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TaN_X coatings deposited by HPPMS on SS316L bipolar plates for polymer electrolyte membrane fuel cells: Correlation between corrosion current, contact resistance and barrier oxide film formation

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ABSTRACT

Tantalum nitride (TaN_x) coatings deposited by High Power Pulsed Magnetron Sputtering (HPPMS) technology at different N_2-to-Ar ratios; i.e. 0, 0.25, 0.625 and 1, corresponding to different N/Ta atomic ratio in the film, were investigated as suitable candidates to improve SS316L bipolar plate's performance and durability for polymer electrolyte membrane fuel cells (PEMFC). The corrosion resistance of TaN_x coatings was evaluated by potentiodynamic and potentiostatic tests carried out under different cathodic potentials (0.8 V_{SHE}, 1 V_{SHE}, and 1.4 V_{SHE}), electrolyte acidities (pH 3 and pH 6) and test durations (5 and 180 min) in order to mimic real fuel cell operation conditions. Corrosion currents observed for all TaN_x coatings were relatively low (1–15 μA cm^{-2}) regardless of N/Ta atomic ratio and applied variable testing parameters. However, considerable differences in Interfacial Contact Resistance (ICR) values were observed after polarization, depending on tested coating material and conditions. The ICR increased with increasing applied potential, electrolyte pH and test duration for the substrate and all TaN_x coatings. Ta coated SS316L exhibited lower ICR (42–82 mΩ cm^2) values than the uncoated SS316L (47–278 mΩ cm^2) at potentials higher than 1 V_{SHE}. A significant rise in ICR was detected for all nitride TaN films after 180 min of polarization at 1.4 V_{SHE} in pH 3, showing ICR values from 362 to 538 mΩ cm^2, depending on N_2-to-Ar ratio. Ta coated SS316L polarized at 0.8 V_{SHE} showed low ICR values, around 25–37 mΩ cm^2. Auger electron spectroscopy (AES) was performed before and after polarization to investigate barrier oxide film formation kinetics. AES study revealed the growth of different composition and thickness oxide layers for each TaN_x coating, exposing the great importance of coating composition on subsequent type of oxide formation. Barrier oxide layer characteristics have been found to dominate the ICR response of TaN_x films after polarization.

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Introduction

A proton exchange membrane fuel cell (PEMFC) converts hydrogen and oxygen gases into electricity with water as the only by-product. Due to its high efficiency and zero emission, PEMFC is of great interest as a clean energy device beyond petroleum [1]. PEMFC is regarded as ideally suited for transportation applications due to its high power density, high energy conversion efficiency, compactness, lightweight, and low-operating temperature (below 100 °C) [2]. PEM driven electric vehicles are currently a technological reality [3] but several components' durability and fabrication costs must be optimized for widespread commercialization [4,5].

One important component in a PEMFC stack is the bipolar plate (BPP) which accounts for about 80% of the total weight and about 30% total stack cost [6,7]. This multi-functional component provides the electrical connection from cell to cell, distributes gases and removes heat from the active areas. Therefore, the bipolar plate material must be chemically stable, highly electrical and thermal conductive; has low contact resistance to the backing, good mechanical strength, low gas permeability and cost-effective for mass production.

BPPs have traditionally been fabricated from graphite due to its excellent corrosion resistance, high thermal and electrical conductivity and availability. However, it is not suitable for transportation applications because it exhibits poor mechanical properties, high manufacturing costs and difficult machinability. In contrast, metallic bipolar plates are suitable options due to their good mechanical strength, high electrical conductivity, low gas permeability, low cost, and easy manufacturing.

Particularly, stainless steel (SS) is considered one of the most promising candidates for transport applications. Nevertheless, chemical stability of SS in humid and acidic conditions of a fuel cell must be improved. The protective passive film formed on its surface does not prevent release of metallic ions leading to membrane poisoning, which reduces the efficiency of the fuel cell. This same passive film significantly increases interfacial contact resistance (ICR) between the BPP and the gas diffusion layer (GDL), compromising the conductivity of the BPP. Recent studies have revealed that a huge amount of total power losses during fuel cell operation are due to high ICR between the BPP and the GDL [8,9]. In order to improve the performance of SS many attempts have been performed including different surface treatments on different types of SS, many of them related with the deposition of transition metal nitrides.

