DOE/GO/10320-Q

DOE/GO10320-4

COMPOSITE ELECTRODES FOR ADVANCED ELECTROCHEMICAL APPLICATIONS

Quarterly Report for the Period July 1 – September 30, 1999

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Date Published -October 1999

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY
Office of Industrial Technologies
Grant No. DE-FG36-98GO10320

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ABSTRACT

The electrochemical industry is one of the most highly energy intensive industries today. However, there have been no significant advances in the electrodes that these industries use. The dimensionally stable anode (DSA), which ELTECH introduced under a license agreement, has been the industry standard for the past twenty-five years. But, DSAs are nearing the end of their technological prevalence. The principal problems with DSAs include high capital and operating costs, and the proprietary nature of the technology. In addition, DSAs experience problems that include: contamination of the process solution by anode materials, failure when the electrocatalytic coating peels from underattack, generally low anode performance due to inherent limitations in operating current density, and short anode lifetime because of corrosion.

The proposed innovation combines the low electrical resistance of copper with the corrosion resistance of electrically conductive diamond to achieve energy efficient, long-lifetime electrodes for electrochemistry. The proposed work will ultimately develop a composite electrode that consists of a copper substrate, a conductive diamond coating, and a catalytic precious metal coating. The scope of the current work includes preparation, testing, and evaluation of diamond-coated titanium electrodes.

PROGRESS

During the tenth and eleventh months of this work, North Coast Crystals (NCC) continued preparing diamond coated titanium substrates, by microwave plasma chemical vapor deposition, for both Eltech Research Corporation (ERC) and Chemionic Enterprises (CIE). However, during the twelfth month, NCC had to completely disassemble its microwave reactor and replace the RF heating coil. We estimate that this reactor will be reassembled by the end of month 14 of this project.

During the tenth, eleventh, and twelfth months of this work, ERC continued evaluating diamond-coated titanium substrates.

Summary of ERC Progress

1. The accelerated lifetesting has been completed for the four samples under test.
2. Samples with diamond film barrier layers and EC-600, oxygen-evolving coating, had lifetimes of almost 3 times that of samples with no barrier layers.
3. Samples with EC100, chlorine-evolving coating, escalated in voltage but then remained relatively stable for a extended period of time indicating good stability of the diamond film.
4. Diamond film alone has potential applications as a high oxygen overpotential anode.

Results & Discussion

The coating preparation and test protocols were described in the previous quarterly report (7/21/99). The lifetests of both EC100 and EC600 coating types continued until the voltage began to escalate unacceptably.

The EC600 coating, containing iridium oxide, is used commercially as an oxygen-evolving anode. The normal failure mode of this anode is by passivation, i.e. the growth of a high resistance layer of titanium oxide between the titanium substrate and the coating. The application of "barrier layers" prior to the application of the active coating is commonly done to extend the lifetime of the anode. The intent of the test was to determine the viability of diamond film as an alternative barrier layer. Figure 1 shows the voltage history for the EC600 coated samples along with a control sample that had no barrier layer applied. The average lifetimes of the duplicate samples, taken when the voltage escalation becomes exponential, indicate that the samples with the diamond film lasted 2.9 times as long as those with no diamond film.

The data clearly indicates that the diamond film does perform as a barrier layer to inhibit the passivation of the titanium substrate. While this data is encouraging, it should be pointed out that other barrier layers used commercially produce lifetimes approximately equivalent to the diamond film results. However, further optimization of the diamond film technology is warranted to try and further extend the lifetime. Also the performance of diamond films in more aggressive environments, such as with fluoride, should be evaluated. Standard barrier layers are generally not effective in for that application.

For coatings containing RuO_2, the principal failure mechanism is loss of the Ru by oxidation. In that case barrier layers are not expected to extend the lifetime. The accelerated test results (Figs.2 and 3) demonstrate this. The escalation in voltage around 50 hours is consistent with previously run samples of EC100 with no barrier layers and is associated with loss of the ruthenium oxide coating. Without a barrier layer, however, the voltage should continue to escalate to well over 10 volts. As seen in Figure 3, though, the anode voltages remain relatively stable at the elevated values for an extended period of time. Finally, around 1500 hours, the anode voltage begins a more rapid escalation as the substrate passivates. Note that the EC100 tests were operated at a current density of only 4 kA/m^2 compared with the EC600 tests at 15 kA/m^2, thus the difference in operating times.

