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An investigation of the typical corrosion parameters used to test polymer electrolyte fuel cell bipolar plate coatings, with titanium nitride coated stainless steel as a case study

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HIGHLIGHTS

- As BPP material TiN degrades into highly resistive titanium oxide.
- The thickness of the formed titanium oxide is increased by higher pH.
- The contact resistance increases with increasing potential.
- The titanium oxide formation is fast in the beginning, but levels out.
- Anodic polarization to 1.4 V_{SHE} was shown to best mimic the anode degradation in an accelerated fuel cell test.

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ABSTRACT

Stainless steel bipolar plates (BPP) for polymer electrolyte membrane fuel cells (PEMFCs) have good manufacturability, durability and low costs, but inadequate corrosion resistance and elevated interfacial contact resistance (ICR) in the fuel cell environment. Thin film coatings of titanium nitride (TiN) of 1 μm in thickness, were deposited by means of physical vapour deposition (PVD) process on to stainless steel (SS) 316L substrates and were evaluated, in a series of tests, for their level of corrosion protection and ICR. In the ex-situ corrosion tests, variables such as applied potential, experimental duration and pH of the sulphate electrolyte at 80 °C were altered. The ICR values were found to increase after exposure to greater applied potentials and electrolytes of a higher pH. In terms of experimental duration, the ICR increased most rapidly at the beginning of each experiment. It was also found that the oxidation of TiN was accelerated after exposure to electrolytes of a higher pH. When coated BPPs were incorporated into an accelerated fuel cell test, the degradation of the fuel cell cathode resembled the plates that were tested at the highest anodic potential (1.4 V_{SHE}).

1. Introduction

PEMFCs have attracted much attention for the conversion of hydrogen and oxygen into electrical energy, heat and water with no emission of pollutants and very high electrical energy efficiency. Two of the most important components of a PEMFC are the membrane electrode assembly (MEA) and the bipolar plates [1,2]. The main purpose of the bipolar plate is to distribute the reactant gases, provide an electrically conductive pathway and facilitate water removal from the cell [3]. Bipolar plates have traditionally been fabricated from graphite or carbon composite materials due to their chemical stability. However, carbon based bipolar plates have poor mechanical properties and high manufacturing costs [4]. In contrast, metals are to be desired because of their very high electrical conductivity and good mechanical properties [5]. However, the chemical resistance of metals is rather poor in the humid, acidic and anodic environment of a fuel cell [6]. Therefore, a corrosion resistant and conductive coating is necessary. Brady et al. [7] wrote a comprehensive research summary concerning the nitridation of metals. They found that transition metal nitrides offer an attractive combination of properties, making them of interest as a protective

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coating for metal bipolar plates.

Wang and Northwood [8] investigated physical vapour deposited TiN on SS 410, using a plasma assisted, reactive evaporation technique. The thickness of the coating was approximately 15 μm with some pinholes observed. In 0.5 M H_2SO_4 at 70 °C, the corrosion current densities were 40 μA cm^{-2} and 20 μA cm^{-2} at −0.1 V_{SCE} and 0.6 V_{SCE}, respectively. In a similar study by Wang and Northwood [9], concerning TiN deposited by PVD on 316 stainless steel, the results were almost analogous to when the substrate was 410 steel, as published in Ref. [8]. Rivas et al. [10] deposited a TiN coating onto an SS304 plate and found that the corrosion rate was surprisingly similar to the base material. In the article it was noted that this was probably caused by pinholes and contamination of the TiN layer. Liu et al. [11] investigated plasma nitriding of titanium sheets at 900 °C and found that the interfacial contact resistance decreased from 175 mΩ cm^2 (pre-nitriding) to 80 mΩ cm^2 (post-nitriding) at 140 N cm^{-2}. Samples were then tested in a 0.5 M H_2SO_4 and 5 ppm HF solution mixture and it was found that the corrosion rates for the coated samples were higher compared to the as-received titanium, suggesting poorer corrosion resistance for the TiN layer. At potentials relevant for fuel cells, the corrosion current densities were in the region of 0.13–0.56 μA cm^{-2} at a high sweep rate of 10 mV s^{-1}.

Kumagai et al. [12,13] deposited TiN nanoparticles electrophoretically on the surface of stainless steel with elastic styrene butadiene rubber (SBR) particles. For a TiN/SBR coating thickness of 50 μm, the contact resistance was about 25 mΩ cm^2 at 140 N cm^{-2}, which was not influenced by polarization tests. The corrosion tests were performed in a 0.05 M H_2SO_2 (pH 2.3) and 2 ppm HF solution mixture at 80 °C and the electrolyte was either saturated with Ar and the samples polarized to −0.1 V_{SCE} or saturated with air and polarized to 0.6 V_{SCE}. In the simulated anodic environment (−0.1 V_{SCE}), the corrosion current density was very close to 0 μA cm^{-2}. In the simulated cathodic environment (0.6 V_{SCE}), the corrosion current density was about 0.1 μA cm^{-2}. A single cell using bipolar plates coated with TiN nanoparticles consequently showed comparable cell performance to a cell employing graphite plates at a current density of 0.5 A cm^{-2}, although no information was provided regarding the degradation in performance over time.

