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

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Todd J. Toops [a, *], Michael P. Brady [a], Feng-Yuan Zhang [b, 1], Harry M. Meyer III [a], Katherine Ayers [c], Andrew Roemer [c], Luke Dalton [c]

[a] Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, TN 37831, USA
[b] University of Tennessee, Dept. of Mechanical, Aerospace & Biomedical Engineering, 1512 Middle Drive, 414 Dougherty, Knoxville, TN 37996-2210, USA
[c] Proton Onsite, 10 Technology Drive, Wallingford, CT 06492, USA

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.

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.

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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

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.

3. Results and discussion

3.1. Characterization of as-nitrided surfaces

X-ray diffraction indicated that TiN was formed on the plasma nitrided Ti anode plate, whereas a mixture of TiN, Ti_2N, and Ti_2O were detected on the thermally-nitrided Ti plate. XPS analysis was consistent with the XRD data. After brief Ar-ion etching (~20 nm) on the plasma nitrided surface of a comparably plasma nitrided test coupon, Ti and N were observed in a 1:1 atomic % (at. %) ratio consistent with TiN. Small signals related to O and C/carbide (~1 at% levels, respectively) were also observed in the plasma-nitrided surface, suggestive of minor incorporation of O and C into the TiN. In contrast, the near surface (~0–20 nm) of the thermally-nitrided Ti plate (measured on the unexposed backside of the test plate post electrolysis operation) contained 30–50 at% C, 20–30 at% O, 10–20 at% N, and 10-30 Ti. Ar-ion etching for 10–15 min (estimated at ~150–250 nm) yielded composition of Ti–33N–12C–8O at%, again consistent with the XRD.

3.2. Initial 48 h, 25 °C PEM-EC performance assessment

Fig. 1a shows the polarization curves from the initial evaluation of the three plates. Both the thermal and plasma nitridation significantly improved the cell performance, with 0.2–0.3 V lower (better performance) than the untreated Ti plate at 1.2 A cm^{-2}. This improved cell performance of the nitrided plates is hypothesized to result at least in part from the reduced interfacial contact resistance of nitride surfaces vs. bare metal, see for example [5,8,12,13]. After 48 h operation at 1.2 A cm^{-2} (Fig. 1b), the untreated Ti and thermally nitrided Ti plates experienced a small increase in voltage, 0.1V range, with the plasma nitrided plate essentially unchanged. Disassembly of the test cells after 48 h operation revealed discoloration of the flow-field lands in the thermally nitrided and plasma nitrided Ti plates (Fig. 1c). Looking at a close-up of the discoloration and comparing it with the metal (untreated) Ti mesh diffusion media used in the test (Fig. 1d), it is clear the observed pattern is similar to the Ti mesh and is likely associated with the contact and/ or pooling of water between the mesh pieces on the lands.
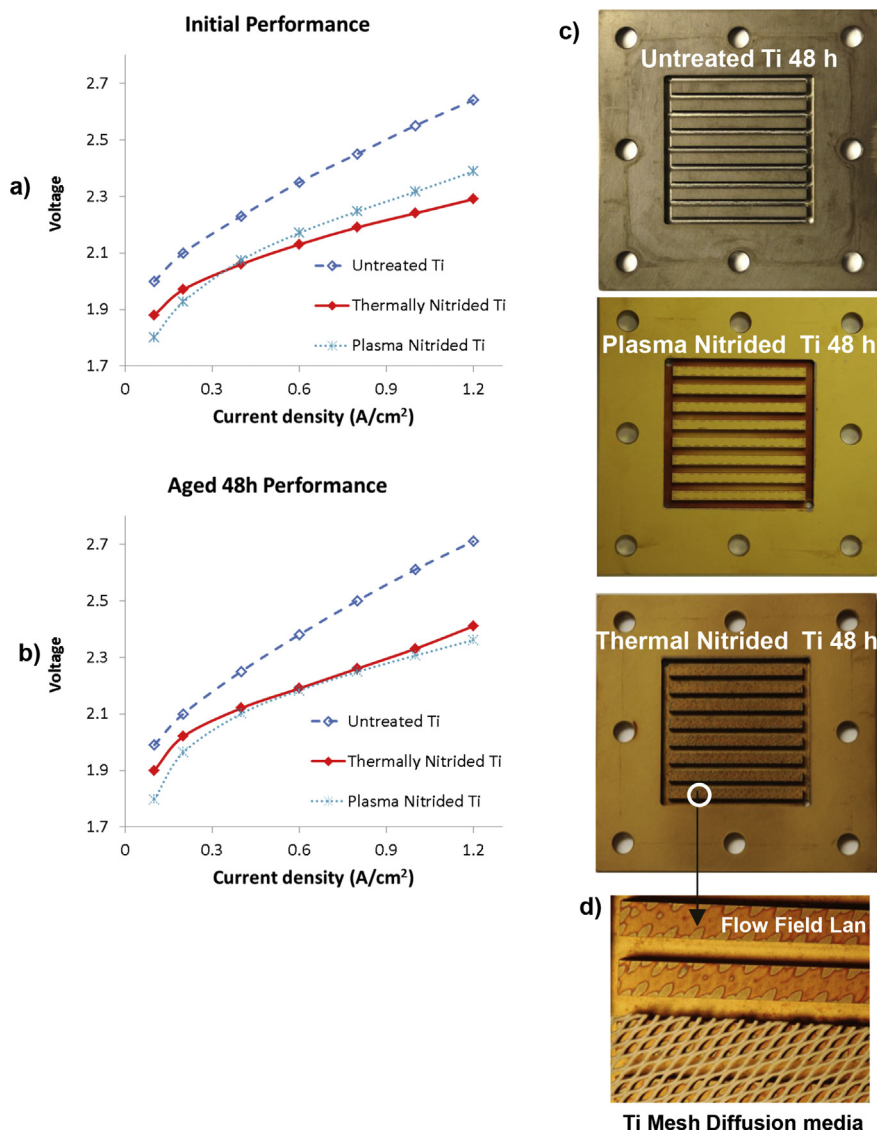

