



Active screen plasma surface co-alloying treatments of 316 stainless steel with nitrogen and silver for fuel cell bipolar plates



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ABSTRACT

Due to their good mechanical and corrosion properties, relatively low cost and ease of manufacture, 316 austenitic stainless steel has been researched as a promising candidate material for bipolar plates in proton exchange membrane fuel cells. However, its interfacial contact resistance (ICR) is about 16 times higher than that of the Department of Energy target ($10 \text{ m}\Omega \text{ cm}^2$), which leads to undesirable fuel cell performance. In this work, active screen plasma (ASP) surface co-alloying treatments with both nitrogen and silver were developed to modify the surface of 316 stainless steel to reduce its ICR required for high-performance bipolar plates. The treated surfaces were fully studied by means of scanning electron microscopy, X-ray diffraction, glow discharge optical emission spectroscopy and energy dispersive spectroscopy. The experimental results demonstrated that a duplex surface layer structure consisting of an Ag-rich surface deposition layer supported by an S-phase case was generated by the ASP surface co-alloying treatment. The ASP co-alloying treated surfaces showed increased corrosion potential and reduced corrosion current density, and significantly improved surface electrical conductivity. This could be attributed to the introduction of metallic Ag particles by this novel surface plasma treatment.

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1. Introduction

Because of the ever-increasing concerns over the depletion of fossil fuel and the aggravation of greenhouse gas emission, considerable research has recently been conducted to develop alternative methods of power generation. Among them, the proton exchange membrane fuel cell (PEMFC) has been considered as one of the most promising candidates in stationary and transportation applications due to its high efficiency, near zero emission, low working temperature and fast start-stop behaviour [1].

Bipolar plates are the key multi-functional components in PEMFCs and graphite has been currently employed to make the bipolar plates due to its good corrosion resistance and electrical conductivity in PEMFC working conditions. However, the inherent poor mechanical properties and the unacceptably high manufacturing cost are barriers to their widespread use.

Compared with graphite, stainless steels (SS) exhibit a much higher mechanical strength and a much lower manufacturing cost, and have attracted massive interest for bipolar plate applications [2,3,4]. It is known that stainless steels possess satisfactory corrosion resistance for many applications. The inherent passive film formed on the stainless steel surface, however, greatly increases the interfacial conduct resistance (ICR), leading to the degradation of output power of fuel cells.

Therefore, surface modification is needed to improve the surface conductivity of stainless steels [5].

Silver is well known for its excellent electrical conductivity and chemical stability, and it has been applied to improve the surface properties of stainless steel bipolar plates via surface modification technologies. Ag coated 316 SS bipolar plates by electrodeposition methods [6,7] show significantly improved surface electrical conductivity. The unavoidable defects (such as pin-holes) in the coating, however, are found to act as the short-cut for the penetration of corrosive solution to reach the substrate in the acidic environment, resulting in the failure of Ag coatings. In view of the shortcoming of coating technology, Feng [8] alloys the 316 SS surfaces by the ion implantation method and the Ag implanted 316 L SS shows enhanced corrosion resistance and polarisation resistance. The ICR value is reduced after the treatment, but it is still much higher than the target set by the Department of Energy (DOE), mainly due to the formation of silver oxide.

Recently, the authors have explored the possibility of improving the surface electrical conductivity of 316 SS by low-temperature active-screen plasma nitriding (ASPN) [9]. The ASPN treatment can significantly reduce the ICR from $158 \text{ m}\Omega \text{ cm}^2$ for the untreated 316 SS to $33 \text{ m}\Omega \text{ cm}^2$, which is still higher than the DOE target of $10 \text{ m}\Omega \text{ cm}^2$. In the present work, a new active screen plasma co-alloying technology has been developed to introduce both nitrogen and silver into 316 stainless steel surfaces aiming at further improving the surface electrical conductivity of 316 SS.

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2. Experimental

Commercial 316 austenitic stainless steel was used in this study as the substrate material and its chemical composition (wt.%) is 0.06C, 17.20Cr, 1.30Mn, 2.20Mo, 11.70Ni, 0.014S, 0.026P, and 0.60Si, with Fe balanced. Samples of 6 mm in thickness and 25.4 mm in diameter were cut from hot rolled bars. The surfaces of the samples to be treated were wet ground from #120 up to #1200 grit using SiC emery paper, followed by polishing using diamond paste from 6 μm down to 1 μm . Prior to plasma treatment, the polished samples were degreased with acetone in an ultrasonic bath for 10 min and finally dried with flowing hot air.

Cross sections were cut from the treated samples and mounted in conductive backlite, followed by the same preparation procedures as described above. An etching agent containing 25% H_2O + 25% HNO_3 + 50% HCl was used to reveal the micro-structure of the cross sections.

Active screen plasma co-alloying with nitrogen and silver (ASPA(N&Ag)) treatments were carried out in a 40 kW Klöckner conventional DC plasma nitriding furnace with a laboratory active screen set-up, the details of which could be found elsewhere [10]. However, in order to achieve co-alloying with not only N but also Ag, the lid of the metal mesh cylinder (i.e. active screen) was fabricated by hot isostatic pressing (HIP), using the powder mixture of 95% 316 L stainless steel and 5% silver. The active screen plasma co-alloying treatments were conducted at 450 °C in a gas mixture of 25% N_2 + 75% H_2 under 4 mbar. These optimal parameters are identified from the previous ASPN treatments reported [9]. This is because the ICR decreases with increasing the ASPN temperature but when the treatment temperature is above 450 °C, the formation of Cr precipitation will take place, thus leading to the serious degradation of corrosion resistance [11,12]. The treatment durations were set for 7 and 15 h. In order to show the effect of Ag, normal ASPN treatment (i.e. ASP alloying with N) was also conducted with the same treatment conditions as for the ASPA(N&Ag) co-alloying treatments but only for 7 h.

