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Evaluation of nitrided titanium separator plates for proton exchange membrane electrolyzer cells☆

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HIGHLIGHTS

- We assess performance of nitrided titanium flow plates in PEM electrolysis cells.
- Nitrided Ti increases performance by 3–13% compared to untreated Ti.
- Nitrided Ti is susceptible to oxidation under anodic PEM-EC operating conditions.
- Even though oxidized, the thermally nitrided Ti demonstrates higher performance.
- Unlike surface abrasion/Pt-plating, nitrided Ti does not incur H_2 embrittlement.

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ABSTRACT

Proton exchanges membrane (PEM) regenerative fuel cell electrolysis of water is of great recent interest as a hydrogen generation technology. Anode side titanium current collectors and separator plates used in these applications typically employ coatings of platinum group metals to achieve durability and performance requirements in the high voltage, oxidizing environment. The present work assessed the potential for lower cost surface modified titanium by both thermal (gas) nitridation and plasma nitridation approaches. The nitrided Ti was found to result in far less hydrogen uptake in coupon testing than did Pt-plated Ti. Short-term (48 h) single-cell performance at 25 °C was approximately 13% better (lower voltage) at 1.2 A cm^{-2} for thermal and plasma nitrided plates vs. untreated Ti. However, at 50 °C and 1.5 A cm^{-2}, the thermally nitrided plate exhibited only on the order of 3% better behavior (lower voltage) compared to the untreated Ti and plasma nitrided Ti. Durability testing for 500 h resulted in only a minor degradation in cell performance, on the order of 1–2% voltage increase, with the best behavior exhibited by the thermally nitrided Ti plate. Despite their relatively stable cell performance, extensive local oxidation of the thermally nitrided and plasma nitrided flow field regions was observed.

1. Introduction

Hydrogen is of great interest for energy storage and production. When combined with renewable energy methods such as solar or wind, electrolysis using proton exchange membrane (PEM) cells to produce hydrogen from water is an attractive option for energy storage [1–4]. As with conventional PEM fuel cells for power production, cost and durability of PEM electrolysis cells (ECs) are a key challenge. In the commercial Proton Onsite 13 kg day^{-1} electrolyzer, stack costs account for over half of total capital costs, with 50% of the stack costs coming from flow field and current collector components [3]. The state-of-the-art PEM-EC flowfield/separator/current collector components are generally made of Ti due to its

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good corrosion resistance in the high voltage conditions encountered (cell potentials in the 2V range), particularly on the anode side where oxidation takes place [2,4]. However, oxidation to form TiO_2 can result in significantly increased cell electrical and thermal resistance and reduced performance [4]. Titanium plates are therefore typically coated with precious or platinum group metals such as Au and Pt [5–7]. Although performance is improved, costs are significantly increased. Additionally, on the high pressure H_2 side of the system (cathode), hydride formation can be significant, which in turn weakens Ti. Applying cost-effective surface treatments that mitigate this behavior is also of interest.

Efforts are therefore underway to find lower cost coating/surface treatment options for Ti plates in PEM-ECs, generally based on variations of nitride phases or refractory/platinum group metal oxides [5,8–10]. Gas and plasma nitridation approaches are of interest due to their ability to coat all exposed plate surfaces with low incidence of pin-hole defects, and have shown promise in PEM fuel cell bipolar plate applications [5,11–13]. Although extensively investigated for PEMFC applications, the literature on separator/current collectors for EC applications is quite sparse [2,4]. A potential additional advantage of nitrided surfaces for PEM-EC applications is the resistance of TiN to hydrogen permeation in high pressure environments [14]. The present work evaluates thermal (gas) nitrided Ti (referred to in remainder of paper as "thermally-nitrided" for simplicity), plasma nitrided Ti, and untreated Ti anode-side separator/current collector plates under PEM-EC operating conditions.

2. Experimental

2.1. Electrolyzer components and assembly

The electrolyzer consisted of a catalyst coated membrane (CCM), with anode and cathode diffusion media on both sides, simple parallel channel flow fields, current distributors and end plates. The Nafion-based CCM had an active area of 25 cm^2, was 175 μm thick with Pt loading of 1 mg cm^{-2} in anode and cathode electrodes. On the cathode side (hydrogen production side), a standard graphite bipolar plate and 250 μm untreated *carbon paper*were used. On the anode side (water feed and oxygen generation), Ti materials were utilized to reduce the corrosion due to the high voltage operation and oxidizing conditions. The diffusion layer was 250 μm Ti mesh with a wire diameter of 0.2 mm. All the flow channels were machined on the Ti-base plates in a rectangular shape with a depth of 3 mm and a width of 2.5 mm.

