage of the metal support was observed after sintering at high temperatures when NiO-YSZ was directly coated on Ni, resulting in cracks and warping of the anode surface (Figure 4-10(b)). In order to overcome this issue, CTE of the metal structure was reduced by first oxidizing the Ni supports into NiO at high temperature. Subsequently, when the NiO-YSZ slurry was coated, due to similar CTE values, no warping of the anode structure was observed. Coating of NiO-YSZ was conducted twice to ensure a smooth surface was obtain for easier electrolyte deposition.

The anode support had to be pre-sintered first before coating, as the high shrinkage occurring within NiO-YSZ during densification would result in cracks formation on the YSZ surface otherwise. Thus, the anode support was sintered to full density at 1400 °C first before a thin layer of the electrolyte layer was subsequently sprayed on the anode support using YSZ suspension and densified at 1500 °C. The spray coating method allowed a thin layer of YSZ to be evenly deposited on the substrate. When thicker layers of YSZ were coated using YSZ slurry or unevenly coated on the anode support, cracks and isolated islands were formed on the material (Figure 4-10(c)). Delamination would also occur when the heating rate was increased to 5 °C/min, thus the heating rate of the fabrication process was reduced to 2 °C/min to reduce thermal stress on the material. These methods ensured that a flat half-cell was fabricated before Pt cathode was painted

on it and sintered at 1000 °C. Figure 4-10(d) showed the final metal-supported SOFC that was fabricated.

Figure 4-10. Process optimization of fuel cell fabrication process

4.2.2. Electrochemical Performance

The electrochemical performance of the SLM-fabricated metal support SOFC was tested at 800 °C and the I-V and EIS curves were shown in Figure 4-11. Based on the I-V curve, the OCV obtained was 0.53 V which is significantly lower than the referenced value of around 1.1 V found in literatures, while the power density obtain was only 11.0 mW/cm². The lower OCV value could be caused by the decreased in partial pressure of hydrogen gas, due to leakage from the Ni structure. From Figure 4-12(a), it was observed that small pores were found on the Ni surface, which was a result of NiO reducing back into Ni during the testing process.

Figure 4-11. I-V curve and power density of the metal supported SOFC

From the Nyquist plot in Figure 4-13, the polarization resistance obtained was $2.5 \Omega\text{cm}^2$, while ohmic resistance was $3.8 \Omega\text{cm}^2$ and based on the bode plot, the dominant factor in the resistance was due to the poor charge transfer at the interface. As each layer thickness during the SLM process was $50 \mu\text{m}$, a thick layer of NiO-YSZ was required to be coated on the top of the Ni structure to achieve a flat and smooth surface for subsequent process. This thick layer of NiO-YSZ restricted the flow of gas to the interface, and thus the reduction NiO to Ni at the interface was limited as shown in Figure 4-12(b). This resulted in the increase in polarization values achieved.

Figure 4-12. (a) Ni structure and (b) NiO-YSZ anode layer after testing

Although the current performance of the SOFC was not optimal and further optimization of the fabrication process is required, this experiment demonstrated the potential of fabricating a functional SOFC using SLM fabricated metal supports.

Figure 4-13. (a) Nyquist and (b) bode plot of metal support SOFC

4.3. Chapter Summary

In this study, a novel method of fabricating porous structures for SOFC metal support by SLM was discussed. A step-by-step process was conducted to identify and understand different factors that would affect the printing process. Laser power, scanning speed and hatch spacing were found to influence the printability of the parts.

After printing the metal support, a functional fuel cell was built on the metal support using more conventional methods. A sequential fabrication process was discussed to resolve issues that were faced when building the cell.

Lastly, the electrochemical performance of the functional SOFC was analyzed. Although the performance of the cell was poor, with OCV reaching only 0.53 V with a low power density of 11.0 mW/cm², this process had shown the feasibility of building a SLM-fabricated metal support SOFC. Further optimization of the fabrication process will be required to obtain better electrochemical performance.

