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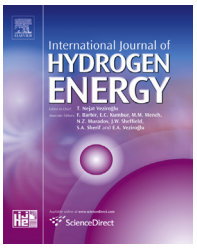

Surface modification of 304 stainless steels to improve corrosion behavior and interfacial contact resistance of bipolar plates

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ABSTRACT

In this study, plasma nitrided stainless steel (SS304) at low and high temperature, treated by Thermo Reactive Deposition (TRD) and then pickled is investigated under PEMFC accelerated condition. Surface characterization is performed by SEM, EDS, XRD, AFM, and GD-OES. Potentiostatic (PS) and electrochemical impedance spectroscopy (EIS) is used to assess corrosion resistance of untreated and treated samples. Interfacial contact resistance (ICR) measurements are carried out to investigate the surface conductivity. The results reveal that TRD treated samples are covered by an inhomogeneous layer that cannot protect the substrate. Corrosion resistance and conductivity of pickled samples improve significantly. The improvements are attributed to a rich chromium layer and the low roughness of the modified passive layer. A bi-layer (outer porous and inner dense layer) structure is proposed as the most appropriate model for the passive film. Contact angle measurements indicate improved hydrophobicity of pickled samples.

Introduction

Bipolar plates (BP's) can be metallic due to their excellent metal formability, relatively high strength, low electrical resistivity, and low gas permeability, as well as reasonable expenses for massive production of fuel cells with very high volumetric and gravimetric power density [1].

During the operation of PEMFC stacks, BP's are exposed to highly corrosive environment. Therefore, a potential drawback with any metal-based PEMFC BP is surface corrosion. Corrosion of BP leads to release of metal ions that can contaminate the electrolyte membrane, and poison the electrode catalysts; thereby exhibiting long-term degradation issues with PEMFC stacks [2].

Stainless steels compared with graphite that is presently a common material for bipolar plates, exhibit much higher mechanical strength and much lower manufacturing cost, thus raising much interest for bipolar plate applications [3,4]. It is well known that stainless steels possess satisfactory corrosion resistance for many applications [5].

The roughness and morphology of the surface, as well as the composition of the passive film influence the interfacial contact resistance (ICR) and the corrosion resistance of the bipolar plate [6,7]. The ICR and the corrosion resistance of the

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stainless steel can be effectively controlled with appropriate surface modifications [8].

Various techniques [9,10] of stainless steel surface modification have been used to improve corrosion resistance and interfacial contact resistance. Transition metals and their nitrides like CrN [11,12], NbN [13] and TiN [12,14] have been fabricated as protective layers of stainless steel bipolar plates, and assessed in simulated PEMFC conditions [15]. Niobium is widely used as a micro-alloying element in steel by means of solid solution formation, precipitation, carbide and coherent phase formation. Also, niobium and its alloys have excellent resistance to a large variety of corrosive environments including mineral acids and most organic acids [16].

The main objective of this study has been to modify the surface layer of SS304 by means of a less expensive and relatively easier method in comparison with other carbide/nitride coating processes, such as chemical vapor deposition (CVD), and physical vapor deposition (PVD). The first step was a plasma nitriding treatment to produce nitride phases and nitrogenated solid solution. The second step was niobizing treatment by TRD to produce niobium nitride phases on the pre-nitrided stainless steels. Finally, a pickling process was used to remove layers of poor corrosion resistance. Such procedures expected to improve corrosion resistance and surface electrical conductivity.

Experimental

Specimen preparation

Commercial SS304 sheets (1.5 mm thick) were cut into strips of 150 mm × 30 mm. The surface of every specimen was ground with SiC papers up to #1200 grit, then degreased with acetone in an ultrasonic bath, and finally dried at room temperature in air.

The nitriding treatment was carried out in a commercial dc plasma nitriding set-up. Samples were set on a plate of cathodic potential. The temperature was controlled by an electrically isolated thermocouple attached to the sample holder. Nitriding took place at two (low and high) temperature conditions to investigate the S-phase effect on the corrosion behavior of SS304. Once nitrided, samples were cooled in vacuum. Table 1 summarizes the parameters of the plasma nitriding treatments.

Nitrided stainless steel samples were coated with niobium nitride using TRD in a powder mixture consisting of 40%ferro niobium, 20%ammonium chloride and 40%alumina at 1100 °C for 8 h. The experimental conditions were chosen after some preliminary testing. After TRD, according to ASTM A 380 standard, specimens were pickled in a solution of 20%HNO_3 and 5%HF at room temperature for 30 min. The process conditions are listed in Table 2.

Table 1 – Processing parameters of plasma nitriding of SS304.

Condition	Parameter
Temperature (°C)	420 and 520
Time (hours)	8
Gas (volume)	$1N_2$,:$3H_2$
Pressure (mbar)	3.5–4
Voltage (V)	450–480
Current density (A)	3.5–6

Surface characterization

Scanning electron microscopy (SEM, LEO 1430) equipped with Oxford energy-dispersive X-ray Spectroscopy (EDS) was used to study and analyze the surface of modified specimens. X-ray diffraction (XRD, using a Rigaku D IIIMAX horizontal-scan powder diffractometer with Cu Kα radiation) was employed for phase detection. Topography and surface roughness values were determined by atomic force microscopy (AFM, Solver Pro., NT-MDT) in contact mode. Bulk and surface profile analysis of the samples were performed via glow discharge optical emission spectrometry (GDOES, GDA 750). The hydrophilicity of the sample surfaces was estimated by measuring the average contact angle using the sessile drop method on a contact angle goniometer at room temperature.

Electrochemical measurements

Potentiostatic (PS) experiments using a Gamry reference 600 instrument were used to evaluate the corrosion resistance of untreated and modified specimens. An acidic solution (1 M H_2SO_4 + 2 ppm HF solution at 80 °C) was used as an electrolyte to simulate the aggressive PEMFC environment [17]. A conventional three-electrode cell was used with a platinum wire spiral as the counter electrode, and a saturated Ag/AgCl electrode connected to a Luggin capillary as the reference electrode. All potentials are reported relative to Ag/AgCl. The temperature of corrosion tests was controlled to ±0.1 °C by a thermostatic bath during electrochemical tests.

Before experiments, all specimens were stabilized at open circuit for 20 min. For PS experiments, typical potentials of real PEMFC working conditions were chosen [17]: −0.056 V and 0.644 V to simulate anodic and cathodic conditions, respectively.

Electrochemical Impedance Spectroscopy (EIS) was carried out were carried out at the same potentials as above with the same Gamry instrument in the frequency range from 100 kHz to 0.01 Hz, and with amplitude of the sinusoidal signal of 10% of the studied potential.

Interfacial contact resistance (ICR)

The Wang method [17] was applied to measure ICR under simulated compaction forces for PEMFC. Specimens were sandwiched between two carbon papers, and the assembly was further put between two copper plates for force loading. A constant current of 1 A was provided by a Solatron 1286 potentiostat. The needed compaction force was applied by weight, while potentials were monitored by a NIMEX-NI3310 multimeter.

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