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Improved Container Electrode Coatings for Na/S Battery Systems

T.K. Hunt

August 1995

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Improved Container Electrode Coatings for Na/S Battery Systems

Final Report

by

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for

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Table of Contents

Abstract

Current sodium sulfur (Na/S) battery systems utilize the fast ion conducting properties of sodium beta"-alumina electrolyte (BASE) to create high energy density sodium-sulfur electrochemical cells which can be used as components of secondary batteries. Since the days when these cells were invented at the Ford Motor Company Scientific Laboratory by J.T. Kummer and N. Weber, problems with container electrode corrosion have troubled the Na/S systems that have been developed in the many laboratories. In an unpublished investigation carried out at the Ford Motor Company laboratory, it was shown that titanium nitride films sputter deposited onto aluminum substrates under the appropriate conditions can exhibit excellent resistance to corrosion by sodium polysulfide melts. In the work carried out here, the corrosion resistant properties of TiN coatings sputter deposited on Al substrates have been investigated. TiN sputter

coated aluminum samples were tested under static conditions in sodium sulfide melts and in Na/S cells under the range of electrochemical conditions needed for battery operation. The sputter deposited coatings produced in these experiments exhibited satisfactory corrosion resistance in the static tests but degraded under full cell operation. Tests of TiN coatings deposited by reactive ion-plating (IP), a common commercial process, showed excellent corrosion and electrical performance in both static and complete cell testing. Charge/discharge testing of sulfur core cells with IP coatings for over 350 cycles to 70% depth of discharge has shown only very minor changes in cell performance and the tests are continuing.

1. Program Objectives

The objective of this program was to enhance the viability of sodium sulfur (Na/S) battery technology by developing a method for producing a durable, cost effective coating that can act as the sulfur electrode of Na/S cells in the sodium polysulfide environment while providing the low impedance electrical connection required for practical batteries.

Sodium sulfur (Na/S) battery systems utilize the ion conducting properties of sodium beta"-alumina electrolyte (BASE) to create the high energy density sodium-sulfur electrochemical cells which can be used as components in secondary batteries. Na/S batteries have long held great promise for a variety of electrical storage applications, including electric vehicles, utility load leveling and spacecraft energy storage for PV systems. Since the days when the Na/S battery was invented at the Ford Motor Company Scientific Laboratory by J.T. Kummer and N. Weber, however, problems with durability have plagued these systems. Durability problems continue to interfere with the development of these batteries in spite of a large, world-wide effort to complete their development. A serious remaining technical problem delaying the wide application of Na/S technology is the excessive corrosion of previous, practical, container electrode materials when they are exposed to the sodium polysulfide melt at the operating temperatures (approximately 325°C - 375°C) required. Few materials have been identified that both stand up to the polysulfide environment and retain their electronic contact with the melt. Initial studies had indicated that titanium nitride (TiN) could be stable under the full range of electrochemical conditions found in these cells and commercial methods for the production of TiN coatings are well known . TiN coatings were therefore chosen as the focus of the investigation.

Corrosion of the sulfur side current-collector electrode damages the system for several reasons; 1) because it erodes the material and puts the physical integrity of the system at risk; 2) because the corrosion products can form surface layers which increase the internal resistance of cells; 3) because the corrosion products tie up a portion of the cathodic reactant; and because soluble corrosion products can be redeposited, clogging the electrode, obstructing transport of active materials and contributing to uneven current distribution. In some cases, uneven current distribution during recharging operation has been a contributing factor in initiating electrolyte failure.