Visually the EC100 samples had lost all of the active coating and there were patches were the diamond film also appeared to have been lost. Representative SEM photos are shown in Figure 4. The first photo shows the "mud-cracked" appearance of the initial EC100 coating that is typical of RuO_2/TiO_2 coatings. Normally when the anode passivates there is residual, intact coating. The second photo shows what appears to be the residual diamond film. Energy Dispersive Spectroscopy (EDS) indicated no evidence of Ru - only titanium from the underlying substrate. The third photo was taken from one of the "bare" areas on the anode surface and is characteristic of the surface of the titanium substrate that was etched prior to application of the diamond film.

The fact that the anode continued to operate well for nearly 1500 hours after loss of the electrocatalytic coating indicates very good stability of the diamond film itself. Thus there is the distinct possibility of utilizing the diamond film as a high oxygen overpotential anode coating for certain applications.

Conclusions

The diamond film does function as a good barrier layer for the protection of a titanium substrate from passivation during operation as an oxygen-evolving anode with an electrocatalytic coating. The diamond film extended the lifetime of a laboratory anode by almost 3 times at least equivalent to commercially available barrier layer technology. The diamond film also had good stability when operated without an active coating, as evidenced by the lifetests where the RuO_2 coating was lost early. This data supports the possible use of diamond films alone as high oxygen overpotential anodes.

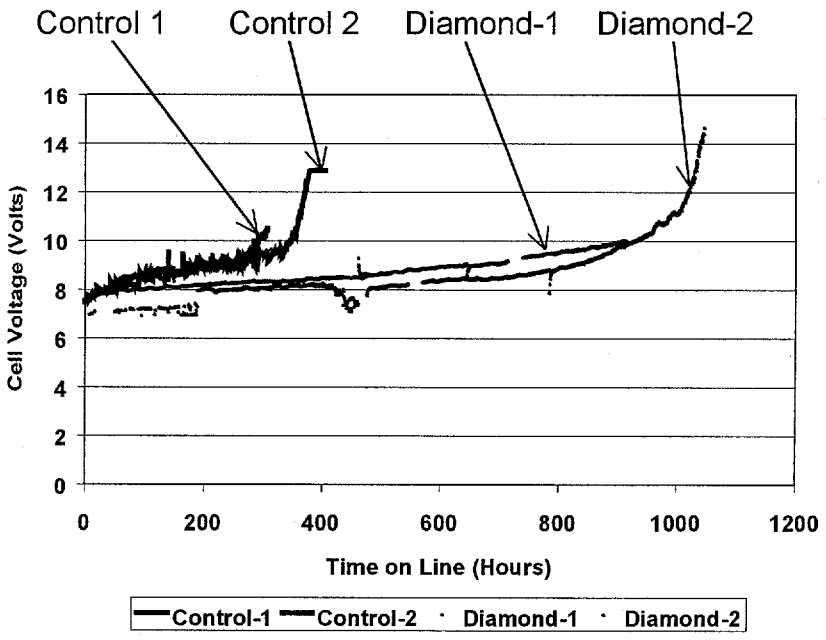


Figure 1: Cell voltage history for EC600 anodes with and without diamond film barrier layers (285 gpl Na_2SO_4 + 60 gpl $MgSO_4$, pH 2.0, 65 °C, 15 kA/m^2)