Fig. 1. Performance evaluation at 25 °C, 1 atm, 100 ml min^{-1} water flow rate. a) initial polarization curves; b) polarization curves after hold at 1.2 A cm^{-2} for 48 h; c) photographs of anode test plates after 48 h, d) close-up of thermal nitrided plate flow field land and Ti metal mesh diffusion media.

3.3. Long-term 500 h, 50 °C PEM-EC durability assessment

The electrolyzer cells were rebuilt with fresh CCM, diffusion media and gaskets, and operated for an additional 500 h using the same cathode side graphite plate and the discolored, 48 h anode side Ti and nitrided Ti test plates (Fig. 2). The cell was operated at a current density of 1.5 A cm^{-2}, and to further accelerate any corrosion effects observed in the initial 48 h performance evaluation at 25 °C, the electrolyzer was operated at 50 °C. This heat was directly controlled at the electrolyzer such that the incoming water was not heated directly; however, because the water was being recirculated, the un-reacted water that was returning to the reservoir was mildly heated after going through the electrolyzer. This resulted in a reservoir temperature of ~40 °C, and since water is being consumed and transferred through the polymer-based membrane to the cathode, it was necessary to refill the reservoir periodically. In the initial 500 h evaluation (performed on the thermally-

nitrided Ti plate), it was determined that the addition of this water could disrupt the electrolyzer performance (Fig. 2e) unless the added water was heated to the reservoir temperature. Water heating was added to the durability evaluation procedure at the 150 h mark of the thermally-nitrided plate and for all subsequent 500 h evaluations.

