Materials and Design 106 (2016) 51–59

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Electrical conductivity and porosity in stainless steel 316L scaffolds for electrochemical devices fabricated using selective laser sintering

Khairul Amilin Ibrahim [a,b,*], Billy Wu [c], Nigel P. Brandon [a]

[a] Department of Earth Science and Engineering, Imperial College London, London SW7 2BP, UK
[b] Faculty of Mechanical Engineering, Universiti Teknologi MARA, Shah Alam 40450, Selangor, Malaysia
[c] Dyson School of Design Engineering, Imperial College London, London SW7 1NA, London, UK

ARTICLE INFO

Article history:
Received 9 March 2016
Received in revised form 24 May 2016
Accepted 25 May 2016
Available online 26 May 2016

Keywords:
Porous electrode
Laser sintering
Binding mechanism
Electrical conductivity

ABSTRACT

Battery electrode microstructures must be porous, to provide a large active surface area to facilitate fast charge transfer kinetics. In this work, we describe how a novel porous electrode scaffold, made from stainless steel 316L powder can be fabricated using selective laser sintering by proper selection of process parameters. Porosity, electrical conductivity and optical microscopy measurements were used to investigate the properties of fabricated samples. Our results show that a laser energy density between 1.50–2.00 J/mm^2 leads to a partial laser sintering mechanism where the powder particles are partially fused together, resulting in the fabrication of electrode scaffolds with 10% or higher porosity. The sample fabricated using 2.00 J/mm^2 energy density (60 W–1200 mm/s) exhibited a good electrical conductivity of 1.80×10^6 S/m with 15.61% of porosity. Moreover, we have observed the porosity changes across height for the sample fabricated at 60 W and 600 mm/s, 5.70% from base and increasing to 7.12% and 9.89% for each 2.5 mm height towards the top surface offering graded properties ideal for electrochemical devices, due to the changing thermal boundary conditions. These highly porous electrode scaffolds can be used as an electrode in electrochemical devices, potentially improving energy density and life cycle.

1. Introduction

Selective Laser Sintering (SLS) is an additive manufacturing technology that has grown rapidly, and has a wide application potential because of its flexibility. These advantages have provided a wide platform in areas such as medical research, e.g. to study the process of hydroxyapatite using laser sintering for bone tissue engineering [1], in manufacturing, e.g. in rapid casting [2] and in civil engineering, e.g. in bridge manufacturing [3]. In spite of these advantages, its application to electrochemical device development has been limited to date. One example of its application in this field is the fabrication of three-dimensional (3D) Li-ion microbattery architectures, where the researchers used 3D printing techniques to create interdigitated electrodes from specially developed inks [4].

Electrochemical devices are capable of converting chemical energy to/from electrical energy at very high efficiency. Such devices include the lithium-ion battery, solid-oxide fuel cell and metal-air battery, amongst others. Currently, the development of these devices has become crucial in order to support de-carbonisation targets, for example through battery electric vehicles [5,6]. This development faces many challenges, for instance the need to safely improve battery energy density and cycle life, [7,8,9,10]. Researchers have been working over a decade to solve the problems in metal-air batteries such as life cycle limitation, non-uniform zinc dissolution during charge and discharge cycle [11], morphological changes of the zinc electrode [12] and dendritic growth at the zinc anode [13]. Moreover, degradation of the air electrode and carbonization problems due to the reaction between electrolyte and air can block the pores of air cathode damaging the electrode architecture [14]. However, there remain opportunities to continue to improve the performance and lifetime of electrochemical devices such as batteries and fuel cells devices through better design and manufacture of the electrodes.

Literature studies have shown several approaches to improving the performance of metal-air batteries such as suppressing zinc dendrite growth in an ionic liquid electrolyte containing highly concentrated cationic and anionic zinc complexes [15] and the use of Co_3O_4 nanoparticles that were synthesized on *N*-doped Vulcan carbon as a hybrid bifunctional electrolcatalyst [16]. Another approach with a particular focus on the anode focused on the production of the electrode as foam [17] or fibrous [18] materials to improve life cycle and energy density. Zhang investigated the performance of the zinc-air system by using solid zinc to produce fibrous zinc anodes. This anode increased the

* Corresponding author at: Department of Earth Science and Engineering, Imperial College London, London SW7 2BP, UK.
E-mail address: k.ibrahim14@imperial.ac.uk (K.A. Ibrahim).

http://dx.doi.org/10.1016/j.matdes.2016.05.096
0264-1275/

discharge capacity by 38%, material utilization by 26% and discharge energy by 49% compared to the gelled atomized powder zinc anode [18]. In another study, Yan et al. fabricated a 3D zinc foam electrodes by pulse electro-deposition of zinc on copper. When tested under 250 mA cm^{-2} discharge-charge currents, 100% depth of discharge was achieved without using any dendrite-suppressing additives. The resulting 3D Zn/Cu foam electrodes remain dendrite free after 10,000 discharge-charge cycles and also demonstrated a good cycling stability where it achieved up to 620 mA h g^{-1} of specific capacity after 9000 discharge-charge cycles in a zinc-nickel system [19]. However, performance gaps remain, meaning that further improvements in the electrode would be beneficial. This could be achieved by the development of a 3D porous electrode using SLS. In this study, the capabilities of SLS to fabricate porous scaffold electrodes have been explored to enhance electrochemical device performance. Scaffold electrodes means a 3D aperiodic structure or non-planar geometries of electrodes that utilize more surface area for chemical reaction to take place [20,21,22].

