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Electrochemical characterization and thermodynamic tendency of β-Lactoglobulin adsorption on 3D printed stainless steel

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ABSTRACT

The electrochemical behavior of 3D printed 316L stainless steel (3DPSS) was investigated in phosphate buffer saline (PBS), containing β-Lactoglobulin (BLG). The charge transfer resistance (R_{ct}) was decreased from 629 to 40 k Ω cm^2 with an increase in temperature from 293 to 323 K in BLG free electrolyte. At each temperature, the exponential decrease in the polarization resistance (R_p) of 3DPSS was a function of BLG concentration. The significant decrease in activation energy 'E_a' (~15 kJ mol^{-1}) upon adding 0.06 g/L BLG attributed to the charge transfer process involved in the adsorption process. The results were further used to quantify the thermodynamic parameters.

Introduction

Austenitic stainless steel is a workhorse material in various industries, including but not limited to biomedical, food and dairy [1–4]. This material has diverse range of applications, due to its fair corrosion resistance, good mechanical strength and excellent biocompatibility [5–7]. In order to maximize the industrial applications of stainless steel, improved corrosion resistance of this material has always been a focus of the research community. To enhance the corrosion resistance of stainless steel, surface modification, application of coatings and use of different inhibitors have been widely discussed in the literature [8–11]. Recently, by tailoring the microstructure of stainless steel, the improvement in the corrosion resistance has also been reported [12,13]. However, all these processes require additional tooling or mechanical treatments, which may not be applicable to many components involving complex geometries. Additive manufacturing or 3D-printing is an emerging metallurgical process which has established a drastic impact on the existing technology due to the development of the most intricate parts with great time efficiency [14,15]. It is a layer-by-layer manufacturing process, involving a localized melting and extremely high solidification rate that can result into very non-conventional microstructure compared to the wrought counterpart [16,17]. Wang et al. [18] reported that 316L stainless steel parts with more strength and appreciable ductility can be manufactured via 3D printing approach, attributing to the significant modification of microstructure. Sander et al. [19] mentioned that the pitting resistance of 3D printed 316L stainless steel was significantly higher compared to the conventional 316L stainless steel. In essence, the fundamental understanding of the material behavior is dependent on its microstructural features which are also influenced by the manufacturing and processing methods. Furthermore, materials behavior is also strongly dependent on its working environment.

In the food, biomedical and pharmaceutical industries, the adsorption of proteins on the surface of metallic components is an important issue [20–24]. Proteins adsorption can subsequently alter the corrosion behavior of the metallic components due to the formation of biofilm on the surface [25]. The adsorption of protein on the surface is an instantaneous, heterogeneous and a complex phenomenon which may involve electrostatic, hydrophobic and/or hydrogen bonding interactions [26]. The quantity and nature of the protein adsorption is dependent on the surface properties of the material i.e. wettability, polar interaction and surface topography [27,28]. Proteins may tend to denature or nature on the surface which may catalyze, moderate or mediate the chemical, electrochemical and/or physical reactions [29–31]. Temperature, pH, ionic strength of the solution and structural stability of the protein are

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some other key factors which also play an important role on the stability of the surface and protein structure. The adsorption behavior of the proteins on metallic surface is considered a chemical interaction, in which the building blocks of amino acids (proteins) interact with hydroxylated sites on the metal surface [32–34]. There are some reports available in the literature addressing the interaction of various proteins with stainless steel and its implications [25,35,36]. Thermal instability of the proteins could also lead to the biofouling of the equipment, particularly used in the food industries [37,38]. The decrease in corrosion resistance of the metallic parts was also found to be related with the physisorption and irreversible chemisorption of the proteins [33,37]. Adsorption of protein through chemisorption process decreases the activation energy which may result due to the decrease in the polarization resistance (accelerated dissolution of the metals). The change in corrosion behavior due to protein adsorption could further affect the surface affinity, structural rearrangement, thermodynamic and kinetic properties of the material [39–41].

The protein, β-Lactoglobulin (BLG) is one of the most prevalent ingredients in the mammalian milk and has been implicated in the fouling of the metallic parts in the dairy industry. With a molar mass of 18,328 Da and isoelectric point of 5.13, it is found naturally as dimer of two monomeric subunits, non-covalently bonded in the bovine milk [42]. In the pH range of 6.0–7.4, the BLG transforms from native to reversible denatured state known as the "Tanford Transition" [43]. This research aims to elucidate the electrochemical response of 3D printed 316L stainless steel (3DPSS) in phosphate buffer saline containing varying concentration of BLG protein. The main objective of this research work is to highlight the influence of BLG protein on the corrosion behavior of (3DPSS). The electrochemical impedance spectroscopy and potentiodynamic polarization tests were performed to observe the effect of temperature on the adsorption characteristics of BLG protein. The electrochemical stability and thermodynamic parameters for the 3D printed 316L stainless steel are also evaluated for the very first time.

