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OPPORTUNITIES FOR FABRICATION OF SOFC ANODE USING SELECTIVE LASER MELTING

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ABSTRACT: Solid oxide fuel cells (SOFC) are electrochemical devices that have the potential to be the future for energy applications. However, current fabrication techniques could not fully optimize the performance of the anode. This paper looks into the opportunities of using additive manufacturing as a possible manufacturing technique for SOFC anode. In particular, selective laser melting (SLM) which is able to produce well-structured metallic products is discussed as a possible technique to fabricate functionally gradient anodes. Although SLM is a possible fabrication method, the limitation of minimum pore sizes produced still needs to be further researched. The study on SLM for SOFC is still at its early stages, and still needs more detailed studies to achieve the desired results.

ANODE OF SOLID OXIDE FUEL CELLS

Solid oxide fuel cells (SOFC) are electrochemical devices that convert chemical energy from gaseous fuel into electrical energy. It comprises of primarily three components: anode, electrolyte and cathode. Gaseous fuel flows through the anode and is oxidized while air is reduced when it flows through the cathode. In contrast to other types of fuel cells, all components in the SOFC are solid and the electrolyte is made of ceramic material that acts as a barrier to prevent the flow of electrons, while transporting ions across. SOFC has the potential to be the future for energy applications being able to achieve higher energy conversion efficiency compared with traditional heat combustion engines and produces lower carbon emission as its byproduct when compared with the burning of coal, reducing the issue on pollution (Wachsman, Marlowe, & Lee, 2012).

SOFC anodes are porous structures that allow fuel to flow through acting as reaction sites for oxidation. Anodes require long three phase boundary distance as well as having suitable diffusion paths for the fuel and exhaust gases for it to work efficiently. Thinner electrolytes which help to lower operating temperature have led to the need for anode-supported SOFC due to their lower mechanical properties. This has resulted in the fabrication of thicker anodes to support the electrolytes. However, thicker anodes will lead to higher overpotential which consists of the concentration polarization resistance and the activation polarization resistance as compared to thin anodes.

As resistance is increased in the anode, higher electrocatalytic activities are required by the anode material to overcome the losses. The anode material must be able to show high electronic conductivity, sufficient electro-catalytic activity, be chemically stable in oxidizing environment and be thermally compatible with other components (Minh, 1993). The choice of anode is

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dependent on the electrolyte that is used and must be compatible with it. Traditionally, anodes are made of conductive metals and the Ni/YSZ cermet is still commonly used as anodes for researches (Jacobson, 2009). The addition of YSZ helps to match the thermal expansion coefficient of the electrode with the electrolyte at the same time utilizing the excellent catalytic properties of Ni. Anodes are commonly fabricated using the tape-casting method (Jiang & Chan, 2004). This process involves spreading of the ceramic powder on a flat surface and stripping it off when dried before laminating with the electrolyte. The composite is then sintered together to obtain the anode structure. However, for lab-based fabrication, powder compacting and die-pressing techniques are still frequently used. The sample will then be sintered at temperature ranging from 1100°C to 1400°C to join the powder particles together. Based on current fabrication techniques, the common pore size achieved is on average 1 µm for the "conduction layer", and about 0.24 µm for the "functional layer", which is the layer allowing gas flow and interface layer with electrolyte respectively (Kim, Hyun, Moon, Kim, & Song, 2005). The smaller pore size reduces the gas permeability but helps to ensure that a dense electrolyte layer could be formed. The size of the pores is dependent on the pore formers used, diameter of the particles used and also the sintering temperature. When two particles are sintered together, parts of their surface will be bonded together, leaving a small gap in between as shown in Figure 1. A higher sintering temperature will result in more surfaces to be bonded, while a smaller particle size will naturally result in a smaller pore. These fabrication processes that could only obtain a homogeneous anode with similar pore sizes would not be able to fully optimize the performance of the anode due to the different reactions occurring at the "conduction layer" and "functional layer".

FUNCTIONALLY GRADIENT ANODE

In order to further enhance the reactivity of anode, anodes with gradient porosity structure were proposed (Holtappels, Sorof, Verbraeken, Rambert, & Vogt, 2006). At the electrode/electrolyte interface, smaller pore size is required to provide a larger surface area per unit volume that contributes to longer triple phase boundary as well as providing support for dense electrolyte fabrication while larger pores are needed near the surface to facilitate efficient gas diffusion. It had been shown that anodes with gradient porosity demonstrated a higher electrochemical performance, showing higher power density, lower ohmic loss and lower total overpotential, compared to homogeneous anodes (Jono, Suda, & Hattori, 2007). Various techniques had been researched on to create a gradient anode such as the multi-step dry pressing (Holtappels et al., 2006), multi-layer screen printing (Jono et al., 2007), freeze-tape-casting (Y. Chen, Bunch, Li, Mao, & Chen, 2012; Sofie, 2007), multilayer tape casting (An, Song, Kang, & Sammes, 2010) and phase inversion method (L. Chen, Yao, & Xia, 2014).

