V.D.2 Novel Structured Metal Bipolar Plates for Low Cost Manufacturing

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University of Hawaii, Honolulu, HI

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Overall Objectives

The technical objective of the Phase II project is to optimize the electrically conductive doped titanium oxide (doped TiO_x) 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 industrial available physical vapor deposition (PVD) systems. It will include the titanium alloy targets optimization, PVD process development for the uniform coating, and if it is necessary, a post deposition reactive ion etching process to obtain the desired surface composition and microstructure.

Fiscal Year (FY) 2016 Objectives

The objective of the project in 2016 is to further develop the PVD process for the doped TiO_x coating deposition and demonstrate the long-term stability of the doped TiO_x coated stainless steel bipolar plates by an in situ durability test in a short automobile stack. The coating process will be focused on the post stamping coating in this phase of the project. In addition, formability of the coated stainless steel foil will be evaluated for the future pre-stamping coating.

Technical Targets

The targets of the technology development include:

1. Low electrical contact resistance with gas diffusion layer (<5 mΩ cm)
2. Low corrosion resistance: <1 µA/cm^2
3. Low cost: <$3/kW by 2020
4. Low cost coolant side coating for low contact resistance (<2 mΩ cm) of cathode and anode plates
5. Capable of roll to roll coating and postcoating stamping

FY 2016 Accomplishments

- Optimized the PVD process for the large amount plate processing with consistent quality.
- Coated full size automobile fuel cell plates, assembled the short stack with the support from Ford. The long-term durability testing is on-going at University of Hawaii.
- Finished the formability tests of the coated stainless steel foil.

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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 stainless steel 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 oxidization 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 cm^2) single cells (Task 1 and 2), and full size, short (10 cells) stack (Task 3) under automobile dynamic driving conditions.

RESULTS

In TreadStone's doped TiO_x coating technology, PVD method is used for the titanium alloy deposition. In the project we have compared the impacts of the titanium alloy target composition and PVD process parameters to the performance of the coated stainless steel plates.

In total, four different Ti-Nb alloy targets are compared. The niobium concentration in titanium alloy targets are 2%, 3%, 5%, and 7% (noted as Ti-2Nb, Ti-3Nb, Ti-5Nb, and Ti-7Nb, respectively). It was found that the through plate resistance (TPR) of the as-coated plate is related with the target composition. As shown in Figure 1, Ti-2Nb and Ti-3Nb coated plates have much lower TPR than that of Ti-5Nb and Ti-7Nb. The hypothesis is that the high niobium content titanium alloy will form high niobium content β-phase that lead to the high TPR.

The difference between Ti-2Nb and Ti-3Nb is shown in the ex situ corrosion test of the coated stainless steel plates. Figure 2 and 3 show the TPR comparison of coated stainless steel before and after corrosion tests. The Ti-3Nb coated plates have small TPR increase after the corrosion tests for 100 h at 0.8 V_{NHE} in pH3 H_2SO_4 + 0.1 ppm hydrofluoric acid solutions at 80°C. On the other hand, there is no TPR increase of Ti-2Nb coated stainless steel plate after the same and more aggressive (at 1.6 V_{NHE} and 2.0 V_{NHE} 20 h) corrosion tests. It is possible that there are still small amount of niobium rich β-phase in the Ti-3Nb coating, which will grow the more resistant niobium oxide during corrosion test. Ti-2Nb coating could be in pure α-phase that surface oxide layer keeps the semi-conductive doped TiO_x phase through the corrosion tests.

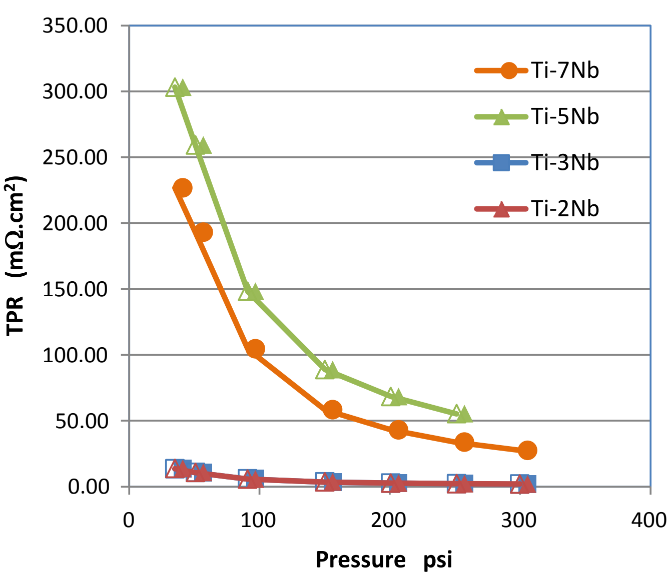


FIGURE 1. TPR comparison of coated stainless steel plate using different Ti-Nb target

Therefore, the project is focused on the coating using Ti-2Nb target to prepare full size bipolar plates for automobile short stack tests. Twenty plates were prepared in the project and were sent to Ford for the stack assembly. Ford used 11 plates to assemble a 10-cell stack in their facility. After the initial testing at Ford, the stack was delivered to University of Hawaii for the durability test. The stack has finished ~600 h test under automobile dynamic testing conditions. One bipolar plate was taken out of the stack after 524 h for middle of life inspection. There was not visible corrosion marks on the plate after the 524 h test. The TPR of the plate has small increase comparing with the original plate (beginning of the life), as shown in Figure 4. But the TPR still meets DOE's technical target (<20 $m\Omega.cm^2$). The project is planned to finish the 2,000 h of this stack.