5. Effect of Laser-modification on SOFC Materials

The use of SLM in fabricating a metal support had been demonstrated in the previous chapter with the subsequent anode, electrolyte and cathode layer being coated on top using a conventional slurry coating technique. However, to further develop a SOFC that can be fully fabricated using laser-based AM technique, how the SOFC materials will interact with laser has to be fully understood before continuing with the printing.

Current fabrication methods typically involve a lengthy sintering process to densify the material at each fabrication step before testing such as the coating method used in the previous chapter. The use of laser as a fabrication tool would greatly shorten these processes by directly densifying the particles either by melting or sintering depending on the intensity of the laser parameters used. Furthermore, the combination with AM processing technique allows gradient-structured electrodes to be fabricated directly by altering the laser parameters and different components can also be directly printed on top of each other.

Another issue with SLM of ceramic components was the formation of cracks on the specimens after the process which greatly reduced the mechanical strength of the part. Among different ceramic materials researched, YSZ material was one of the more frequently studied for its use in SLM, due to its use in a wider range of applications. Bertrand *et al.* first showed that YSZ was successfully fabricated by SLM, however, the resulting density obtained was only 56% [77] which is not ideal for SOFC, whereby a dense electrolyte layer is required. Further studies by Liu *et al.* studied the effects of preheating the powder bed on the crack formation as well as the microstructure achieved [108]. The microstructure obtained by laser scanning would also be different

from that of conventional sintering process. Thus, it is important to understand the effects that laser has on the material and whether it is beneficial or detrimental to the overall electrochemical performance, before proceeding to print it by laser-based AM.

In this chapter, the influence of laser on two common SOFC material was discussed. NiO-YSZ and YSZ anodic and electrolyte material were tested by scanning a laser beam across the material surface to study the changes that occurred.

5.1. Effect on NiO-YSZ Anode Material

Laser surface treatment of materials have been used in a wide range of applications including surface cladding, surface roughening or texturing and surface melting [109]. Due to the high energy density heat source that is generated from the laser, it can be used to change the metallurgical and mechanical properties of the material. NiO-YSZ which is a commonly used anodic material in SOFCs were traditionally sintered at high temperatures of 1300-1400 °C for a mechanically stable structure to be achieved.

Dhalenne *et al.* first demonstrated the use of laser floating zone method on NiO-YSZ to produce well-aligned eutectic lamellar structures [110]. Utilizing the formation of these lamellar NiO-YSZ eutectics through laser floating zone method, Laguna-Bercero *et al.* further produced channeled Ni-YSZ cermets through reduction, which enhanced the long-term stability of the material and provided a pathway for efficient gas diffusion [111].

In addition to the lamellar eutectic obtained, laser processing technique can also help to eliminate the long sintering process required in previous applications, through the use of a localized energy beam to heat up the particles causing it to melt or sinter

together. Therefore, in this research, the use of laser as a heating source for surface densification of powdered NiO-YSZ was studied.

5.1.1. Influence of Laser on Surface Microstructure

The absorptivity of laser by different materials had been discussed by Tolochko *et al.*, which showed the different laser wavelengths that are suitable for different types of materials [59]. In order to better understand the type of laser suitable for NiO-YSZ material, the first study would examine the effect of two different laser sources on NiO-YSZ.

The two different laser sources used were Nd:YAG fibre laser and CO₂ laser system, with a wavelength of 1.06 μm and 10.6 μm respectively. Similar laser processing parameters were used for comparison between the two laser sources and the resulting scanned tracks were shown in Figure 5-1. Fibre laser processed specimen in Figure 5-1(a) showed obvious melt tracks which overlapped the previous ones, demonstrating that sufficient energy was supplied to the powder for it to behave in a liquid-like behavior before solidification took place. In contrast, a smoother surface was achieved in Figure 5-1(b) by CO₂ laser, although some regions did not appear dense due to the low energy supplied. This issue could be resolved by reducing the hatch spacing in subsequent scanning.