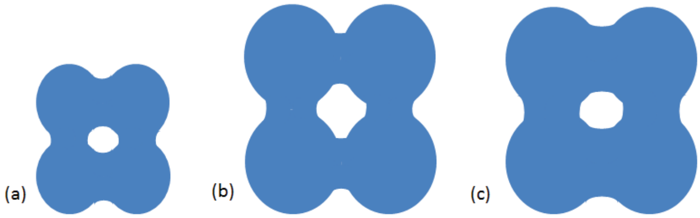

Figure 1. Effect of sintering on pore size (a) smaller particle size, (b) low sintering temperature, (c) high sintering temperature

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 in NiO-YSZ (Holtappels et al., 2006). In order to obtain the gradient structure, the process has to be repeated and the different layers sintered together. For the multi-layer screen printing method, different sizes of pore formers are added to NiO-YSZ paste to vary the porosity obtained before joining the different layers by screen printing (Jono et al., 2007). In tape casting, the films were fabricated with porosity being controlled by the concentration of carbon black added before being laminated together to form the anode (An et al., 2010). Although these methods had managed in successfully fabricating a gradient anode, but the pores created are random and it requires individual layers to be fabricated separately before joining them together. The graphite-assisted phase inversion process is a process that requires repeated immersion of the anode tube in various solvents for the phase inversion reaction to occur creating various porosity (L. Chen et al., 2014). However, this process requires continual immersing of the tube to obtain the desired porosity with no control of the uniformity of the pore sizes created. Freeze-tape-casting process is a novel process that combines tape casting and freeze casting concepts to tailor continuously graded pore structure (Y. Chen et al., 2012; Sofie, 2007). The process involves tape casting of the solvent mixture, dry freezing it and undergoing sublimation to remove the ice crystals. The porous structure is created when the ice crystals change into gas and can be altered by varying the solids loading and freezing temperature. Although unique pore shapes can be made with this technique, the fabrication process still requires joining of different layers together as a post process.

Current fabrication methods are able to obtain the functionally gradient anodes. However, these processes are largely repetitive in steps and require different layers to be fabricated separately. This had reduced the ability to mass produced SOFC anodes which could lead to its commercialization. In addition, the pore size and location fabricated via current methods are usually random and could result in closed pores that are ineffective towards gas diffusion. This would reduce the optimize performance that can be obtained by the anode.

ADDITIVE MANUFACTURING FOR ANODE

Selective laser melting (SLM) is a new promising technique that can be used to eliminate the problems faced by conventional method. Additive manufacturing is a manufacturing method that is rapidly gaining interest. It allows the user to fabricate complex designs with interior features due to its layer by layer nature. SOFC anodes with pre-designed pores or structures could be manufactured with the help of SLM, which is able to produce metallic structures. In SLM, the CAD file of the structure is first designed and inserted into the machine which will then slice it into different layers. Next, the machine will print out the design one layer at a time. The machine process can be viewed as a two-step process whereby the powder is first deposited and spread evenly on the platform. Next the laser will scan the pre-determined path, melting any metal powder in its way. The process will then be repeated until the final product is achieved. This layer by layer addition of material allows for customized structures to be manufactured and would be suitable to fabricate a well-structured anode.

Pore Size

Porous structures have been extensively studied using SLM due to its ability to manufacture controllable porosity by varying the processing parameters (Li, Liu, Shi, Du, & Xie, 2010). Most of the applications currently studied are for use in the medical field. The fabrication of an artificial bone structure is one such application whereby a porous titanium structure of pore size 400-800µm having fine networks of titanium oxide was successful in realistically mimicking the real bone structure after chemical treatment (Pattanayak et al., 2011). In SLM, different pore sizes are pre-defined by the user through the CAD drawing, thus a structure consisting of various pore sizes at the required location can be easily fabricated. This is in contrast with the current fabricating techniques used in anodes, which does not allow control of the position of the pores.

Although the SLM machine is able to manufacture a well-aligned structure with various porosities, however the minimum size of the pores achievable is at least 100 µm. The width of the melt track and subsequently the minimum pore size obtained is determined by the power of the laser, hatch distance, scan speed as well as the laser spot size (Stoffregen, Fischer, Siedelhofer, & Abele, 2011). It had been shown that the smallest distance between two thin walls of width 140 µm for stainless steel is 200 µm and below this distance, the walls are connected (Yadroitsev, Shishkovsky, Bertrand, & Smurov, 2009). The larger pores manufactured by SLM would reduce the surface area in which the gaseous fuel will be in contact with the anode, lowering electro-catalytic activities. The thickness of a button cell SOFC anode is usually about 500 µm to 1mm, thus having a pore size of about 100 µm would limit the variation in pores that can be achieved and would not be of help in enhancing the performance of the anode.