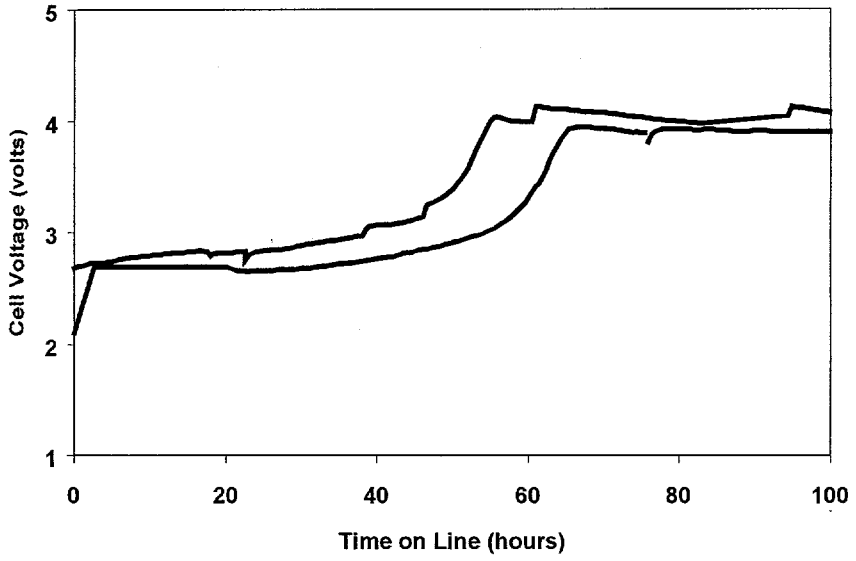


Figure 2: Figure 2: Initial cell voltage history for EC100 anodes with diamondfilm barrier layers (150 gpl H_2SO_4, 65 °C, 4 kA/m^2)

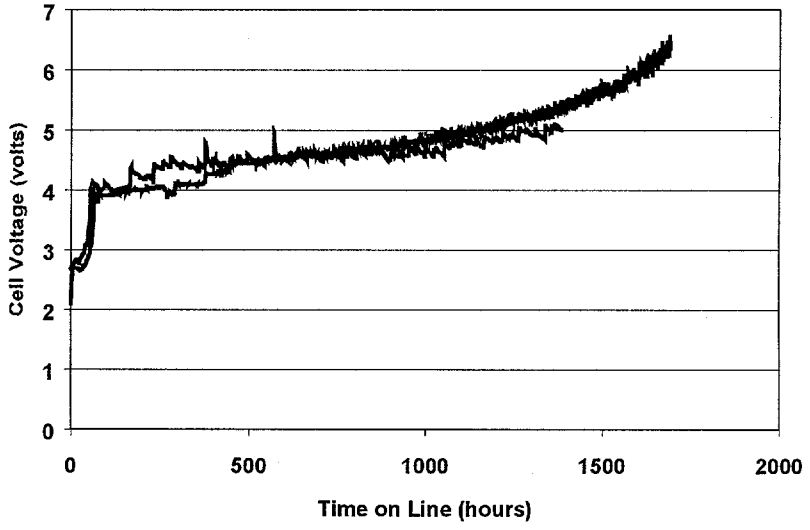
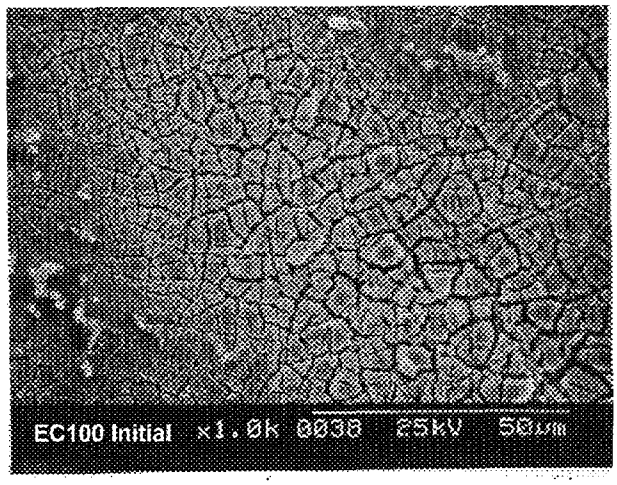


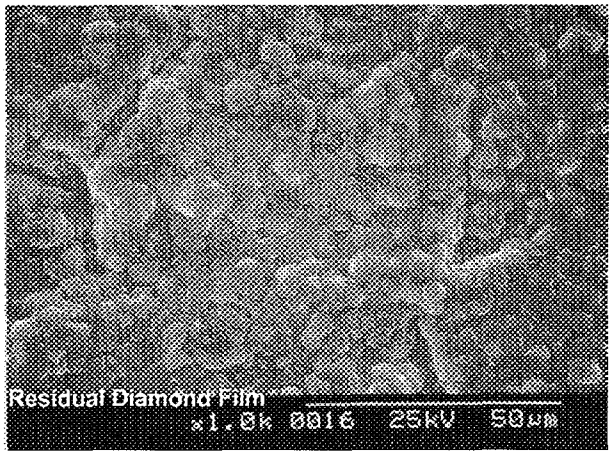
Figure 3: Extended cell voltage history for EC100 anodes with diamond film barrier layers (150 gpl H_2SO_4, 65 °C, 4 kA/m^2)