However, at higher magnification in Figure 5-2(a), the process that took place seemed to be liquid-state sintering of the particles instead of full melting as small crystallites were observed being bonded together. Nano-sized gaps were observed between each crystal, resulting in a less dense structure. This was due to the low absorptivity of laser energy by NiO-YSZ, which only allowed its surface to reach the melting point, instead

of the whole particle. In contrast, the specimen processed by CO₂ laser showed higher densification as observed in Figure 5-2(b). Instead of individual crystals, the microstructure showed the appearance of grain growth as depicted by the black line, showing that melting had occurred on the material's surface. From this study, CO₂ laser had been shown to be more suitable energy source for heating NiO-YSZ material as compared to fibre laser due to better absorptivity of the laser energy. These results were consistent with those presented by Tolochklo *et al.* which showed that the absorptivity of CO₂ laser by oxide materials was approximately 20 times higher than with fibre laser [59].

Figure 5-1. Melt track of NiO-YSZ using (a) fibre laser and (b) CO₂ laser

Figure 5-2. Microstructure of NiO-YSZ processed by (a) fibre laser and (b) CO₂ laser

5.1.2. Influence of Laser Power on Microstructure

After determining that CO₂ laser system was a better heat source for NiO-YSZ material, the next experiment studied on the microstructural changes that occurred to the specimen surface when processed at various laser power settings. A noticeable change in the specimen was the glassy metallic green surface obtained after laser scanning. This was due to the vitrification of ceramic material when supercooled from the liquid phase which resulted in the glass surface [112].

Dendrite features were observed in all specimens fabricated as shown Figure 5-3. A lower scanning speed ensured that more energy was absorbed by the material, resulting in larger grains being formed, thereby no grain boundaries were observed compared to Figure 5-2. As the laser power was increased, the grains became more aligned. From Figure 5-3(a)-(d), the microstructure evolved from having a random configuration to one which was more aligned in the same direction. The appearance of the dendrite features was affected by the energy density of the laser used. According to Hao et al, the difference in microstructure observed was due to the different degrees of constitutional supercooling experienced by the material [113]. In his study of a single line track, the three distinct microstructures could be observed separately at the center, midpoint and edge of the track. Pena *et al.* also showed that as the growth rate increase, dendrite microstructures were formed which transits from a planar to cellular regime, whereby the size of colonies were getting smaller until it became homogeneous [114]. In relation to this study, the different laser power resulted in the difference in growth rate of the microstructure and due to the convection flow within the liquid phase which melts off secondary arms [113], only primary arms with no branches were observed.

The realignment of the microstructure was due to the growth of the grains according to the thermal gradient.

Figure 5-3. Microstructural change in NiO-YSZ surface layer using CO₂ laser at (a) 20 W; (b) 40 W; (c) 60 W; (d) 80 W

The cross-sectional view showed the depth of influence of the laser, whereby different microstructures were observed at varying depth as shown in Figure 5-4 (a) – (c). When compared to a conventionally sintered cell in Figure 5-4 (d), which showed a random structure, the laser-modified specimens showed distinctly different microstructure. Near the surface which laser was scanned, particles absorbed the most energy and experienced full melting. This resulted in a columnar microstructure near the surface which was due to the growth direction being perpendicular to the solidification front. As heat energy was used at the interface, the lower regions received lesser energy for

melting and sintering, thus resulting in partial sintering of the particles away from the interface.

Figure 5-4. Cross section of the specimen having 3 different microstructures. (a) columnar microstructure; (b) equi-axed dense microstructure and (c) partially sintered particles and (d) a conventionally sintered cell

5.1.3. Comparison of Electrochemical Performance

Electrochemical performance between SOFCs fabricated using cells that were laser-modified with a power of 20 W was compared with a normal cell that was fabricated conventionally without laser modification to determine the effect of laser influence on SOFC. Overall, the laser-modified SOFC demonstrated a lower performance in Figure 5-5 with the OCV at 0.75 V compared to 0.84 V, which was obtained using a normal cell. This also resulted in a lower power density of only 9.15 mW/cm² compared to 19.0 mW/cm². From the results, it was clear that the performance was poor in Figure 5-5, due to the presence of micro-cracks within the anode structure due to the large thermal gradient caused by the laser processing technique. The polarization resistance was also found to be larger than the conventional one at 14 Ωcm^2 compared with 9.9 Ωcm^2 . In addition, it was shown that the adhesion of the electrolyte layer to the anode layer was not as good, resulting in a shift in the ohmic resistance.