Experimental

The 3D printed 316L stainless steel (3DPSS) samples used in this study were fabricated using Renishaw AM250 unit equipped with ytterbium continuous laser beam (wavelength 1060 nm) developed at 200 W. All the samples were built under same operating conditions with a hatch distance of 100 μm and layer thickness of 30 μm. The manufactured samples were circular disks having 1.58 cm diameter and 0.5 cm thickness. In order to ensure the chemical composition of the build samples, the energy dispersive X-ray spectroscopy analysis was carried out and the results are presented in Table 1. Before performing all the tests, the surface of each sample was polished using SiC papers (180–1200 grit size) under running water. To obtain mirror like surface, the samples were then polished on the canvas by using 3 μm fine diamond suspension. Furthermore, the samples were degreased via ultrasonication in ethanol for 15 min and rinsed in deionized water before drying in N_2 gas stream. The samples were stored in a desiccator for further use.

The phosphate buffer saline (PBS) solution was prepared by dissolving PBS tablets (Sigma Aldrich) in deionized water, which was used as electrolyte. The chemical composition (in g/L) of PBS was 0.8 NaCl, 0.35 $NaHCO_3$, 0.2 $MgSiO_4$, 0.14 $CaCl_2$, 0.06 KH_2PO_4 and 0.06 Na_2HPO_4. Afterwards, the known concentration of 0.02, 0.04 and 0.06 g/L β-Lactoglobulin (Sigma Aldrich) was added into the PBS solutions for electrochemical testing.

Table 1
Chemical composition of 3D printed 316L stainless steel used in this study.

Elements	Cr	Ni	Mn	C	Mo	S	P	Fe
Wt.%	18.1	11.2	1.8	0.03	2.5	0.03	0.05	Balance

Electrochemical tests were performed in three electrode cell system connected with the Gamry interface 1000E potentiostat. In this cell, polished 3DPSS samples (exposed surface area = 1.27 cm^2) were used as working electrodes. The saturated calomel electrode (E_o = +240 mV vs SHE) and a high purity (99.9%) platinum coil were used as reference and counter electrodes, respectively. All the tests were conducted in the naturally aerated electrolytes. The experiments were performed at different temperatures (293, 303, 313 and 323 K). The open circuit potential (OCP) of the electrode was measured initially for 4 h to achieve the 0.01 mV/min potential stability. The impedance spectra were recorded in the frequency range of 100 kHz–1 mHz by applying 5 mV r.m.s amplitude sinusoidal AC signal at OCP (0 V DC potential). The potentiodynamic polarization scans were obtained within −0.5 V to +1.0 V (vs. OCP) potential range at 0.5 mV/s scan rate.

Results and discussion

Electrochemical impedance spectroscopy (EIS)

In order to analyze the electrochemical processes occurring at the electrode/electrolyte interface, electrochemical impedance spectroscopy (EIS) tests were conducted. The samples were immersed in the electrolyte for 4 h prior to EIS scans to achieve quasi-steady state conditions at the electrode/electrolyte interface. The Bode plots are shown in Fig. 1 presenting the experimental results for 3DPSS in PBS electrolyte containing varying amount of BLG at different temperatures. The measured impedance spectra, as a function of frequency are related with the current response associated with the reversible charge transfer and adsorption processes occurring at the electrode surface, when a small sinusoidal AC potential is applied.

Different model circuits are presented in the literature for mechanistic interpretation of impedance data [44–47]. To simulate the adsorption behavior of protein at the metal surface, the equivalent electrical circuit (EEC) model includes two time constants as proposed by Omanovic and Roscoe [47]. This EEC model incorporates two hierarchical parallel constant phase elements in series with the solution resistance (R_s) as shown in Fig. 2. This can be used to predict the interfacial adsorption/desorption behavior of BLG and its interaction with 3DPSS surface. The high frequency impedance was attributed to the charging/discharging of double layer (Y_{dl}) and charge transfer resistance (R_{ct}). The low frequency impedance was represented by 'Y_f' and 'R_f' indicating the capacitive and resistive behavior related to passive film, respectively. The constant phase elements were incorporated because of the charge distribution within the double layer (due to specifically adsorbed species) and on the passive film. The deviation of impedance slope from −1 and the phase angle from −90° in the Bode plots suggest the annexation of constant phase elements in the EEC. In this case, these effects can be related with the surface characteristics i.e. double layer formation and specifically adsorbed species in association with the uniformity of passive film [47].

The second time constant corresponded to the dielectric characteristics of the passive film and the associated processes involved with the transport of electroactive species to/from the inherent oxide film attributing to its dissolution tendency. Table 2 provides the quantitative information of the impedance behavior measured from the fitting of simulated EEC model over the experimental spectra.

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