

V.C.3 Novel Structured Metal Bipolar Plates for Low Cost Manufacturing

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control the etching depth and can be easily integrated with the deposition process in the low cost, high volume production system.

Task 3: The objective of this task is to demonstrate full size bipolar plates and conduct the test of the coated stainless steel metal plates in an automotive short stack (20 cells). The stack test will focus on the prestamped plates and TreadStone will apply the nanostructured conductive titanium oxide coating on the stamped plate (poststamping coating).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

The targets of the technology development include the following.

- Low electrical contact resistance with gas diffusion layer (<5 mΩ cm)
- Low corrosion resistance: <1 μA/cm²
- Low cost: \$3/kW by 2017
- Low cost coolant side coating for low contact resistance (<2 mΩ cm) of cathode and anode plates
- Capable of roll to roll coating and postcoating stamping

Overall Objectives

The technical objective of the Phase II project is to optimize the electrically conductive titanium oxide coating technology that has been developed in the Phase I project, and to demonstrate its performance in an automobile short stack. The objective is to optimize the technology for the full size, high volume production using industrially available physical vapor deposition (PVD) production systems. It will include the titanium alloy target material optimization, PVD process development for the uniform coating, and if it is necessary, a post deposition reactive ion etching (RIE) process to obtain the desired surface composition and microstructure.

Fiscal Year (FY) 2015 Objectives

Task 1: The objective of this task is to identify the best composition of titanium alloy target as the coating material for proton exchange membrane fuel cell applications. The PVD and wet chemical etching process that was developed in the Phase I project will be used in this task for the titanium alloy composition optimization.

Task 2: The objective of the PVD process development is to obtain a uniform Ti alloy thin film (~0.1 μm thick) coating without the wet etching process. The deposition condition will be optimized to avoid or minimize the composition segregation of the Ti alloy coating. Alternatively, if it is difficult to eliminate the composition segregation, plasma non-reactive ion (argon) etching or RIE will be used to obtain the uniform thin film layer of Ti alloy on the stainless steel (SS) substrate. The plasma etching process can precisely

FY 2015 Accomplishments

In Task 1, we have identified the Ti alloy target materials that have low electrical contact resistance and exceptional corrosion resistance in accelerated stress tests. It was found that the electrical contact resistance and durability of both Ti-Ta and Ti-Nb coated stainless steel can meet DOE's targets. We also finished an 1,100-hour durability test of Ti-Nb coated SS plates in a single cell performance test. There was no degradation of the plates after the test. In Task 2, we have compared the properties of direct current magnetron sputtering and cathodic arc deposition processes. It was found that the coating deposited by sputtering has lower electrical resistance and higher durability after a chemical etching treatment. More investigations have also been conducted in

the dry etching process for surface layer modification. It has demonstrated the feasibility of using dry etching for coating surface modification. Ford Motor Company evaluated the performance of the Ti-Nb coated SS plate. Ford duplicated TreadStone's results and agreed to provide a stack for the durability demonstration in an automobile fuel cell stack of Task 3. The detailed stack testing plan was determined and TreadStone is in the process of finishing the coating of the plates provided by Ford for the stack durability test.



INTRODUCTION

The thrust of the proposed work is to use the nanostructured, electrically conductive titanium oxide layer grown on the titanium alloy surface to protect SS metal plates from corrosion. This technology will go beyond TreadStone's current gold-dot technical solution to meet the latest metal plate technical requirements, which are aimed at cost reduction and performance improvements to guarantee lifetime performance of fuel cell vehicles.

APPROACH

The scope of the Phase II project is focused on the titanium alloy target material development, PVD process development for the titanium alloy surface coating layer deposition. The electrically conductive titanium oxide coating will be grown by thermal oxidation under controlled conditions. The surface layer composition and microstructure will be determined. The coated stainless steel plates will be tested by ex situ evaluation and in situ tests using small (16 cm²) single cells (Task 1 and 2), and full size, short (20 cells) stack (Task 3) under automobile dynamic driving conditions.

RESULTS

Task 1

In Phase I of the project, we tested the Ti-Nb alloy target with an Nb concentration of 3 at%, 5 at%, and 7 at%. It was found that the Ti-Nb alloy with 3% Nb (Ti-3Nb) has the lowest resistance. It was verified by the phase diagram of Ti-Nb that Ti-Nb will be in single α -phase with the Nb concentration below 2 at%. At higher concentration, a high Nb content β -phase (up to 40 at% of Nb) will show up. The surface oxide layer on this β -phase may have a high electrical resistance.