However, when comparing the bode plot in Figure 5-5(c), it was observed that the dominant effect of the polarization resistance shifted from the high frequency to intermediate frequency range. This signified that the with laser modification, charge transfer kinetics was improved. This was likely due to the columnar microstructure found at the interface that promoted charge transfer. However, oxygen adsorption/dissociation seemed to be compromised with such microstructure.

Figure 5-5. Comparison of (a) I-V, (b) Nyquist plots and (c) Bode plots for laser-modified and normal SOFC

5.2. Effect on YSZ Electrolyte Material

Among the many electrolyte materials used to date, YSZ has been the most widely used, due to its chemical stability and excellent ionic conductivity at high operating temperatures [53]. However, the performance of SOFCs can be attributed directly to the conditions of the YSZ electrolyte such as the thickness [115], mean grain size [116] and density of grain boundaries at the interfacial surface [117].

The efficient transportation of oxygen ions across the electrolyte is important in determining its overall fuel cell performance. Knoner *et al.* had shown that fast transport of oxygen ions occurs at grain boundaries [118]. However, De Souza *et al.* found no evidence for fast diffusion along grain boundaries, instead it was found to hinder oxygen transport [119]. Shim *et al.* further demonstrated an enhanced surface exchange rate with higher concentration of grain boundaries as compared with the bulk, resulting in a smaller cathodic impedance [120]. This improvement was attributed to the higher concentration of vacancies near the surface with increased grain boundaries and the grain boundaries that intersects with external surfaces being a preferred pathway for oxygen ions. On the other hand, Peters *et al.* had shown that electrical conduction decreases with smaller grain size due to poor charge transport at the grain boundaries [116]. Therefore, an electrolyte with a hybrid microstructure which incorporates the advantage of possessing larger grain sizes within the bulk region for fast ionic transportation, and smaller grains at the surface region increased surface exchange rate will be beneficial to the reduction of the overall resistance.

A relatively faster and more efficient way of changing surface microstructure can be obtained using a low-intensity laser. As the localized heat source travels across the

substrate, the area scanned would receive higher thermal energy, allowing only the surface material to experience melting and rapid solidification, resulting in a change in grain sizes. The use of laser on YSZ is not uncommon, and had been regularly used in the field of thermal barrier coatings to provide a dense thin layer with micro-grains for better thermal insulation properties [121]. Laser glazing of the YSZ surface has been also used to eliminate surface porosities and defects as well as improve surface roughness [122].

5.2.1. Influence of Surface Laser-modification on Electrochemical Performance

Laser scanning on the surface of YSZ substrates transfers large amount of thermal energy into the material instantly which induce high thermal stresses on the surface causing cracks, especially in ambient conditions, whereby temperature gradient is large. When higher laser power was used, huge cracks were formed, splitting the substrate into multiple pieces. As the laser power used was lowered, penetration depth of the crack was reduced, keeping the substrate intact, even though cracks were still observed on the surface. Figure 5-6 showed the difference in surface morphology when a laser of higher intensity was used instead of low intensity. From Figure 5-6(a), which showed the YSZ surface after higher intensity (30 W) laser scanning, it was observed that the surface had experienced melting as evident by the smoother surface coupled with the visible scanning tracks. However, micro and nano-cracks were also observed on the surface. This caused isolated islands being formed when platinum was sputtered as electrodes, resulting in a loss of conductivity across the surface and overall poor performance in the initial testing due to the small reactive area. To alleviate the thermal stress and cracks formation issue, the intensity of the laser power used was further

reduced to 20 W such that the no visible cracks were observed after laser scanning as shown in Figure 5-6(b). The surface morphology obtained was similar to that of Figure 5-6(c), which was without laser modification. Therefore, lower laser intensity which ensured the absence of cracks and conductivity across the cathode's surface was used for subsequent experiments.