Figure 4: SEM Photos of Surface of EC100/Diamond Film Anodes

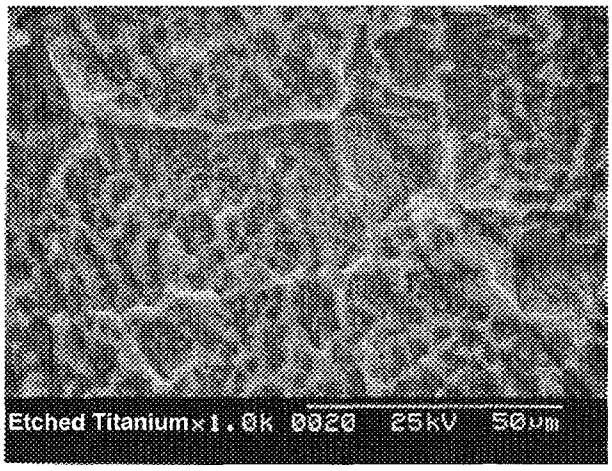
EC100 Initial: View of the EC100 Coating as applied prior to lifetesting.



Residual Diamond Film: Portion of Lifetested sample where EC100 coating was removed and there was still diamond film



Etched Titanium: Area of lifetested sample where both the EC100 coating and the diamond film had been removed exposing the titanium substrate that was etched prior to coating.



SUMMARY OF CIE PROGRESS

1) We are able to achieve good diamond coating on the sand blasted titanium surface. We have identified an outside vendor with better sandblasting process control to reduce contamination. A good contamination free surface is necessary to achieve good diamond coating.
2) The acid etched surface provides a good diamond coating. We have optimized the plating conditions for acid etched, diamond interlayered titanium surfaces. We have well-adhered plating but the platinum plating uniformity is still a problem.
3) We have tried to increase the boron dopant level to achieve better platinum plating uniformity but the NCC reported problems with diamond adhesion. We decided not to increase the boron doping level.
4) Lifetime tests are preliminary and needs to be verified with further experiments. The life time test shows that the diamond interlayered platinum plated sample shows moderate lifetime improvement. The tests also indicate that there is less platinum loss with diamond interlayer.

We have provided more details in the following paragraphs:

1) Diamond Coating:

a) Sand Blasted Surface: In this quarter, we have used another vendor who can provide a better quality surface free of contamination. NCC shows satisfactory diamond deposition. We are interested in a good diamond coating on a sand blasted surface because this is the typical surface preparation procedure for electrode manufacturing.

2) Platinum Plating:

a) Acid etched Titanium surface coated with "Good Diamond": We are able to plate platinum that does not peel off. The plating rate need to be considerably lower than on the diamond interlayered sample for good adhesion. We have plated on the diamond interlayered sample with surface roughness of 40 microinches and we still need to check on the surface roughness of 100 microinches. We believe that will be not a problem.

We still have problem with the platinum plating uniformity. The conductivity of the diamond coated surface is related to the boron doping distribution. We tried to increase the boron doping with the intention of increasing the conductivity and also better platinum distribution. North Coast Crystals (NCC) experienced problem with poor adhesion of diamond with higher level of born doping. Even if NCC is successful in depositing of diamond with higher level of boron, CHEMIONIC has problem of poor platinum adhesion. We decided not to increase the boron level for future samples. We still need to resolve problem related to platinum plating uniformity.

3) Lifetime Tests:

Accelerated life tests are normally carried out at twice or thrice the normal operating current density. This test will help to compare performance between different sets of electrodes with different characteristics. We have assembled the complete test facility to run several electrodes and compare performance at similar experimental conditions.

We ran two platinum-plated samples. One sample is acid etched to 100 microinches and platinum plated. The other samples is acid etched to 40 microinches, diamond interlayered and platinum plated. The platinum weight is approximately the same on both the samples.

The results are preliminary and further experiments need to be done. The lifetime tests shows that the diamond interlayered samples lasted about 10-15% more than the one without the diamond interlayer. The results also indicate a lower platinum weight loss with the diamond interlayer. The significance of these results is not clear yet because, the remaining platinum after the life time test is not well adhered to the surface. This is typical of titanium under attack by the solution. With the diamond the solution should not penetrate and attack the titanium. We are investigating surface to see whether diamond is still intact or attacked.

Future Work

During the 13^{th}, 14^{th}, and 15^{th} months of this work, NCC, ERC, and CIE will complete fabricating and testing these electrodes.