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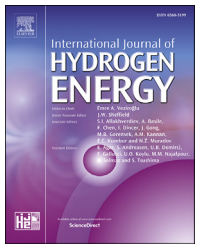

Surface and corrosion properties of modified passive layer on 304 stainless steel as bipolar plates for PEMFCs

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ABSTRACT

In this study, the relation between surface chemistry and corrosion properties of modified 304 stainless steels (304SS) was investigated. 304SS samples were submitted to plasma nitriding performed at two different temperatures: 420 °C (low) and 520 °C (high). Then, a thermo reactive deposition (TRD) was used in a mixture of ferro niobium, alumina and ammonium chloride. Finally, a pickling treatment was performed to access high corrosion resistant surfaces. Surface treated samples, both before and after pickling, were investigated by using Scanning Electron Microscopy (SEM) and Potentiodynamic (PD) techniques. X-ray Photoelectron Spectroscopy (XPS) was performed for the analysis of the surface layers of the samples after pickling.

The surface layers were mostly comprised of iron and chromium oxides and hydroxides. XPS results proved the presence of a surface layer mostly constituted by iron oxides and oxyhydroxides for both the treated samples that resulted more homogenous for the sample nitrided at low temperature. Chromium was detected by XPS in the predominant form of oxide on the surface of the sample nitrided at low temperature.

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Introduction

Bipolar plates constitute the backbone of hydrogen fuel cell power stacks. They isolate the individual cells, conduct current between cells, facilitate water and thermal management through the cell and provide conduits for reactant gases as well as to remove reaction products [1]. Metallic bipolar plates are a suitable choice because they possess high potential to reduce costs and enhance power density, good mechanical strength, high electrical conductivity, high gas impermeability and easy manufacturability at low cost compared to graphite materials which increases their competitiveness in the fuel cell market [2,3]. The main challenge of a metallic bipolar plate, however, is that the corrosion-resistant metals, such as stainless steel (SS),

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develop a passive oxide layer on the surface. The native passive film is composed of Fe and Cr oxides. After polarization under the accelerated and simulated anode conditions, the composition changes to mainly Cr oxide due to dissolution of iron [4]. Although this passive layer protects the bulk metal from the progression of corrosion, it also causes high surface contact resistance [5]. Stainless steels are in general covered by a stable and well adhering passive film which protects the bulk material from further corrosion [6]. Unfortunately, it causes also an undesirable effect of high surface contact resistance under PEM fuel cell operating conditions owing to the semiconducting properties of surface oxides [7]. This causes the dissipation in heat of a considerable amount of electric energy and reduction of the overall efficiency of the fuel cell power stack. Surface analysis, particularly performed by X-ray Photoelectron Spectroscopy (XPS), was extensively used to analyze the passive films formed on both ferritic and austenitic stainless steels, providing evidence of chromium enrichment in the passive films and of the bilayer nature of the passive films on these alloys [8,9]. This bilayer structure shows the p-type behavior derived from the inner Cr oxide layer and the n-type behavior resulted from the outer Fe based oxides and hydroxides species [9].

In our previous work [10] we modified the surface layer of 304 stainless steels in order to improve corrosion behavior and interfacial contact resistance of bipolar plates. The surface treatment consisted in plasma nitriding followed by TRD niobizing and pickling processes. These samples were investigated by SEM-EDS, XRD, AFM, GD-OES, potentiostatic and electrochemical impedance spectroscopy (EIS) under PEMFC accelerated conditions. EIS spectra were best fitted by an equivalent circuit that matched with a double layer structure at the surface of modified samples [10]. The present work is a continuation of previous work to fill the gap in our knowledge on the nature of modified surfaces. We want to verify our newly proposed equivalent circuit, derived from EIS measurements and other methods. For this reason, we planned to perform some characterization analysis of the surface of modified samples to find a relation between their surface condition and corrosion resistance.

Experimental

Specimen preparation

A 304 stainless steel (304SS) sheet was purchased from Iran Steel, a certified and well-known Iranian company in this field. This steel has the following chemical composition (wt%): 0.025 C, 17.96 Cr, 8.07 Ni, 1.48 Mn, 0.32 Si, 0.05 P and Fe as the balance. Nitriding treatments were carried out on 1.5 mm thick strips of 304 stainless steel in a commercial dc plasma nitriding set-up. The temperature was controlled by an electrically isolated thermocouple attached to the sample holder. Plasma nitriding was performed at two different temperatures: 420 °C (low) and 520 °C (high), in order to investigate the effect of nitriding temperature on the corrosion behavior of modified 304SS. These samples are labelled as 420 N and 520 N. Nitrided stainless steel samples were coated with niobium nitride by using thermo reactive deposition (TRD) in a mixture of 40% ferro niobium, 20% ammonium chloride and 40% alumina at 1100 °C for 8 h. These samples are referred to as 420NbN-NP and 520NbN-NP. After TRD, these specimens were pickled in a solution of 20% HNO_3 and 5% HF at room temperature for 30 min. Subsequently, samples were rinsed by deionized water and ultrasonically washed in acetone. Finally, all specimens were dried soon after the cleaning process. These samples are labelled as 420NbN-P and 520NbN-P. The detailed conditions of preparation are mentioned elsewhere [10].

Surface characterization

Scanning electron microscope (SEM, LEO 1430) equipped with Oxford energy-dispersive X-ray spectrometer (EDS) was used to investigate the surface morphology of the investigated specimens. The surface chemical composition of the samples after pickling treatment (420NbN-P and 520NbN-P) was determined by X-ray Photoelectron Spectroscopy using a VG Microtech ESCA 3000 Multilab spectrometer, equipped with a standard Al K_α excitation source ($h\nu = 1486.6$ eV) and a multi-channeltrons detection system. The hemispherical analyzer operated in the CAE mode (pass energy = 20 eV). The binding energy (BE) scale was calibrated by measuring C 1s peak (BE = 285.1 eV) from the adventitious carbon, and the accuracy of the measure was ±0.1 eV. Photoemission spectra were collected in an ultra-high vacuum (UHV) chamber with a base pressure lower than 1×10^{-6} Pa. Data analysis was performed by the VGX900 software using a nonlinear least square curve-fitting procedure. A properly weighted sum of Lorentzian and Gaussian component curves was used, after background subtraction according to Shirley and Sherwood [11]. Surface relative atomic concentrations were calculated by a standard quantification routine including Wagner's energy dependence of attenuation length [12] and a standard set of VG Escalab sensitivity factors. The uncertainty on the atomic quantitative analysis is about ±10%.

Electrochemical measurements

A Gamry reference 600 instrument was used to record potentiodynamic (PD) curves in order 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 [13]. A conventional three-electrode cell was used with a platinum wire spiral as a counter electrode and a saturated Ag/AgCl electrode, connected to a Luggin capillary, as a reference electrode. All potentials are reported relative to Ag/AgCl. The temperature of corrosion experiments was controlled to ±0.1 °C by a thermostatic bath during PD tests. Before experiments, all specimens were stabilized at open circuit potential for 20 min. All corrosion experiments were performed at simulated PEMFC condition from −250 mV vs. open circuit potential to +1.2 V at a constant scan rate (0.32 mV s^{-1}). The reproducibility of the results was checked by performing polarizations of at least three samples under the same experimental conditions.

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