Figure 5-6. Morphological observation of YSZ surface after (a) high (30 W), (b) low (20 W) intensity laser scanning and (c) as-fabricated

Figure 5-7 illustrated the comparison of electrochemical performance measurements of laser-modified and as-fabricated SOFCs. From Figure 5-7(a), OCV values obtained range from 1.03 to 1.08 V, and the power density achieved from tested SOFCs was highest in specimen B at 2.38 mW/cm^2 while specimen A only achieved 1.86 mW/cm^2 at 450°C , demonstrating an increment of 28%. In general, the performance of SOFCs had shown to improve after laser scanning on the cathode side of the YSZ electrolyte,

with the increase in power density. This improvement in performance could be justified by the lower polarization resistance observed in the laser-modified specimens as shown in Figure 5-7(b).

Based on the equivalent circuit used to fit the EIS measurements, the polarization resistance showed a decreased of approximately 4 times from $513 \Omega/\text{cm}^2$ in specimen A to $124 \Omega/\text{cm}^2$ in specimen C. Therefore, it could be seen that laser modification on the electrolyte surface had led to a positive effect by helping to reduce the polarization resistance of the cell.

The bode plot can be further used to provide insights to the factors that dominated within the polarization resistance. In general, the phase angles at high (10^6 - 10^3 Hz), intermediate (10^3 - 10^0 Hz) and low frequencies (10^0 - 10^{-1} Hz) are associated with charge transfer, surface exchange of oxygen adsorption/dissociation processes and gas diffusion processes respectively, which can be used to help understand the reaction kinetics of the cell. From the bode plot in Figure 5-7(c), the most prominent effect of the polarization resistance was found to be in the lower frequency region of 10^1 for all the specimens. However, it was also observed that the polarization resistance was slightly suppressed after the use of laser on the surface. Thus, it can be deduced that the resistance was mainly affected by the oxygen adsorption/dissociation process that shifted the curve to the higher frequencies. When higher power setting was used in specimen D, the increase in polarization resistance was due to the increase in defect on the surface, while specimen B and C showed much better results due to the lower intensity modification on the surface.

From the cross-sectional image of the specimen after laser modification in Figure 5-8, it was found that the microstructure near the surface which interacted with the laser, showed finer grains as compared to the unaffected region. This was likely due to the recrystallization that happened when laser was scanned across the surface. The smaller grain size near the surface allowed for more efficient surface exchange kinetics, while the bulk region of the electrolyte also allowed oxygen ions to diffuse efficiently through the bulk electrolyte, which led to a reduction of overall polarization resistance [123].

Figure 5-7. (a) I-V, (b) Nyquist plots and (c) Bode plots for laser-modified and as-fabricated YSZ electrolytes. A, B, C, D represents electrolyte surfaces modified by laser using 0 W, 10 W, 15 W, 20 W respectively.

Figure 5-8. Cross-section of laser-modified YSZ electrolyte

5.3. Chapter Summary

In this chapter, the effect of laser on SOFC materials were studied. For the anode material, NiO-YSZ, it was found that CO₂ laser system was a better energy source compared to fibre laser due to the better absorptivity experienced by the material leading to significant melting and grain growth of the microstructure. The microstructure obtained on the material's surface also showed the growth of dendrite features which were affected by the laser processing parameters. When comparing the performance of the laser-modified anode surface with a conventionally-fabricated cell, the overall performance was observed to have decreased. However, the charge transfer kinetics showed significant improvement, while oxygen adsorption/dissociation was affected.

For the study on electrolyte material, laser-modified YSZ electrolytes were compared with as-fabricated cells. It was found that while higher intensity resulted in cracks on the surface which was detrimental to overall performance, lower power intensity can result in a reduction in polarization resistance. The improvement was due to the better oxygen adsorption/dissociation process that resulted from the smaller grain sizes near the interface.

Therefore, from these results, it was shown that the use of laser on SOFC materials could result in some positive effect on the electrochemical performance. Although this work only studied the effect of different components separately, based on these results, it was shown that laser-based AM is still a viable option in using it as a fabrication tool for SOFC.

6. Conclusion and Future work

6.1. Conclusion

In this thesis, a series of studies to develop a process which utilized laser-based AM techniques to fabricate SOFCs was conducted. First, this study started with the fabrication of a metal support for SOFC that was printed using SLM. A functional SOFC was constructed on the metal support and tested for its electrochemical performance. Next, the influence of laser on common SOFC materials was also studied by scanning the laser on NiO-YSZ and YSZ anode and electrolyte material.