2. Results Summary

The result of this program effort has been a demonstration that TiN coatings deposited on aluminum electrode support structures are able to perform well not only during static corrosion tests in the polysulfide melt at cell operating temperatures, but also during active Na/S cell tests running over 300 cycles to approximately a 70% depth of discharge. The full cell tests have been performed at Silent Power, Inc. (SPI) facilities in Salt Lake City, Utah[1]. Three cells using TiN coatings produced by commercial reactive ion-plating were placed on accelerated cycle life test and run through charge/discharge cycles (at a rate of ~2/day) under procedures as normally conducted on advanced cell designs by Silent Power. One of the three cells showed degraded performance with an onset after 90 cycles and it was subsequently taken off test after 180 cycles. The other two cells have performed very well through 300+cycles as of 18 July 1995 and they are continuing under test as this report is written. At present, Silent Power plans to continue these tests at least through December 1995. The observed performance is excellent and appears to indicate that the enhanced durability postulated at the program outset is likely to be achieved in practice. The issue of the cost to produce coatings by the ion-plating and sputtering methods tested has not yet been carefully addressed, but the use of reactive ion-plating for deposition of TiN coatings is a standard commercial operation used routinely for coating industrial cutting tools and drill bits. It is expected that mass production methods can lead to acceptable production costs.

3. Background

Container Electrode Problems

The molten sodium polysulfide which forms on the sulfur side during the discharge of a Na/S secondary battery is highly corrosive and the problem is exacerbated under the electrochemical stress of cyclic battery operation. Many materials have been tested as coatings and structural members for the cathodic

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[1] The cell tests discussed here were carried out at Silent Power, Inc., 163 West 1700 South, Salt Lake City, Utah 84115, under the direction of James R. Rasmussen.

electrode/container which typically holds these reactants (for examples, see section 9 for references to the Ford work in this area). Among these materials have been stainless steels, chromium and nickel chromium alloys and coatings of them on base metals, doped TiO_2, doped calcium titanate and lanthanum strontium chromate. Surface modified materials such as boronized metals have also been tried. Most of the materials which have been shown to withstand corrosion by the sodium polysulfide melt are also, unfortunately, electronic insulators and so are not useful for collecting the current from the carbon felt in which the sulfide melt is generally held. The few electron conducting materials, such as carbon and molybdenum which can survive the corrosive environment, have generally been found to be impractical either for cost of assembly or mechanical durability considerations. Early testing appeared to show that stoichiometric titanium nitride coatings, deposited appropriately on aluminum, appear to provide an exception to these 'rules'. The program described here was intended to follow up on those tests and if the early results were confirmed, to establish conditions under which practical coatings could be reliably produced. This task was accomplished.

In an investigation carried out at the Ford Motor Company laboratory it was observed that titanium nitride films, sputter deposited onto aluminum substrates under specific conditions could exhibit excellent resistance to corrosion by molten sodium polysulfide. In previous experiments, using the same test conditions, on TiN coatings deposited on other materials, also conducted at Ford, extensive corrosion was observed[2]. Because TiN also shows excellent electronic conductivity (higher conductivity than pure Ti) it was considered to be a possible candidate for a durable container electrode coating. In those experiments, current collectors of TiN sputter deposited on aluminum alloy samples were exposed to polysulfide melt at 350°C for periods up to 2 months. During this time the samples were polarized anodically and cathodically and were cycled at current densities sufficient to expose the TiN surface to the entire span of

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[2] K. Kinsman and W. Winterbottom, "The Use of Coatings in High Temperature Battery Systems", Thin Solid Films, <u>83</u>, p 417-428 (1981).

melt compositions between sulfur and Na_2S_3 to which parts of the container can be exposed locally during normal operation of a Na/S cell.

As with most coatings deposited by physical means such as sputtering, ion plating (IP) or chemical vapor deposition (CVD), TiN exhibits a porous structure in which small pores penetrate the entire thickness of the film, potentially exposing the substrate to the corrosive chemical environment. The presence of such pores in the protective coating on most substrate metals other than aluminum would bar serious consideration of this coating method. Corrosion of steel or titanium at these pores would lead to severe undercutting and the resulting lateral chemical attack would dislodge the coating. When exposed to the polysulfide environment, however, aluminum reacts to form a self-limiting layer of aluminum sulfide. The ability of TiN coated aluminum to operate in the cathodic container environment can thus be understood by considering the schematic diagrams shown in Figures 1 and 2.