In order to achieve a small pore feature using SLM, several methods can be used. First, the parameters can be adjusted so that instead of a obtaining a fully dense structure, uncontrolled porosity can be introduced into the struts whereby the gas is able to flow through. Secondly, the balling effect can be intentionally created on the surface of the struts so that there is a larger surface area for interaction for the anode. Studies have shown that spherical balls of 10 µm could be formed without affecting the quality of the melt (Li, Liu, Shi, Wang, & Jiang, 2012). Lastly, small additives can be added into the powder mixture that will sublimate when heated to create smaller pores of sizes 2 µm to 5 µm (Wang, Shen, & Gu, 2011). This process can help to form a porous structure when the gas escape from the melt pool or when there is not enough energy for it to escape, a bubbly surface feature can be obtained. Although the largest controlled pore size that is fabricated by SLM currently is significantly larger than required, novel ideas can be used to enhance the surface of the struts either through balling or smaller pores that facilitate the reactivity of the anode. These smaller features would be closer in dimension to those that are obtained through traditional methods

Gradient Material Composition

The material of anodes are usually homogeneous due to the traditional fabrication process, however a gradient material composition would help in its performance by having the "conduction layer" made of conductive material while the "functional layer" comprising of materials with thermal expansion coefficient that matched the electrolyte. The addition of YSZ to Ni helps reduce the thermal coefficient of the anode from 13.3×10^{-6} $cm.cm^{-1}K^{-1}$ to 10.4×10^{-6} $cm.cm^{-1}K^{-1}$ (Aruna, Muthuraman, & Patil, 1998), making it more thermally compatible with the electrolyte and prevents delamination. It also helps to lower polarization resistance and extend the length of the triple phase boundary where electro-catalytic activities occur into the anode (Virkar, Chen, Tanner, & Kim, 2000). Traditional fabrication techniques for anodes can only produce anodes with a uniform and monolithic microstructure. However, researches have shown that most of the electro-catalytic activities of anode happen near the electrolyte interface. A thin "functional layer" paired with a separate "conduction layer" made from different materials had been shown to exhibit excellent performance with a maximum power density of 208 mW/cm^2 at 700°C (Gross, Vohs, & Gorte, 2007). Conventional fabrication of anodes is not able to utilize this feature to its advantage. Hence there is a move towards creating a graded structured anode whereby the layer closest to the electrolyte would contain a higher composition of YSZ in order to increase electro-catalytic activities and reduce thermal coefficient. On the other hand, the upper layers require as little YSZ added as possible to maximize the conductivity of the anode. Various methods have been attempted in the fabrication of graded anodes such as the fabrication of a functional layer on top of the substrate by air brushing (Y. Chen et al., 2012) and lamination of different layers together (Gross et al., 2007). Although these techniques have shown to be able to fabricate a graded anode structure, it is often a complicated process that also requires each layer to be fabricated individually before joining them together.

SLM with its layer by layer addition of materials allows for faster and easier fabrication of the graded structures. The required material's powder needs to be first arranged in the powder feed chamber according to the desired position of the material in the anode. The re-coater will next deposit these powders layer by layer onto the platform. As the powder has already been arranged beforehand, user interaction is minimized during the machine's operation, simplifying the whole process. The successful fabrication of Waspaloy, a nickel-based superalloy, with increasing amount of zirconia from 0% to 10% (Mumtaz & Hopkinson, 2007) and a varying composition of stellite, copper and tungsten alloy with a gradient resolution of 30 μm (Yadroitsev, Bertrand, Laget, & Smurov, 2007) have shown that fabrication of graded structures is possible using SLM. By varying the material in the z-axis, graded anodes with various compositions can be fabricated easily in one step as compared to traditional methods and help to maximize the performance.

CONCLUSION

The current fabrication methods are still limited in ways to enhance the performance of the anode. SLM showed great promise as a new technique that is able to enhance the structure of the anode, through giving it more flexibility in structural design. Although the minimum pore sizes that can be achieved by the SLM are still considered large, further research could be done to minimize the size of the pores. In addition, the optimized pore size and shape that enhances performance can be looked into to better utilize the benefits of SLM. The potential of fabricating fuel cells using SLM are still in its infancy and will perhaps give rise to a more efficient method of generating energy.

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