From the printing of a porous metal support structure for SOFC, it was found that the major factors that affected the printability of the structure were the laser power, scanning speed and hatch spacing. A porous metal structure was further developed after optimization of the printing process. Next, during the fabrication of a functional SOFC on top of the metal support, a series of processes was demonstrated and discussed which resolved issues faced when building the cell. Although the performance of the metal-supported SOFC was not ideal, reaching a power density of only 11.0 mW/cm^2 , it demonstrated the feasibility of using AM as a fabrication tool for SOFCs.

The influence of laser on NiO-YSZ material resulted in the formation of dendrite features at the surface with columnar grains growing from the interface. The microstructure was found to be influenced by the laser processing parameters. When comparing the performance of these laser-modified SOFCs, it showed a decrease in overall performance. However, the charge transfer kinetics was found to be significantly improved with the new columnar microstructure at the interface.

Lastly, the effect of using laser to modify YSZ electrolytes on its cathode surface, showed that the polarization was reduced due to the better oxygen adsorption/dissociation process that resulted from the smaller grain sizes near the interface.

In conclusion, although the development of a SOFC using laser-based AM techniques is still in its infancy stage, the experiments conducted in this thesis showed that there is still a potential for this fabrication technique. The influence of laser on SOFC materials had shown some positive effects on the performance which can be enhanced by further optimization of the process.

6.2. Future works

In this thesis, a laser-based AM technique was proposed for the fabrication of SOFC. However, a fully functional SOFC was not yet established using AM techniques and only the metal support was successfully printed. In order to incorporate the use of AM into SOFC, the following works are proposed.

- Optimization of metal support design

The metal support was successfully printed using SLM as demonstrated in the thesis, however, the structure was based on a simple basic shape. Thus, more efforts could be placed into optimizing the structure and fabricating more complex designs. The newer designs could also incorporate the requirements of a flow channel and make it an integrated component, while also being a mechanical support for the fuel cell.

- Direct printing of SOFC materials using laser-based AM

The influence of laser on SOFCs' materials showed that laser-based AM is a promising technology that can not only fabricate but also the process can enhance some aspects of the fuel cell. Due to the poor thermal properties of ceramic materials, efforts need to be made to eliminate the occurrence of cracks. This is particularly important for the electrolyte, which requires a dense structure. Pre-heating of the powder bed can help eliminate the occurrence of cracks, while having a higher packing density of the powder bed, prevents excessive shrinkage of the material during fabrication.

Appendix A

Flowability of the powder is essential for a successful build especially when using AM as a fabrication technique. As AM uses a layer by layer technique, how well a layer of powder is dispersed determines the successfulness of the build.

Powder under pressure experienced irreversible changes in the powder particles such as resulting in agglomeration or caking of the particles, by the creation of strong bonds between these particles that restricted the flow of the powder. Most powders would experience such issue when being stored in a container. Pressure exerted was created by the weight of material above it over an area of powder which increased with depth. Hence, flowability test was conducted on the two different NiO-YSZ powder samples with different morphologies to determine the effect of such pressure on the flow. During the test, spherical powder was observed to behave more like a fluid with a near constant surface level in Figure A-1(a), while the granular powder exhibits an uneven surface level with the top pile of powder toppling down during rotation causing an avalanche as demonstrated in Figure A-1(b).

Figure A-1. Image of (a) spherical and (b) granular NiO-YSZ powder during rotation

When comparing a non-viscous liquid such as water rotating in the drum, the surface level would remain horizontal, while a solid block moves up the drum as it rotates before tipping over. Powdered materials possess behavior that is somewhere between solid and liquid which builds up to a maximum (break energy) before flowing to a lower energy state (rest energy). By measuring the change in potential before and after the powder creates an avalanche, the flowability of the powder can be determined. Higher avalanche energy will result in poor flow of the powder as evidence by liquids such as water having zero avalanche energy.