In order to avoid the high Nb content β -phase in the Ti alloy coating layer, we prepared two types of Ti alloy target with lower (2 at%) dopant element concentration, which are 2 at% Nb (Ti-2Nb) and 2 at% Ta (Ti-2Ta), respectively.

These targets were used for the Ti alloy coating on SS foil, using the PVD process. The electrical contact resistance (in the form of through plate resistance, TPR) was measured. The TPR of the as coated SS foil using a sputtering process was very high (300–700 m Ω cm², comparing with the target of <10 m Ω cm²). Surface chemistry analysis indicated that the composition of the bulk of the coating layer is same as the target material, but the surface layer (~10 nm deep) is pure Ti without Nb or Ta alloy element. The reason for this composition segregation on the surface during sputtering process is unknown.

The surface pure Ti layer was removed by a wet chemical etching process using 3% hydrogen fluoride (HF) solution, the same way as that in Phase I of the project, then thermally oxidized in air to obtain a more stable surface oxide layer. The coated SS foil was first evaluated by potentiodynamic and potentiostatic corrosion tests in pH 3 H₂SO₄ + 0.1 ppm HF solution at 80°C. Figure 1 shows the potentiodynamic curves of Ti2Nb and Ti2Ta coated stainless steel (Ti2Nb-SS, Ti2Ta-SS, respectively) with the scanning rate of 10 mV/min. It was found that both Ti2Nb and Ti2Ta coated SS had low corrosion current. The typical transpassivation corrosion peak of stainless steel between 0.8–0.9 V_{NHE} (0.6–0.7 V_{Ag/AgCl}) almost disappeared, which indicates that the Ti alloy coating can effectively protect the SS substrate. The corrosion current of Ti2Ta coated SS is much lower than that of Ti2Nb coated SS, which could indicate that the Ti2Ta-SS has a better corrosion resistance than that of Ti2Nb-SS.

The curves of the potentiostatic test of Ti2Nb-SS and Ti2Ta-SS are shown in Figure 2. It shows that the corrosion

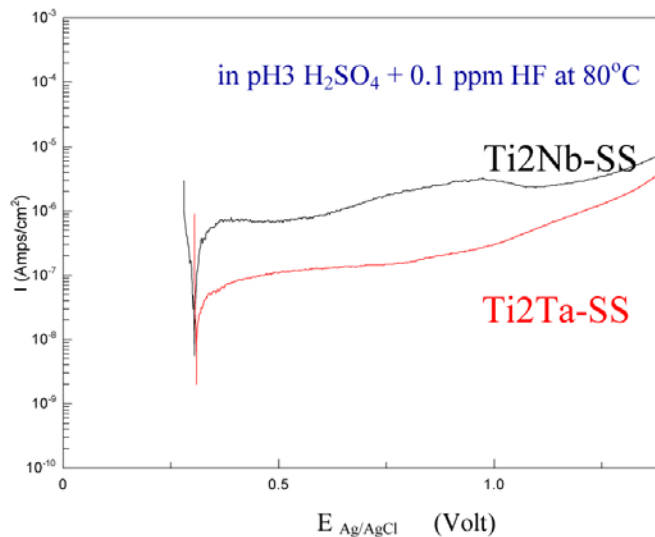


FIGURE 1. Potentiodynamic curves of Ti2Nb-SS and Ti2Ta-SS with the scan rate of 10 mV/min

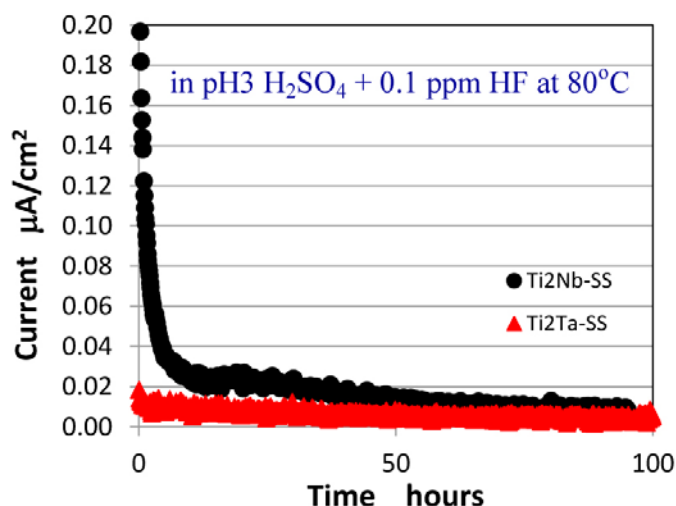


FIGURE 2. Potentiostatic curves of Ti2Nb-SS and Ti2Ta-SS under the polarization of potential of $0.8 V_{NHE}$