The initial performance behavior at 50 °C and 1.5 A cm^{-2} of the untreated Ti plate in the 500 h durability assessment was similar to the plasma nitrided Ti plate, with the thermally nitrided Ti plate cell voltage only about 3% better (lower). As shown in Fig. 2, all test plates showed an initial minor increase in cell voltage in the first 100 h of operation, with the voltage continually increasing (again minor effect) for the untreated Ti (2.42V at 0 h vs. 2.46 V at 500 h, 1.5 A cm^{-2}) and plasma nitrided Ti (2.42V at 0 h vs. 2.48 V at 500 h, 1.5 A cm^{-2}) plates, and essentially flat for the thermally nitrided Ti (2.35V at 0 h vs. 2.37 V at 500 h, 1.5 A cm^{-2}).
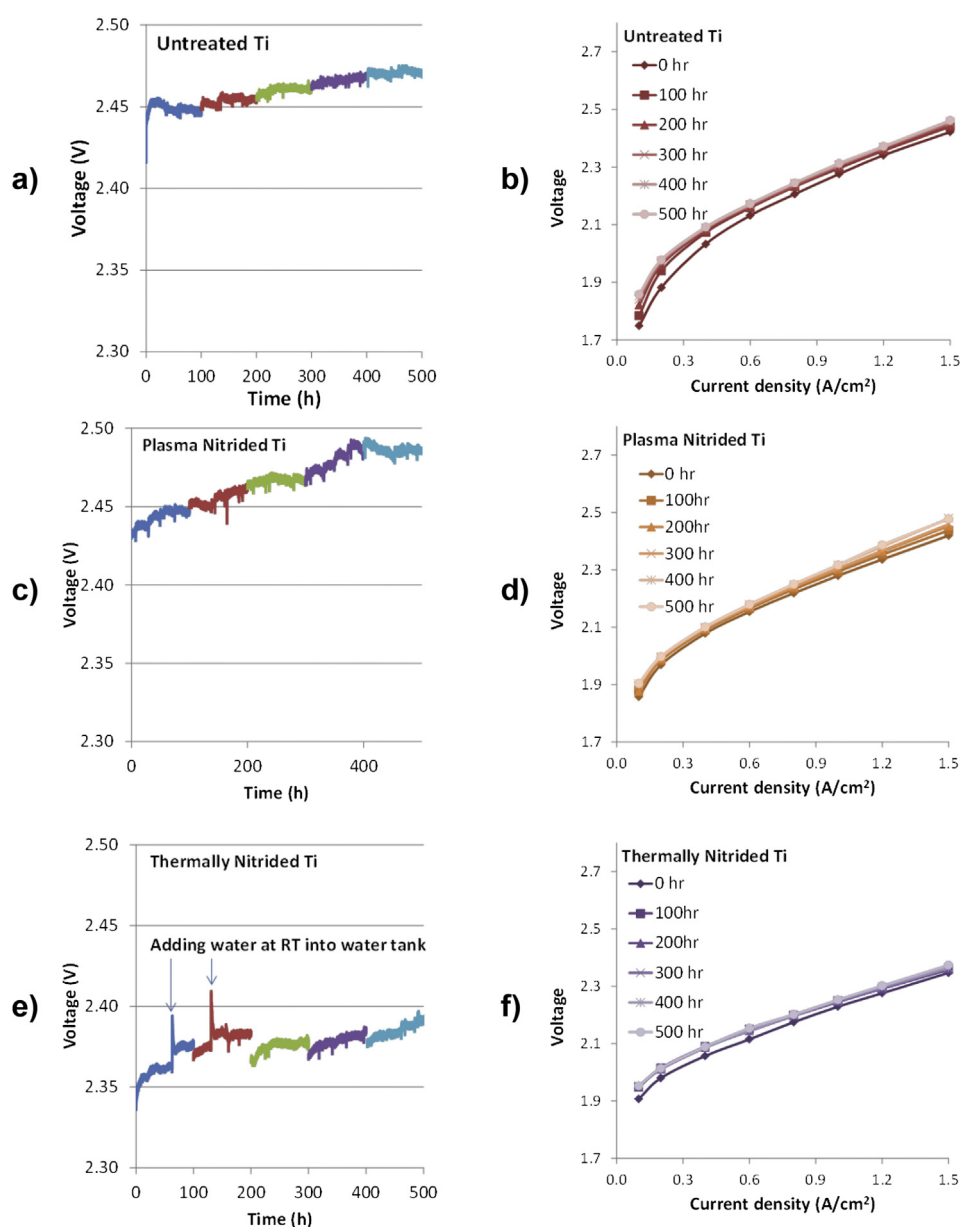