After the plasma alloying treatments, scanning electron microscopy (SEM, Jeol 7000) and X-ray diffraction (XRD, Bruker D8 Advance) with Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) were employed to characterise the surface morphology and microstructure of the treated surfaces. Elemental depth profiles were determined by glow discharge optical emission spectroscopy (GDOES).

The corrosion performance of both the treated and the untreated samples for comparison was evaluated by potentiodynamic polarisation tests. A standard three-electrode system was used with a saturated calomel electrode (SCE) as the reference electrode. The electrolyte used was a sulphuric acid aqueous solution (0.5 M H_2SO_4 + 2 ppm HF), and all the corrosion tests were conducted at room temperature. More details of the polarisation tests can be found in the previous publication [9]. The surface electrical conductivity of all the samples was measured using interfacial contact resistance (ICR) according to Wang's method [13] and the compaction pressure used for the ICR measurement was 1.4 MPa (140 N/cm^2).

3. Results

3.1. Surface morphology

The surface morphology of ASPA(N&Ag) and ASPN treated samples was observed by SEM. It can be seen from the low magnification images (Fig. 1(a), (c), (e)) that the surfaces are roughened after treatments with surface relief. This is a typical characteristic of the formation of S-phase mainly due to lattice expansion of grains with different orientations caused by the supersaturation of nitrogen [14]. Under low magnification, the whole surface of 7 h treated ASPN (Fig. 1(a)) and 15 h treated ASPA(N&Ag) (Fig. 1(e)) is covered by fine white particles but it is interesting to find that only some areas of the 7 h ASPA(N&Ag) treated surface are covered by the fine white particles, which seem to

correspond to the surface relief or grains (denoted by a white dash line in Fig. 1(c)).

The above varying contrast with grains observed on 7 h ASPA(N&Ag) treated samples could be explained using the mechanism proposed by Corujeira Gallo & Dong [15]. In their work, similar varying contrast with grains was observed under certain ASPN treatment conditions. This is mainly because the mass transfer of nitrogen in active screen plasma nitriding follows the following steps: deposition of iron nitride—their decomposition—inward diffusion of N. The diffusion of nitrogen in austenite grains and hence the decomposition of the deposited fine iron nitride particles on different grains are orientation dependent; the competition between the deposition rate and the diffusion rate determines the resulted surface morphology. If the deposition rate is much higher than the decomposition rate even for grains with most favourable (001) orientation for diffusion, more and more deposited particles will be piled up. Eventually, a thick deposition layer covers the whole surface, leading to the bright contrast on the low magnification SEM pictures (Fig. 1(a) and (c)); on the other hand, if the deposition rate is lower than the decomposition rate even for grains with least (111) favourable orientation for diffusion, no large deposited particles would leave on the surface, thus leading to the dark contrast when observed under low magnification SEM. Only at a specific deposition rate, some grains are covered by such white deposited particles because they had unfavourable (111) orientation for diffusion.

The deposition rate and the decomposition rate are governed by many different aspects, such as the treatment temperature, duration and the chemical composition of the lid. For example, when treated under the same temperature (450 °C) for the same time (7 h), the deposition rate of iron nitride is faster in ASPN using a 316 SS screen than in ASPA(N&Ag) using a composite screen consisting of 316 L SS doped with Ag because of the presence of Ag in the lid and hence in the deposited layer. Hence, the whole surface of the former was covered by the white particles whilst only some surface areas of the latter showed similar white particles. The different surface morphologies observed for 7 h and 15 h ASPA(N&Ag) treated surfaces might be explained by the longer time for the latter than for the former. This is because the diffusion coefficient of nitrogen in 316 SS was found to reduce with the increase of low-temperature plasma treatment duration [16] and hence the amount of deposited particles would be expected to increase with prolonged treatment time.

The detailed surface morphology taken from the rectangles shown in Fig. 1 can be found in the high magnification SEM images (Fig. 1(b), (d), (f)). Many fine particles were observed on the surface of the 7 h ASPN treated sample with the shape of polyhedron and the size of about 250 nm in diameter (Fig. 1(b)). Particles can also be found on the surface of the 7 h ASPA(N&Ag) treated surface; however, their size reduces to about 130 nm in diameter. With the increase of the treatment duration to 15 h, the size of the particles becomes un-even and the average size increases to around 250 nm on the surface of the 15 h ASPA(N&Ag) treated sample.

The high magnification backscatter surface image of 15 h ASPA(N&Ag) treated 316 SS (Fig. 2(a)) reveals two different materials deposited on the surface, which can be deduced from the different contrasts. The EDS spectra taken from the two areas with different contrasts (Fig. 2(b)) reveal that the bright area (Spectrum 1) is rich in Ag whilst the dark area (Spectrum 2) is rich in Fe. Considering that the spatial resolution of EDS ($\approx 1 \mu\text{m}$) is larger than the thickness of the surface deposition layer ($< 0.5 \mu\text{m}$), the EDS peaks of Fe, Cr, Ni and Si might come from the S-phase case underneath. Therefore, these bright particles might be metallic Ag particles as revealed from previous TEM observation [17].

3.2. Surface layer structure

3.2.1. XRD phase identification

The phase constituent of ASPA(N&Ag) and ASPN treated samples was analysed by XRD (Fig. 3). The typical peaks of S-phase can be seen

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