current of both Ti2Nb-SS and Ti2Ta-SS are very low ($<0.2 \mu A/cm^2$) which easily meet the target defined by DOE ($<1 \mu A/cm^2$). As with the potentiodynamic test, Ti2Ta-SS has a lower corrosion current than that of Ti2Nb-SS.

The electrical properties of Ti2Ta-SS and Ti2Nb-SS were compared by the TPR measurement with the plate in contact with TGP-H-060 Toray Paper. The TPRs of the Ti-2Nb and Ti-2Ta coated SS are lower than that of Ti-3Nb coated SS developed in Phase I of the project. The TPR difference between Ti-2Nb and Ti-3Nb is more significant after $1.6 V_{NHE}$ corrosion test in pH 3 H_2SO_4 - 0.1 ppm HF solutions at $80^\circ C$. As shown in Figure 2, Ti-2Nb coated SS has a lower resistance after the test despite the much longer corrosion time (24 hours) than that of Ti-3Nb (6 hours).

It was found in Phase I that the thermally oxidized Ti alloy coated SS has much better stability under the high potential corrosion conditions for proton exchange membrane fuel cells, despite the fact that the thermally oxide plates have higher electrical resistance. The higher stability of the oxidized coating may lead to the potential benefit that the thermally oxidized plate resistance at the end of life is lower than that of nonoxidized plates. Therefore, this process is continually used in this phase of the project. The thermal oxidization of the coated SS increases TPR compared to the etched plates. But the increase of Ti-2Nb coated SS is much smaller than that of Ti-3Nb coated SS. The corrosion stability of Ti-2Nb coated and oxidized SS was evaluated with the electrochemical corrosion test at $0.8 V_{NHE}$, $1.6 V_{NHE}$ and $2.0 V_{NHE}$ in pH 3 H_2SO_4 - 0.1 ppm HF solutions at $80^\circ C$ for 24–100 hours. It was found that the thermally oxidized Ti-2Nb coated SS is very stable. It did not have a TPR increase after those corrosion tests (within measurement error). In comparison, Ti-3Nb coated SS had shown a TPR

increase after 0.8 V and 1.6 V corrosion tests as reported in Phase I of the project. The hypothesis is that the high Nb content β -phase is left on the surface after etching process will grow a high Nb content surface oxide layer. This oxide surface layer may have high electrical resistance and the resistance will keep increasing during corrosion due to the thickness increase of the oxide surface layer. On the other hand, the elimination of the β -phase in Ti-2Nb successfully avoids this issue.

The Ti2Nb alloy coated stainless steel plates were further evaluated in a single cell durability test. The cell hardware was from Fuel Cell Technologies, with $16 cm^2$ active area and serpentine flow field design. The cell was tested around $30^\circ C$ at constant current (maintain the cell voltage between 0.70 V and 0.75 V). The total test time was 1,100 hours. The surface contact resistance of the plate was measured with TGP-H-060 Toray Paper before and after the single cell durability test. Figure 3 shows the cell voltage curve during the test and Figure 4 shows the comparison of the electrical contact resistance of the cathode and anode plates before and after the single cell test. It shows that the surface contact resistance of the plates (with flow field channels) is below $4 m\Omega cm^2$ at 150 psi, which meets DOE's target ($<10 m\Omega cm^2$). After the 1,100-hour test in single cell, there was no contact resistance increase.