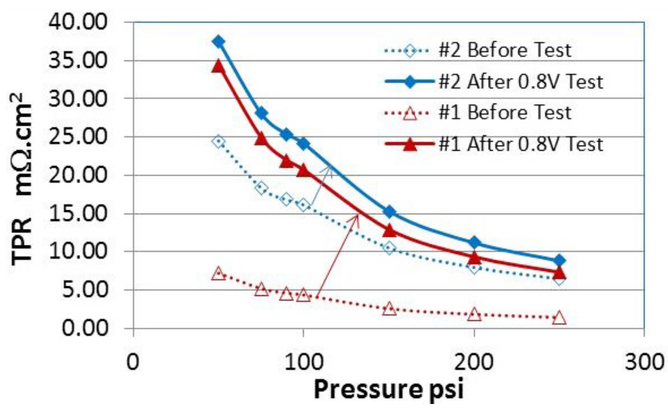


FIGURE 2. TPR comparison of stainless steel plates coated with Ti-3Nb alloy processed at different conditions (#1 and #2) before and after the corrosion tests at 0.8 V_{NHE} in pH3 H_2SO_4 + 0.1 ppm hydrofluoric acid solutions at 80°C

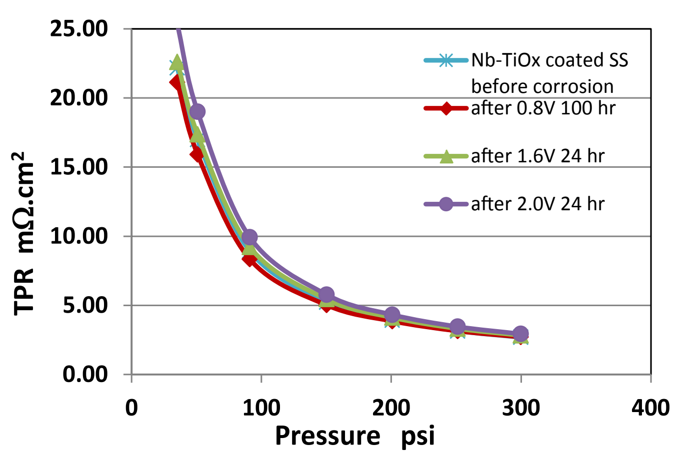
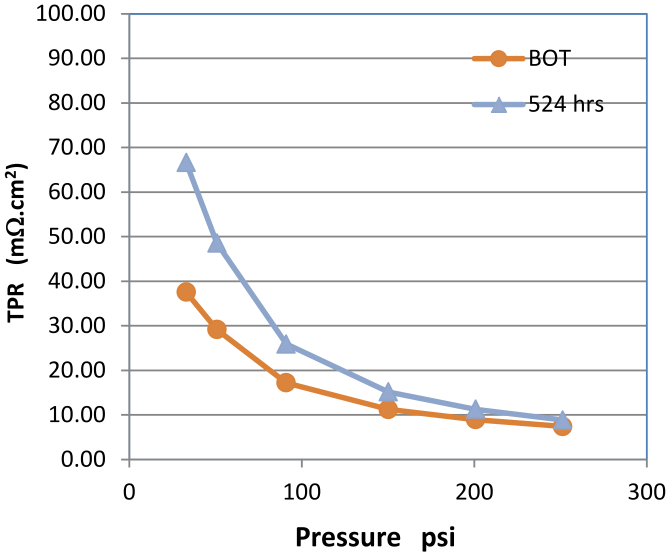


FIGURE 3. TPR comparison of stainless steel (SS) plates coated with Ti-2Nb alloy before and after corrosion tests in pH3 H_2SO_4 + 0.1 ppm hydrofluoric acid solutions at 80°C



BOT – Beginning of test

FIGURE 4. TPR comparison of the bipolar plate before and after 524 h stack test

The formability of the titanium alloy coated stainless plates is evaluated in this phase of the project. It was found that coating thickness has major impacts on the plate formability. It was found that a thick Ti-Nb alloy coating layer will crack after stamping. After comparing stainless steel foil with different thickness Ti-Nb alloy coating, it is concluded that the titanium alloy coating thickness has to be less than 0.2 µm to avoid the coating layer crack during stamping. On the other hand, the stainless steel substrate may have some micro-cracking or micro-tearing during stamping. The substrate micro-cracking behavior is highly related with the flow field and forming-die designs. For the pre-stamping coating process, it is desired to have proper stamping process to avoid the substrate micro-cracking. With this condition, it is feasible to develop the pre-stamping coating of the doped TiO_x coating with a thin (<0.2 µm) Ti alloy coating.

CONCLUSIONS AND FUTURE DIRECTIONS

TreadStone demonstrated the low electrical contact resistance and superior corrosion resistance of the semi-conductive Nb doped TiO_x grown on Ti-2Nb alloy sub-layer coated on 316L stainless steel plates. The experimental results of this precious metal free coating technology indicates the potential of this technology for polymer electrolyte membrane fuel cell applications. Additionally, it was found in the project that the coating performance depends on the processing conditions. Some critical questions have to be answered before the development of the large volume production for automobile applications.

Further technology development should be focused to provide answers to these questions.

- ***PVD process optimization:*** The Ti alloy sub-layer deposition process has to be optimized for high volume production. It is desired to eliminate the hydrofluoric acid etching process used in Phase II project for low cost manufacturing, and fabrication cost of the coating technology need to be analyzed.
- ***Doped TiO_x surface layer growth mechanism:*** It was found in Phase II project that the properties of doped TiO_x surface layer grown on Ti alloy sub-layer is highly related with the titanium alloy composition and the processing conditions. It is necessary to understand the mechanism of the doped TiOx layer growth on the titanium alloy sublayer surface. This understanding is critical for quality control of the bipolar plate production process.