After rotation of the powders at 0.6 rpm for 150 avalanches, the avalanche energies of the powders were recorded. From Figure A-2, spherical powder exhibited lower average avalanche energy of 7.73 kJ/kg, while the granular powder showed around 3 times higher average avalanche energy of 21.56 kJ/kg. Based on the avalanche energies recorded, granular powder would have a poorer flowability resulting in an uneven distribution of the powder on the platform. Both powders were then further deposited using the recoating system from SLM250 HL as shown in Figure A-3 to further prove the relationship between flowability and avalanche energy. From Figure A-3(a), it could be observed that spherical powder with lower avalanche energy had successfully spread a thin even layer of powder across the platform. On the other hand, granular powder appeared as small clumps on the platform that were unevenly spread. Therefore, spherical powder would be more suitable for use in additive manufacturing, due to its ability to create a thin, even layer.

Figure A-2. Avalanche energy graph of both spherical and granular particles

Figure A-3. Spreading of (a) spherical and (b) granular powder on the platform

Appendix B

In this preliminary study, NiO-YSZ material was printed using SLM 250HL. The focus of this experiment was to determine the printability of this material by printing small cubes using different laser parameters. Although NiO-YSZ was an anode material that required a porous structure for SOFC application, the printing of a dense structure was conducted instead. This was due to the fact that the material will experience reduction to become Ni-YSZ during testing which will create smaller pores, that would be more efficient for catalytic activities to occur.

Figure B-1. NiO-YSZ samples built using SLM

Figure B-1 showed the printing of NiO-YSZ material on a steel substrate. The parts produced were fragile and difficult for handling and removal. Specimens built using higher energy densities, were more tightly bonded to the substrate as the material and the substrate were both melted and bonded together. However, loosely bonded parts that resulted in delamination occurred in parts that were subjected to lower energy densities. Compared to Ni parts fabricated previously, NiO-YSZ parts were weak and fragile, breaking apart when a small force was exerted, demonstrating the brittleness of the material. Thus, upon retrieval some parts were unintentionally broken or brushed off.

Based on the remaining specimens, it was observed that the specimens built were different from what was designed. Overall, the printed parts were shorter than designed, with the edges being slightly taller than the center region. This could be due to low powder bed density which resulted in insufficient powder left within the center region. When the border region was first scanned, thermal energy was transferred to the powder as well as the trapped air between powder particles. The rise in temperature caused air within the powder to expand, resulting in dispersion of powder as laser scanned, which was observed as fumes during the printing process. As the process was continued layer-wise, this error became cumulative. When the error was large enough, the penetration depth of the laser was not able to bond additional layers with the previously melted layers, thus the finished product differed from designed. In addition, shrinkage of the material caused subsequent scanning to have insufficient material for melting, thus the edges were built taller than the other parts.

In addition, surface cracks and small pores can also be observed on the surface of the specimens in Figure B-2 due to thermal stresses experienced by the material. Under further magnification in Figure B-3, coral-like microstructures were observed with gaps found between each particle demonstrating that the effect of rapid solidification which resulted in limited grain growth. The dendrite arms that extended from the particle's center was due to the grain growth direction being influenced by the thermal gradient. In order to prove that these features were as a result of rapid solidification, the specimens were reheated to 1400°C and a dense microstructure was shown obtained as shown in Figure B-4.

Figure B-2. Overview of printed specimen's surface

Figure B-3. Surface morphology at higher magnification

Figure B-4. NiO-YSZ after reheating at 1400°C

Figure B-5. NiO-YSZ built using two different parameters for top and bottom layers

Next, in order to improve the printability of the material, two different scanning parameters within a single specimen was used for the print. The bottom layers were scanned using higher energy density to ensure that the material had bonded well with the substrate, forming the “new” base for the next parameter, so that subsequent layers could be built upon NiO-YSZ material. Figure B-5 showed the results of this new processing method, whereby the surface profile achieved was flatter and even.

From this study, it showed that the printing of NiO-YSZ using SLM is a potential fabrication process for SOFC. Although a 3D-printed anode was not yet achieved using SLM, based on previously mentioned study, this could be done by manipulating the printing process.

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