Fig. 2. Measured voltage at 1.5 A cm^{-2} during the 500 h durability evaluation and associated polarization curves. Test condition at 50 °C, 1 atm, 100 ml min^{-1} water flow rate. a), b) untreated Ti; c), d) plasma nitrided Ti; e), f) thermally nitrided Ti.
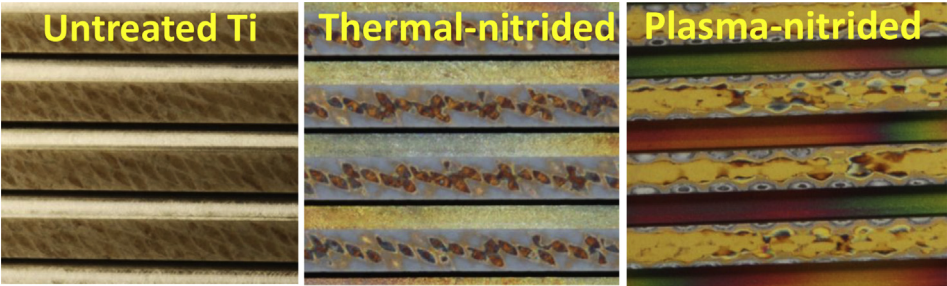
Fig. 3. Optical images of the anode test plates after the 500 h durability measurements showing significant discoloration of the flow field lands.

3.4. Characterization of nitrided surfaces after 500 h electrolyzer operation

After the 500-h durability evaluation, the electrolyzers were disassembled and the plates were once again investigated. Extensive discoloration and degradation of the nitrided flow-field land surfaces following the pattern of the Ti mesh diffusion media were again observed, as was similar surface discoloration on the untreated Ti plate (Fig. 3). The attack was primarily confined to the flow-field land surface regions in contact with the Ti mesh diffusion media, although discoloration in the plasma nitrided Ti plate was also observed in the bottoms of the flow fields between the lands (Fig. 3).

Extensive XPS studies were conducted on the discolored flow-field land surface regions of the thermally nitrided Ti plate (Fig. 4). The XPS data indicated that the discoloration was associated with oxidation of the nitrided surface, consistent with local regions of N- and C- modified TiO_2 formation (phase 1 in Fig. 4) rather than direct dissolution of the nitrided surface. Ar-ion etch profiling indicated that nitride was still present underneath the TiO_2 regions, with the higher N-containing phase 2 regions marked in Fig. 4 (Ti–O–N–C phase) increasing in surface area with increasing etch depth. The depth of oxidation is estimated to be at least on the order of several hundred nanometers.

Oxidation of Ti–N phases under the high voltage anode-side operating conditions of PEM-EC water electrolysis to form TiO_2 is not unexpected, based on corrosion studies of TiN and Ti_2N in a range of environments [15–20]. The key question for separator/current collector plates is the degree to which the nitrided surface can incorporate oxygen and remain sufficiently electrically conductive to achieve durability targets. The results of the present work indicate that both plasma nitrided TiN surfaces and mixed
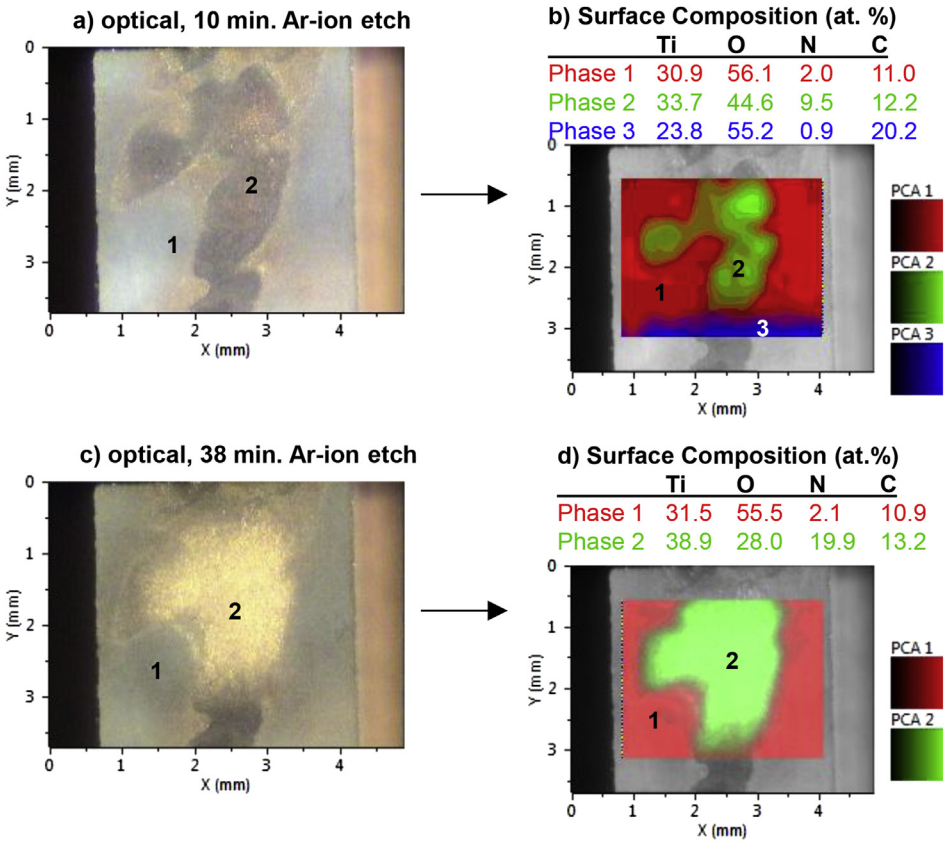