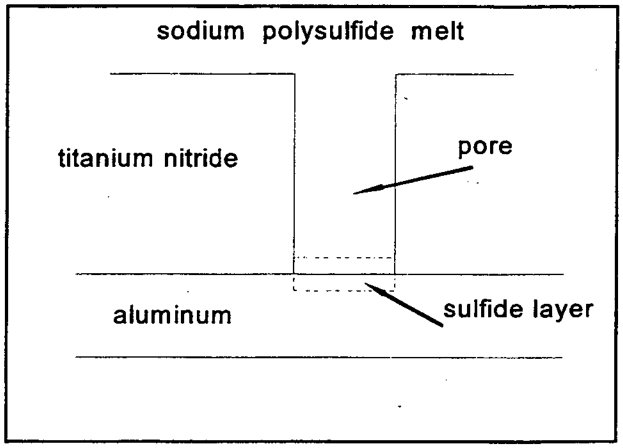

Figure 1 Schematic diagram of porous coating showing passivated aluminum sulfide layer.

Due to cost and timing considerations, the initial testing of samples in this program was done under "static" conditions in which the samples were exposed to molten polysulfide at operating temperatures but without the application of cell voltages. In the 2nd year of the program, the investigation of the resistance to corrosion by polysulfide melts of TiN coatings sputter deposited on Al substrates was further extended to determine the applicability of these films for corrosion protection

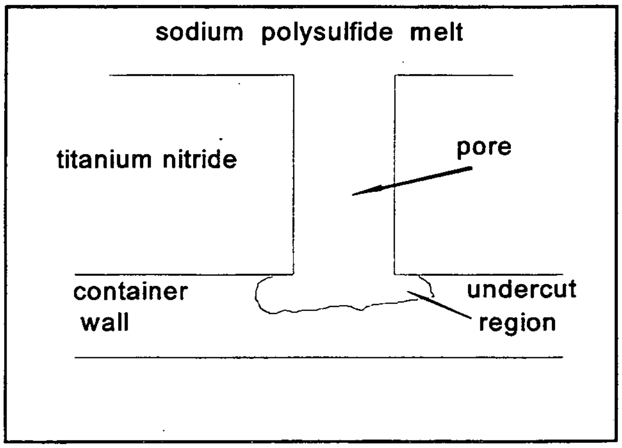

Figure 2 Schematic diagram of coating showing undercut region due to non-self limited attack of the base layer.

under state-of-the-art Na/S cell operating conditions. TiN coated aluminum samples were tested, and continue to be tested, under the range of electrochemical conditions appropriate for Na/S battery operation using conventional volt-ammetry. It is intended that they be subsequently examined for the effects of corrosion optically and electrically. These tests are being conducted under standardized conditions by Silent Power, Inc., a major corporation in the Na/S battery field, so that the results may be compared directly with data on the current state-of-the-art coatings and materials. Because the static tests (soaking in polysulfide at 350°C) exhibited good corrosion resistance, complete cells using container electrodes coated in this way were produced and run under conditions of electrochemical stress to confirm the utility of this approach. The initial experiments used reactively sputtered TiN films conforming as closely as possible to the original conditions used at Ford. Following those tests, commercial ion-plated films (using a deposition process currently expected to be less expensive than sputtering) have been examined for longer periods with good results. These results are described in section 7 of this report.

4. Experiments

The static corrosion experiments performed under this program are covered here as described in the quarterly reports issued. The cell tests have been and are still being carried out after the conclusion of the formal performance period of this program and they are covered here by inclusion of the reports and data collected by Silent Power, Inc. on the coatings delivered to them under the program.