Feng et al. [14] carried out plasma immersion ion implantation of titanium with nitrogen at 100 °C and 370 °C. The high temperature ion implantation exhibited the best performance. The ICR value of this sample was 23.2–6.4 mΩ cm^2 under 120–210 N cm^{-2} pressure. The contact resistance increased significantly after corrosion testing (a 0.5 M H_2SO_4 and 2 ppm HF solution mixture at 80 °C). For the high temperature sample in a simulated cathode environment, with air bubbling at 0.6 V_{SCE}, the corrosion current density varied in the range of 1–3 μA cm^{-2}. At −0.1 V_{SCE} with hydrogen bubbling, this sample exhibited a negative corrosion current density of about −15 μA cm^{-2}, i.e. practically no corrosion. Interestingly, the titanium metal ion concentrations in the solutions were measured after the 10 h, high temperature corrosion tests. In the anodic test the ion concentration was 115 ppb and in the cathodic test the ion concentration was 155 ppb.

TiN_XO_Y films with various amounts of oxygen were deposited by Kim et al. [15] on SS 316L substrates by inductively coupled plasma assisted reactive sputtering at different oxygen gas flow rates. The ICR value was 2.5 mΩ cm^2 at 150 N cm^{-2} when the oxygen content was below 12 atomic %. Corrosion tests were performed in a 0.1 M H_2SO_4 and 2 ppm HF solution mixture at 80 °C. The corrosion resistance of the film was increased significantly by introducing a small amount of oxygen into the TiN film. At 0.6 V_{SCE} and with air bubbling, the corrosion current density was 2.7 mA cm^{-2}. With hydrogen bubbling at −0.1 V_{SCE}, the corrosion current densities varied in the range 0–0.75 μA cm^{-2}. It is suggested in the article that oxygen atoms are likely to be located at the column and the grain boundaries, thereby preventing corrosive media from penetrating into the substrate, whilst not deteriorating the through plane electrical property of the film.

Lee et al. [16] deposited TiN on SS 316 by arc ion plating. The coatings were tested electrochemically in 0.1 M H_2SO_4 at 80 °C. The TiN coating layer was reportedly dissolved in the simulated PEMFC environments and it was claimed that the corrosion of the TiN coating occurred mainly due to the low intensity of the TiN (111) plane. H. Sun et al. [17] used closed field unbalanced magnetron sputter ion plating (CFUBMSIP) to produce dense and well adhered TiN coatings. The steady state corrosion current was measured to approximately 10 μA cm^{-2} at 1 V_{SHE} in 0.5 M H_2SO_4 at 70 °C. The contact resistance after corrosion testing was measured to be more than 230 mΩ cm^{-2}. Turan et al. [18] deposited TiN on SS 316, which had already been formed into bipolar plate–like shapes. The specimens were corrosion tested in 0.5 M H_2SO_4 at 80 °C by polarization from −1.2 V_{SHE} to 0.8 V_{SHE} at 1 mV s^{-1}. The contact resistance varied in the range of 10–25 mΩ cm^{-2} (mainly related to TiN thickness) before corrosion testing and increased excessively after the corrosion testing.

Nam et al. [19] coated TiN films on SS 316 by magnetron sputtering physical vapour deposition. Electrochemical tests were performed in aerated 1 M H_2SO_4 and 2 ppm HF solution at 70 °C. After exposure for 186 h it was found that only the coating deposited at the highest bias voltage of −150 V had a surface resistance of less than 10 mΩ cm^2. Jeon et al. [20] synthesized TiN coatings by closed-field unbalanced magnetron sputtering (CFUBM). Potentiodynamic polarization tests were performed in an aerated solution of 1 M H_2SO_4 and 2 ppm HF at 70 °C. The TiN coating that was deposited at a partial pressure of 0.4 mTorr N_2 had the lowest porosity and surface resistance (10 mΩ cm^2) after testing at open circuit for 20 days. Ren et al. [21] made a fuel cell stack of titanium bipolar plates with a TiN coating. The stack performed well, but the contact resistance before and after stack testing was not published.

From the literature it seems that the performance of TiN coatings is dependent not only on the deposition procedure, but also the parameters used for electrochemical testing. Only a few studies performed both electrochemical measurement testing and fuel cell testing. The aim of this work was to study the test variables used in electrochemical testing such as applied potential, pH and test duration and to compare these ex-situ results with those from in-situ fuel cell testing. The US Department of Energy (DoE) has set certain goals with respect to performance and cost of fuel cell bipolar plates for 2017 and 2020 [22] and propose electrochemical test conditions of pH 3 and applied potentials not exceeding 0.8 V_{SHE}.

2. Experimental

2.1. Preparation of samples

The TiN coatings of 1.0 μm thickness were deposited by Teer Coatings Ltd. (Miba Coating Group) by means of a Teer UDP 650 Closed Field Unbalanced Magnetron Sputter Ion Plating system. Prior to coating, the SS 316L coupons (35 × 35 × 0.1 mm) were ultrasonically cleaned in acetone for 15–20 min, followed by drying in warm air. The samples were arranged into the jigging and introduced into the coating chamber, which was then pumped down to a pressure of 0.0027–0.0047 Pa (2.0–3.5 × 10^{-5} torr). Argon gas was then admitted by a mass flow controller, allowing the chamber to reach a pressure between 0.107 Pa (8.0 × 10^{-4} torr) and 0.27 Pa (2.0 × 10^{-3} torr). The coupons for the TiN coatings were first ion cleaned by applying a pulsed DC bias voltage of approximately −400 V, during which the magnetrons were all