The aim of the study is to investigate the influence of selected process parameters on the additive manufacturing of 316L stainless steel (SS 316L), with the aim of fabricating porous scaffold parts. Such porosity can improve the active surface area compared to planar electrode structures, increasing electrochemical reaction rates [20,21,22], and also deliver higher mass transfer rates within electrode structures. Having such porous metal parts can lead to increased metal surface area for chemical reaction. Later, other active materials can be deposited between void spaces.

Kamath et al. demonstrated how to fabricate metal parts with a density of more than 99% from SS 316L via control of laser power and scanning speed [23]. A comparison study of different powder grades (three different particle size distribution) also has been demonstrated with the aim of fabrication of high density SS 316L parts [24]. Whilst more work has been reported on how to achieve high density parts [25,26], there are few studies that discuss how to achieve such porous parts. Such examples include the work conducted by Cijun et al. Here they demonstrated the correlation between process parameters (laser scanning speed and energy density) and microstructure (grain size and mechanical properties) of laser sintering for porous bone scaffolds [27]. However, this work focuses on the sintering of β-tricalcium phosphate bioceramic as the materials for laser sintering, not the SS 316L.

Process parameter selection is the most important component in this study. More than 20 process parameters can be explored, such as laser power, laser spot size, hatch space, size of powder particle and layer thickness. They can be classified into four main categories which are material properties, laser parameters, scanning process parameters and environmental parameters [28]. Other researchers who have looked at the influence of process parameters have found that each has influence on specific properties. Kamath et al. highlighted the influence of scan speed followed by laser power on the density of metal parts [23]. In another study, Simchi and Pohl concluded that the density of built parts was an exponential function of the specific energy input of the laser; where a specific energy input is defined as laser power divided by scanning speed and sintered area [29]. Additionally, Noriko et al. reported the major influence on the SLS build arising from the interaction between laser power, scan speed and scan spacing [30]. From the literature studies, it was concluded that laser power and scan speed are the crucial parameters in determining the porosity of the fabricated parts.

This study includes analysis of the relationship between the laser power, scan speed and energy density on the electrical conductivity of fabricated structures, such conductivity being a pre-requisite for electrochemical device applications. There are two types of porosity to take into consideration when producing scaffold structures. The first is the designed porosity, i.e. the porosity intrinsic to the scaffold design. This is a relatively large length scale, typically 10^{-3} m. The second is the internal porosity of metal parts that make up the structure, typically of the order of 10^{-6} to 10^{-4} m. This internal porosity is generated as a result of the parameters used during the SLS process. In this study we focus only the second form of porosity.

Table 1
Matrix of parameter selection, showing the variation in energy density with laser power and scan speed.

	Laser Power (W)				
Scan Speed (mm/s)	30	45	60	75	90
300	4.00	6.00	8.00	10.00	12.00
600	2.00	3.00	4.00	5.00	6.00
900	1.33	2.00	2.67	3.33	4.00
1200	1.00	1.50	2.00	2.50	3.00
1500	0.80	1.20	1.60	2.00	2.40

* Energy density is shown in unit of J/mm^2.

2. Experimental methods

A SS 316L powder, average particle size of 25 to 50 μm and standard chemical composition as supplied by Concept Laser was used in this study. A Concept Laser Mlab Cusing with a laser spot size of approximately 25 μm was used to fabricate samples.

A set of 25 cylindrical samples, of diameter 4 mm and 10 mm in height, each fabricated using a different range of laser powers (30 W to 90 W) and scan speeds (300 mm/s to 1500 mm/s) were produced. Both parameters are correlated, as shown in Eq. (1) [1].

$$\text{Energy density}\left[\frac{J}{mm^2}\right] = \frac{\text{Laser Power [W]}}{\text{Scan Speed}\left[\frac{\text{mm}}{\text{sec}}\right] \text{x Spot size [mm]}} \quad (1)$$

The range of parameters used in the build were set in a matrix form as shown in the Table 1 together with the corresponding energy density. For the purposes of sample identification, they were labelled as laser power-scan speed (e.g. sample 30–1500 means that the sample was built using a laser power of 30 W and a scan speed of 1500 mm/s).

The array of samples on the build plate is shown in Fig. 1. The red arrow to the right represents the increment in laser power (from low to high) while the green arrow in the downward direction represents the increment in scan speed (from low to high). As shown, samples were arranged in a wave pattern. This is to avoid a non-uniform metal powder spread when the distance, d, is too close.

A systematic analysis was performed, including: 1) optical microscopy analysis on the surface of samples; 2) bulk porosity measurement; and 3) electrical conductivity measurement for each sample to investigate the effect of the laser parameters on the properties of the fabricated metal parts.

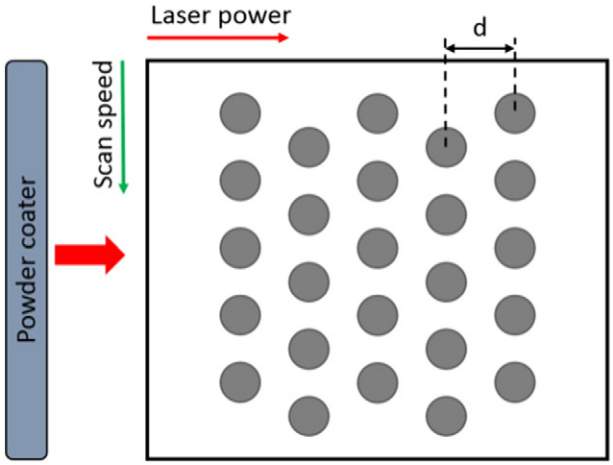

Fig. 1. Array of 25 samples on the build plate based on the matrix in Table 1.