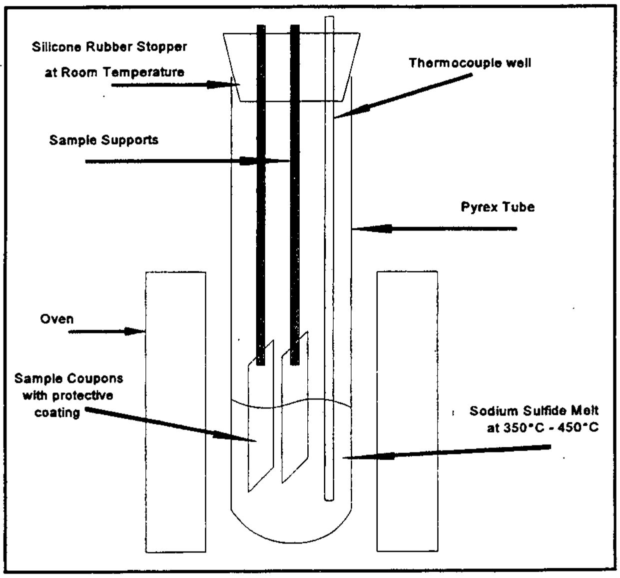

Figure 3. Schematic of Sodium Sulfide Exposure Test Cell.

Static Exposure Testing

During the first year of the program, the reactive sputtering apparatus was transferred from the Ford Scientific Laboratory to ERIM, reconfigured and over 60 sputtered TiN samples were prepared using a variety of sputtering conditions. Soak testing for corrosion in molten Na_2S_4 which had originally been planned as a task to be carried out by Sandia under a CRADA, ultimately could not be arranged due to program conflicts there. The soak corrosion tests were then set up at ERIM and exposure tests of up to 500 hours at 350°C were conducted on a series of sputtered samples. The coating samples were deposited on 1 cm x 3 cm 6061 aluminum coupons which were held in an all aluminum clamping arrangement and suspended with approximately half of the coated sample immersed in the melt to permit examination of effects at the melt boundary and easy visual inspection of the effects of the exposure. The arrangement is shown schematically in Figure 3. The sodium tetrasulfide, Na_2S_4, melt material was obtained from Johnson Matthey. Because the sulfide is reactive with moisture in air as well as corrosive in powder form, all handling was done in a glove bag that was evacuated, flushed and reflushed with argon prior to opening the supplier's containers and transferring the material to the apparatus shown in Fig. 3. The temperature of the heater oven was ramped up slowly to the test temperature, generally ~ 350°C and held there for the duration of the test. The test cell temperatures were recorded daily. Following the test period, the samples were removed, washed in water to remove traces of the melt and examined visually for evidence of corrosion. The sheet resistance of the samples was also measured before and after the exposure to identify samples for which corrosion fully penetrated the surface coating. The resistance of the bare aluminum coupon material, as examined from the surface through the sulfide layer, was substantially higher following the sulfide exposure, thus permitting this test.

Coating Deposition - Sputtering

The coatings whose test results led to this investigation were deposited by reactive ion sputtering. The process utilizes a pure titanium sputtering target in a D.C. magnetron sputtering system (Varian S-Gun).

The sputtering gas is primarily argon, as usual, but an actively controlled amount of nitrogen is introduce to the gas stream. The sputtered Ti atoms encounter the N_2 en route to the substrate and after reacting with the nitrogen land as TiN molecules. The control requirements for this process are very demanding. Since stoichiometric films require deposition under gas flow/power conditions which are inherently unstable, active computer control based on mass spectrometric readings of the nitrogen level are used. Excess nitrogen coats the sputtering target with TiN and this drastically reduces the sputtering rate, while too little nitrogen for a given ion current does not allow sufficient interaction to carry out the chemical reactions to produce the TiN. Because good TiN stoichiometry appeared from the previous Ford experiments to be necessary to prevent undercutting corrosion, the apparatus to carry this through was set up at the outset.