Three simple parallel channel Ti anode plates were evaluated and characterized: untreated grade 2 Ti, thermally-nitrided grade 2 Ti, and plasma nitrided grade 2 Ti. Thermal nitridation was accomplished in an infrared quartz lamp furnace system for the test plate using a thermal cycle of 1000 °C for 30 min in flowing 4% H_2/N_2 gas. The plasma nitridation was conducted by a commercial vendor. The process used was a standard plasma deposition as used for nitrided tools and other applications, which resulted in a several microns range TiN surface layer (specific processing parameters are considered proprietary). The same graphite plate on the cathode side was used for all studies.

2.2. Electrolyzer evaluation system and procedure

The electrolyzer evaluation system was comprised of a power supply, temperature and flow controller, distilled deionized (DDI) water tank, water pump, water removal system, and hydrogen mass-flow monitor. The electrolyzer was controlled with a Model HCP-803 test stand (Bio-Logic) with an electronic load of up to 100A, and a data acquisition system. Water was removed from the hydrogen (cathode) stream prior to evaluating the flowrate by implementing a simple two-phase separation followed by an in-line desiccant filter. Non-metallic fittings and tubing were utilized throughout the system to minimize introduction of non-electrolyzer component metals during the evaluation.

In the experiments, the DDI water flow rate and the operating temperature of the electrolyzer were controlled at 100 ml min^{-1} and 25–50 °C, respectively. The water was flowing in excess and was thus returned to the reservoir after the electrolyzer. After a 12 h conditioning period, each bipolar plate was evaluated with a fresh CCM and gaskets at 25 °C. These initial polarization curves were performed while holding the current density constant and measuring the resulting voltage; the current density was increased from 0.1 to 1.2 A cm^{-2}. At each current density, the operation was held for 5 min and the performance was derived based on its voltage average; this was repeated three times with the final polarization curve being reported. The current density was then held at 1.2 A cm^{-2} for 48 h followed by an additional polarization curve measurement. The electrolyzers were then disassembled and the plates were inspected and photographed, and then rebuilt with a fresh CCM, diffusion media and gaskets.

After another polarization curve evaluation (0.1–1.5 A cm^{-2}), a 500 h durability test was started. The current density was held constant at 1.5 A cm^{-2} and the voltage of the electrolyzer was recorded. After each 100 h, the electrolyzer performance was evaluated using the same protocol as described above. Every 40 h it was necessary to refill the DDI reservoir, which results in small variations in the voltage due to the change in water temperature; this was the case even though the DDI water being added was introduced at a temperature approximating the reservoir temperature, ~40 °C.

2.3. Materials characterization

Nitrided Ti test plates were characterized by x-ray diffraction and X-ray photoelectron spectroscopy (XPS) depth profiling using a Thermo Scientific K-Alpha X-Ray Photoelectron Spectrometer equipped with a Thermo Scientific EX06 argon ion gun. The XPS data were collected and processed using the Thermo Scientific Advantage XPS software package (v.4.61). Peak fitting was performed using mixed Gaussian/Lorentzian peak shapes and a Shirley/Smart type background.

2.4. H_2 uptake measurements

Ti in contact with high pressure H_2 on the cathode side can react to form a hydride and thus is another degradation mechanism with which to be concerned. As another basis of evaluation, representative grade 2 Ti materials were exposed to high pressure H_2 to determine the effect of nitriding and other treatments on hydrogen uptake/hydride formation, and key consideration in electrolyzer applications. Four samples were loaded into a high pressure vessel and exposed to a constant pressure of H_2 at 800 psig and 150 °C. The four samples were– as-annealed Ti with no surface conditioning; annealed, surface abraded, and Pt-plated Ti; plasma-nitrided Ti; and thermally-nitrided Ti(Note, the thermally-nitrided Ti coupon was accomplished by a commercial vendor, process details proprietary, and yielded a similar, conventional TiN/Ti_2N surface structure as the quartz-furnace thermally nitrided single-cell Ti test plate studied) The coupons had a total surface area of 7.5 cm^2 and sample weights were recorded periodically throughout the exposure that was up to 1700 h or until material failure occurred.