Task 2

In this period, we have evaluated the Ti alloy coating using sputtering and cathodic arc deposition process. The TPR of as coated SS foils was measured. It was found that between the as coated stainless steel plate, sputtering coated

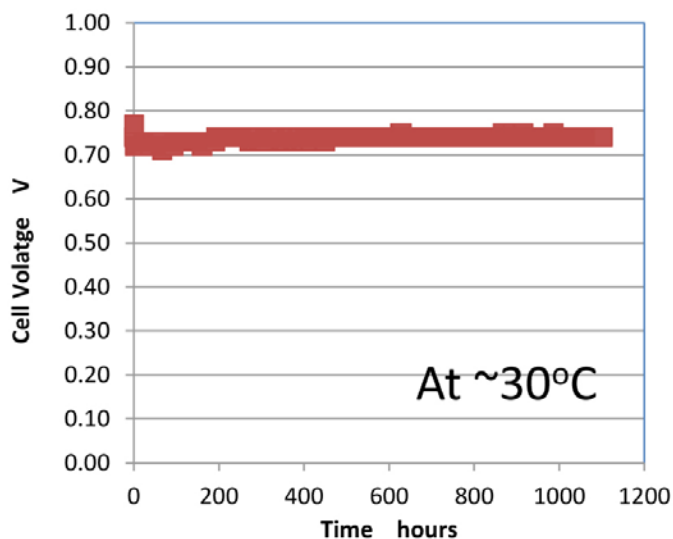


FIGURE 3. Comparison of TPR of Ti-2Nb, Ti-2Ta, and Ti-3Nb coated stainless steel foil

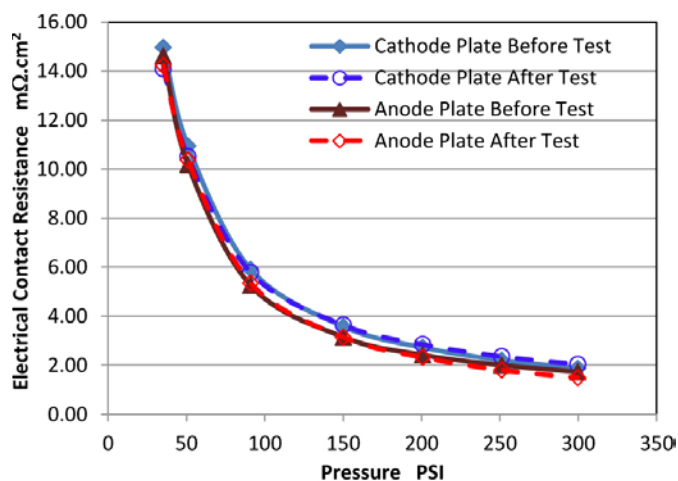


FIGURE 4. Comparison of TPR of Ti-2Nb and Ti-3Nb coated stainless steel foil after corrosion test at $1.6 V_{NHE}$

TABLE 1. TPR ($m\Omega cm^2$) Comparison of As-Coated SS with Ti-2Nb Alloy Using Sputtering and Cathode Arc Methods

Pressure PSI	35	51	91	150	201	250	300
Sputtering	1,037.33	806.95	633.21	479.48	399.86	329.19	274.14
Cathodic Arc	38.74	27.22	14.35	8.36	6.12	4.81	4.02

SS has much higher TPR than that of cathodic arc coated SS, as shown in Table 1.

On the other hand, sputtering can deposit a very thin coating layer and has a high target utilization rate for low cost production. Cathodic arc coated surface is very rough, with many micron-scale particles on the surface. The surface chemistry analysis by X-ray photoelectron spectroscopy indicates that the surface layer of SP-Ti2Nb-SS does not contain niobium, but the surface layer composition of cathodic arc coated Ti2Nb-SS (CA-Ti2Nb-SS) is the same as the target material (2 at% of Nb in Ti).

Despite the lower TPR of the as-coated cathodic arc coated Ti2Nb-SS, its TPR will increase after the corrosion test due to the continuous growth of the titanium oxide surface layer. The through plate resistance after $2 V_{NHE}$ 24-hour corrosion is near $50 m\Omega cm^2$, which does not meet DOE's target. Thermal oxidization can stabilize the surface oxide layer, but the TPR of a CA-Ti2Nb-SS plate is $33 m\Omega cm^2$ at 150 psi, that does not meet DOE's target. Wet etching of CA-Ti2Nb-SS could reduce the TPR, but the TPR of a thermally oxidized plate ($23.8 m\Omega cm^2$) still can't meet the requirement. In addition, the TPR will keep increasing after the corrosion test (to $30.3 m\Omega cm^2$ after $0.8 V_{NHE}$ 70 hours). The reason for the higher TPR and unsatisfied stability of cathodic arc deposited coating is not clear, further development is needed to invest the feasibility of using cathodic arc as the coating method. At this stage of

the project, we will focus on sputtering deposition despite the surface composition segregation issue.