Fig. 4. Optical images after 10 and 38 min. Ar-ion etching (a,c) of the flow-field land surfaces of the thermal nitrided Ti anode plate after 500 h durability test. Corresponding XPS surface composition maps shown in b,d. The phase 3 region in the 10 min maps is considered an etch edge artifact.
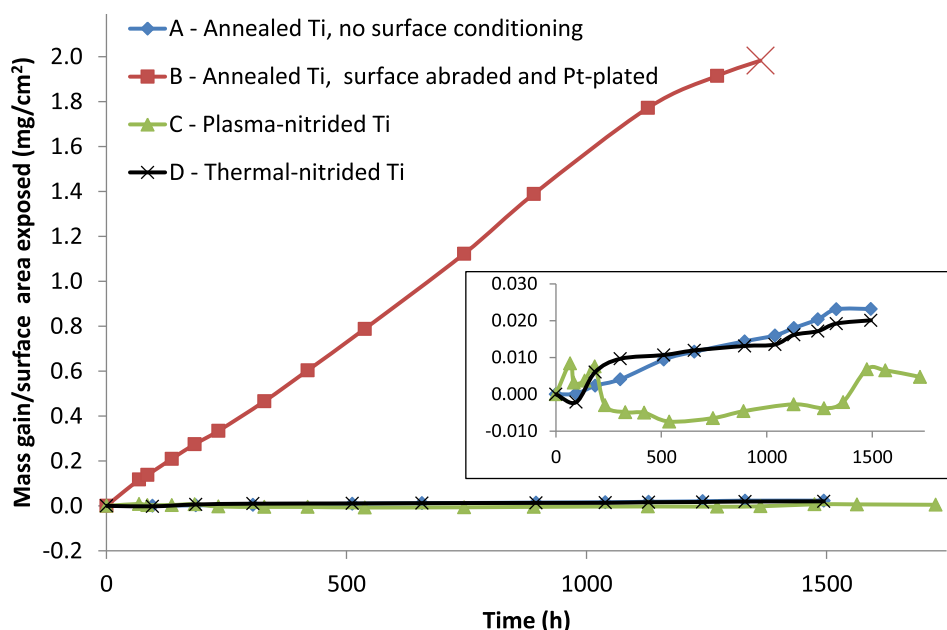
Fig. 5. H_2 uptake normalized to the exposed surface area for Ti samples at 800 psig H_2 and 150 °C. Samples were: A – as-annealed Ti with no surface conditioning, B – annealed, surface abraded, and Pt-plated Ti (failed at 1350 h), C – plasma-nitrided Ti, and D – thermal-nitrided Ti. See inset for comparison of B, C, and D.