O. Lavigne et al. deposited two thin (100 nm) chromium nitride PVD coatings on SS316L bipolar plates [9]. The first coating (coating 1) was a mixture of Cr_2N and Cr, the second (coating 2) a single phase CrN. The electrolyte used was an aqueous solution containing 0.07 M of Na_2SO_4 to limit ohmic drop with the addition of a small amount of H_2SO_4 (to adjust the pH to about 4). The electrolyte was either purged with H_2 and samples polarized to +0.05 V_{SHE} or purged with air and samples polarized to +0.85 V_{SHE} at 60 °C to simulate anode and cathode side environment, respectively. In the simulated anodic environment, the corrosion currents of both coatings were very low (~10^{-8} A cm^{-2}). In the simulated cathodic environment, corrosion currents were in the range of ~10^{-7} A cm^{-2} and ~10^{-6} A cm^{-2} for coating 1 and coating 2, respectively, after 25 h of polarization. The ICR values after polarization tests at 140 N cm^{-2} compaction pressures were 30 mΩ cm^2 and 10 mΩ cm^2 for coating 1 and coating 2, respectively.

S.H. Lee et al. investigated the corrosion and electrical characteristics of CrN and TiN coatings deposited by cathode arc ion plating on SS316L substrate [10]. A 0.1 M H_2SO_4 solution with 2 ppm F^- at 80 °C was purged continuously with hydrogen gas and air to simulate anodic and cathodic PEMFC environment. While TiN coating was dissolved during corrosion testing and showed a corrosion current of 29 μA cm^{-2} at 0.6 V_{SCE}, CrN exhibited lower corrosion currents of 6 μA cm^{-2} at cathode potential. In comparison to uncoated SS316L, CrN- and TiN-coated SS316L exhibit lower ICR value. H. Sun et al. tested 1 μm TiN coating deposited on SS316L by closed field unbalanced magnetron sputter ion plating (CFUBMSIP) at higher cathodic potential of 1 V_{SHE} [11]. Under these simulated conditions, the corrosion current registered was 11 μA cm^{-2}, slightly higher than US DoE target of 1 μA cm^{-2}. The ICR value measured after corrosion testing increased up to 230 mΩ cm^2.

Wang et al. prepared a molybdenum nitride (Mo–N) diffusion coating on the surface of SS304 by a plasma surface diffusion alloying method [12]. The coating was tested electrochemically in 0.05 M H_2SO_4 + 2 ppm F^- solution at 70 °C and ICR measurements were taken before and after polarization. The corrosion currents of Mo–N coated 304SS were around 1 μA cm^{-2} at both −0.1 V_{SCE} anodic potential and +0.6 V_{SCE} cathodic potential, reducing the corrosion current density of uncoated SS304 by nearly one order of magnitude. ICR values measured after polarization at 140 N cm^{-2} compaction pressures were 27.26 mΩ cm^2 and 100.98 mΩ cm^2 for coated- and uncoated-SS304.

C. Choe et al. used inductively coupled plasma assisted reactive magnetron sputtering to deposit TaN_x coatings at various N_2 flow rates on SS316L samples [13]. The electrochemical properties of the samples were investigated in a 0.05 M H_2SO_4 + 0.2 ppm HF solution at 80 °C and polarized to −0.1 V_{SCE} (H_2 bubbling) and +0.6 V_{SCE} (air bubbling) to mimic anode and cathode potential, respectively. TaN_x coated samples exhibited excellent corrosion resistance that satisfied the DoE requirement with a lowest current density value of 0.3 μA cm^{-2} (at 0.6 V, cathodic condition) and 0.01 μA cm^{-2} (at −0.1 V, anodic condition). Lowest ICR value of 11 mΩ cm^2 was obtained at highest N_2 flow rate. The literature on transition metal nitride coatings is extensive. However, the coating materials, deposition techniques and more importantly, testing parameters are so diverse that making conclusions and establishing a tendency becomes rather complicated.

The corrosion resistance of tantalum (Ta) is higher than any other metallic material and comparable to that of noble metals. The high chemical stability and inertness of Ta and its alloys is ascribed to the growth of an extremely impervious tantalum pentoxide (Ta_2O_5) surface barrier layer [14]. Accordingly, Ta based coatings can be potential candidates to improve SS bipolar plate's performance and durability in PEMFC. There are a few studies about Ta and TaN films deposited by chemical vapour deposition (CVD) and magnetron sputtering based techniques and their performance in