It was found that the surface layer composition of the sputtered Ti-2Nb coating is pure Ti. Nb only exists in the subsurface layer (below 10 nm from the surface). A chemical etching step is necessary to obtain the Ti alloy on the coating surface. In this project, different etching methods have been evaluated, including wet etching using diluted HF solution, and vacuum etching (dry etching) using various chemicals. Dry etching uses fluorine or chlorine containing compounds that can react with titanium in a vacuum. Because of the high vapor pressure of titanium fluoride and titanium chloride, the reaction product can be continually removed from the plate surface and maintain the continuing etching process. This process has been readily used in the semiconductor industry. Compared to wet etching, dry etching is more controllable to remove very thin layer (nanometers). In addition, dry etching has the advantage to be easily integrated with the PVD process as a one-pass coating/surface treatment process for low cost manufacturing.

We evaluated three dry etching processes. One uses XeF_2 vapor; the second uses HF- H_2O vapor at low vacuum. The third uses plasma reactive ion etching using CF_4 . Vapor etching has the advantage of low capital cost but may have the challenge of the uniform etching of large size plate in high volume production because of mass transport limitations. On the other hand, plasma etching generates the reactive species between electrodes. It is easier to achieve uniform etching with the planar electrode reactors.

The TPRs of XeF_2 (with Ar as carrier gas), HF- H_2O vapor and CF_4 plasma etched Ti-2Nb coated SS plates are shown in Figure 5. It was found that all three methods can effectively reduce the TPR of Ti-2Nb coated SS plates. This experiment shows the feasibility of postdeposition surface

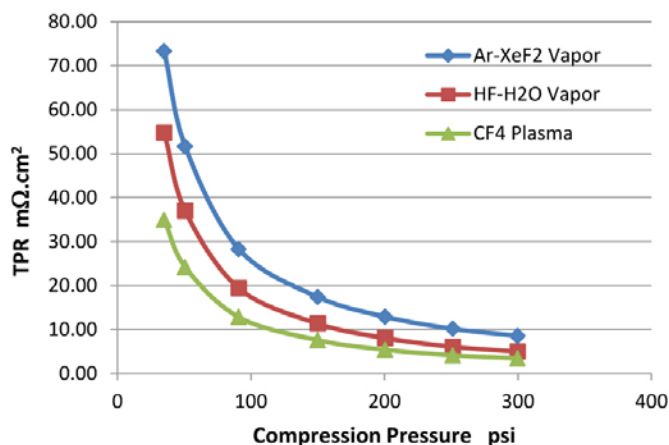


FIGURE 5. Comparison of TPR of Ti-2Nb coated dry etched using different processes

modification using the dry etching process. Although its TPR is not as low as the as wet etched Ti-2Nb coated SS, the resistance can still meet the application requirements ($<10 \text{ m}\Omega \text{ cm}^2$) using HF vapor and plasma etching processes. Further corrosion resistant tests of these coated materials will be conducted in the following months of the project.

It was found that XeF_2 , HF vapor etching and plasma enhanced RIE can effectively remove titanium alloy. However, it was found that the etching rate for Ti is much higher than that of Nb and Ta. The Nb and Ta concentration of the dry etched surface layer is very sensitive to the etching condition, and difficult to control. We have detected the Nb concentration up to 20–50% on the dry etched surface. The electrical contact resistance of such high alloy content surface is too high for proton exchange membrane fuel cell applications.

Another phenomenon we have observed in dry etching is the impurity enrichment on the surface. The typical metallic impurity in titanium is iron. Because of the low vapor pressure of iron fluoride and chloride, iron cannot be removed in dry etching. Other minor impurities may have the same issue in the dry etching process. Figure 6 is a scanning electron microscope (SEM) picture of a plasma RIE treated Ti2Nb coated SS surface. It clearly shows the grain boundary of the Ti2Nb coating layer. At higher magnification, it seems that the grain boundary stands out of the grain surface. The hypothesis is that the etching rate of the grain boundary is slower than that of the grain because of the enrichment of iron and other impurities with low etching rates. The stand-out grain boundary may have a negative impact to the surface charge of the plate with the gas diffusion layer.