$TiN/Ti_2N/Ti_2O$ thermally nitrided surfaces can oxidize during the first 48–100 h of electrolyzer operation, with a concomitant decrease in cell performance (V increase). However, particularly for the thermally nitrided surface, better initial performance and relatively stable behavior from 100 to 500 h of operation was observed. This result suggests that the Ti_2N phase may perform better in PEM-EC applications than the TiN phase, although the available literature (in other corrosion environments) is mixed with regards to which phase may be more corrosion resistant [15–17,20]. In particular, the thermally nitrided surface exhibited better performance than the plasma nitrided one, and examination of the anode side plates post-test showed oxidation of both the flow-field channel bottoms and flow-field land surfaces in contact with the Ti-metal mesh for the plasma nitrided plate, whereas the flow-field channel bottoms appeared unattacked for the thermally nitrided Ti (Fig. 3).

What is not clear from the present work is whether advantages of the thermally nitrided surface can be retained to meet PEM-EC durability targets. Extensive oxidation to form TiO_2 was observed in land surface contact regions with the Ti mesh diffusion media. The key question is whether sufficient electrical contact can be maintained by the local land regions that are not as extensively initially oxidized, as well as the flow-field channel bottoms. Longer term studies will be necessary to more definitively answer the question of whether nitrided Ti surfaces provide sufficient benefits for PEM-EC separator/current collectors. Design modification and/or nitridation of the Ti metal diffusion media in the simple cell design evaluated in the present work may also result in less local oxidation attack, potentially meeting cost and durability targets.

3.5. Effect of nitrided surface on hydrogen uptake and embrittlement

As another basis of comparison of the potential benefits of surface treatments of titanium parts in PEM-ECs [14,21], representative titanium coupons were exposed to high pressure H_2 as described in Section 2.4. Fig. 5 shows the level of protection that can

be achieved through the nitriding processes described in Section 2.1. The untreated annealed Ti (sample A) shows only a minimal amount of H_2 uptake; however, untreated Ti has low surface conductivity and thus a surface enhancement is desirable for PEM-EC applications. A common practice is to plate Ti with Pt, which typically requires a surface abrasion technique to enhance adhesion. A side effect of this increased conductivity is the dramatic rise in H_2 uptake as noted in Fig. 5, sample B (annealed, surface abraded, and Pt plated). This sample delaminated after 1350 h of exposure at 800 psig and 150 °C with notable curvature apparent after 350 h. The plasma-nitrided sample, C, showed little uptake during the entire 1700 h exposure, with minimal visible signs of any attack occurring. The thermally-nitrided sample, D, behaved similar to the untreated sample, A, as only a minimal amount of H_2 was absorbed. The inset in Fig. 5 illustrates that the plasma-nitrided sample offered the best protection from H_2 embrittlement, but the untreated or thermally nitrided samples offered more than adequate protection from the H_2 uptake. This screening for H_2 embrittlement susceptibility suggests that nitriding offers substantial benefits for reduced susceptibility to H_2 uptake compared with surface-abraded and Pt-plated Ti, again the key question is whether the local susceptibility to oxidation of the nitrided Ti surfaces can be tolerated in long-term operation without unacceptable loss of performance.

4. Conclusions

Anode side plates of untreated Ti, thermally nitrided Ti, and plasma nitrided Ti were evaluated under PEM-EC operating conditions. It was determined that:

1) Nitrided Ti surfaces offer up to 3–13% range initial performance improvement compared to untreated Ti in single-cell evaluation.
2) Nitrided Ti surfaces are susceptible to oxidation under anode-side PEM-EC operating conditions.
3) Unlike surface abrasion and Pt-plating, nitriding does not increase susceptibility to H_2 uptake and embrittlement, making it

attractive as a method to increase surface conductivity in PEM-EC plates.

4) Longer term studies and optimized Ti diffusion media/flow field design will be needed to definitively determine if nitrided Ti plates offers sufficient durability and cost benefits to replace more expensive precious metal and platinum group metal coatings on Ti. This includes the evaluation of nitrided diffusion media which may decrease the oxidation/discoloration observed in the plates.

Acknowledgments

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