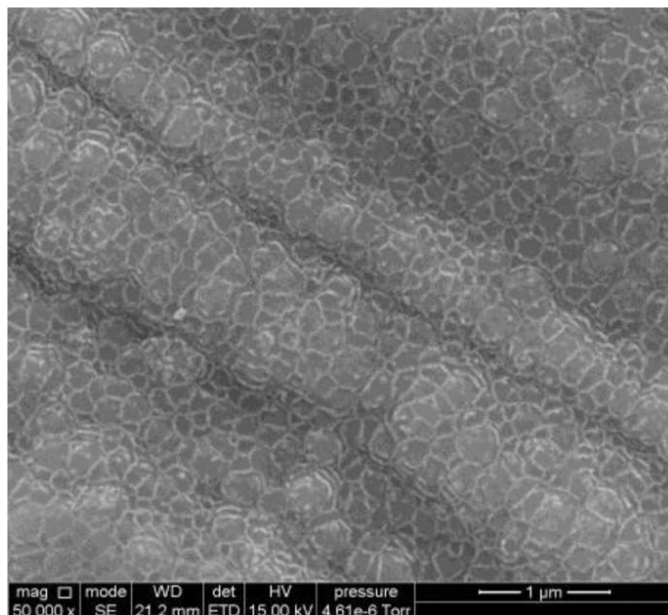


FIGURE 6. SEM picture of RIE treated surface of Ti-2Nb coated stainless steel

Task 3

After demonstrating the superior stability and low electrical resistance of the coated stainless steel plates, we sent the Ti2Nb alloy coated SS samples to Ford for their evaluation. After ex situ corrosion and electrical contact resistance tests, they were satisfied with the performance of TreadStone's coating and agreed to provide metal plates and membrane electrode assemblies (MEAs) for the stack durability test for the project. The plate will use Ford's standard design, instead of the latest high performance flow field design to protect their intellectual properties. However, Ford only has a limited amount of MEAs for this plate design and it is difficult to obtain new MEAs from their supplier, W.L. Gore. So, Ford recommended the following adjustments in the stack test plan.

- Test a 10-cell short stack, with power of 2–2.5 kW.
- Ford will assemble the stack, conduct the initial performance test (~100 hours) before it ships to the University of Hawaii.
- The University of Hawaii will conduct a 1,500–2,000-hour test, depending on the MEA degradation rate. No plates will be taken out during the test.
- Testing protocol is the combined public drive cycles, e.g., Environmental Protection Agency (city and highway) and New European Drive Cycle.
- The stack will be sent back to Ford for inspection after the 1,500–2,000-hour test.
- If the performance is satisfactory and Ford still has available MEAs, the stack may be assembled again with new MEAs for the second 1,500–2,000-hour test.

Ford sent 20 pieces of formed bipolar plates to TreadStone for coating in June 2015. However, we experienced issues in the Ti-2Nb alloy sputtering with our PVD partner in June and July. The coated SS plates are more difficult to etch compared with the plates coated in the early part of the project, and the finished plates have high resistance. TreadStone processed over ten batches of Ti alloy coated SS through the project before processing the bipolar plates from Ford. All of these batches were processed between October and April; the humidity was low in the northeastern United States and none of those batches had etching problems. We learned from the PVD partner that their system took a longer time to reach the desired vacuum for the process in the latest batches in June and July. The hypothesis is that high humidity in the summer has an impact on the coating properties. There is a coating on the inner wall of the vacuum chamber in the PVD system. It may absorb moisture from air during the loading/unloading period, then it may slowly release water vapor during the Ti alloy deposition process and lead to the high oxygen content in the alloy coating. The etching behavior of the high oxygen

content Ti alloy layer could be different from the normal coating because of the big difference of the etching rate of titanium metal and titanium oxide.

Due to the limitation of its system, TreadStone decided to wait to resume plate coating until September/October, when humidity is lower in the Northeast.

CONCLUSIONS AND FUTURE DIRECTIONS

The stable performance of the Ti-2Nb and Ti-2Ta coated stainless steel at high potential ($1.6 V_{\text{NHE}}$ and $2.0 V_{\text{NHE}}$) is very significant for the practical application in proton exchange membrane fuel cells. It means that this coating has the capability to withhold the high potential transient conditions, which is the key barrier for precious metal free coating technologies, such as nitride and graphite coatings.

The dry etching process can be used to optimize the surface chemistry composition. But it has to be carefully controlled so that only a very thin (nanometers) layer is removed to avoid too high an Nb or Ta concentration and minimize the impurity enrichment on the Ti alloy surface.