Coating Stress State

The state of compressive or tensile stress in the sputtered films was monitored in each deposition run, by co-depositing the material on a microscope cover slip. The sign of the stress in the film can be readily determined by noting the direction of the curvature induced in the thin cover slip. If desired, this approach can be made quantitative for the stress determination.[3] Early indications during this study suggested that moderate compressive stress in the films was correlated with superior resistance to sulfide corrosion in the static tests. Excessive compressive stress however was shown to lead to detachment of the depositing film from the substrate and thus loss of any chance at corrosion protection. Tensile stress leads to cracking and frequently also to delamination of the coating. Unfortunately while a correlation with stress state was present, the correlation was not sufficiently tight to permit using stress as a positive indicator of appropriate film conditions.

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[3] "Stress Related Effects in Thin Films", J.A. Thornton and D.W. Hoffman, Thin Solid Films, 171 (1989) p 5-31.

Coating Deposition - Ion Plating

In the ion plating process, a plasma of the coating ions is created using an electron beam heating source which not only vaporizes the target material but also ionizes the material. The ions are then either deposited ballistically or driven to the substrate by a (generally high) voltage. Deposition occurs at higher pressures than in conventional sputtering. The combination of the extremely hot ions and the applied voltage causes the substrate to be generally quite hot during the process, with temperatures of 500°C to 750°C common. Ion bombardment is widely recognized as one of the most effective ways to clean surfaces and it is an inherent feature of the ion plating process. As a result, "one of the most important advantages of ion-plating is its ability to produce highly adherent coatings on metal substrates."[4] The deposition rate can also be very high, reaching up to 25 micrometers/minute a rate much higher than conventional sputtering permits. Since protective layers as thin as 2 - 5 μ are expected to be sufficient, coating times by ion-plating should allow processing arrangements that will be cost effective. The ion-plated coatings used in this program were provided to the program by Balzers Tool Coating Inc., 901 Erie Avenue, North Tonawanda, New York 14120-0708[5].

5. The Proposed Scope of Work and Technical Approach for Year 2

The use of chemically inert, electronically conducting surface coatings for the container electrode of sodium sulfur batteries had been explored in a continuation of an effort initially carried out at the Ford Motor Company Scientific Laboratory. TiN coatings were deposited by reactive sputtering of pure titanium metal in a nitrogen partial atmosphere. The choice of substrate was expected to be crucial to the success of physically deposited coatings since such coatings almost invariably have pinhole perforations which will allow the reactant sodium polysulfide species to reach the substrate and base of the coating.

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[4] "Physical Vapor Deposition", P.63, Airco Temescal Publ. 1976.

[5] The technical contact at Balzers was Tom Flatau, Tel. (716) 694-6012. Balzers produced the test coatings at no charge to the program.

If a substrate material which passivates in this chemical environment is chosen, the integrity of the rest of the conducting coating can be maintained and durable performance achieved.

The work carried out here continued the development of corrosion resistant coatings for the sodium polysulfide 'container' electrode of the sodium sulfur battery system. During the first half year of the program, the capability for sputtering titanium nitride coatings was developed at ERIM and a series of coatings produced to establish the conditions needed for producing essentially stoichiometric TiN films. The corrosion testing was originally anticipated to begin at the Sandia National Laboratory using primarily static soak exposure testing of samples in a polysulfide melt at cell operating temperature followed by inspection. The general arrangement was as shown in Figure 3. The plans called for this testing to be carried out as a task sponsored by the Advanced Battery Consortium, but this failed due to a long delay in the implementation of a CRADA at Sandia.

For the reasons mentioned, and as described in the quarterly reports submitted during the 1993-1994 phase, static testing was carried out at ERIM. Following the successful testing of both sputtered and ion-plated coatings under static conditions, tests under the typical electrochemical loading cycle of Na/S cell operation were proposed and arranged with SPI's laboratory in Salt Lake City, Utah under the direction of James Rasmussen and Scott Olsen.

6. Coating Tests

The static tests were continued during the second year as preparation and screening for the Na/S cell tests to be conducted by SPI. The descriptions of the results of the static corrosion tests carried out on selected coupon samples are given below in the form presented in the quarterly reports submitted at the time.

January - March 1993

Run 1. TiN coated aluminum sample coupons #'s 62 and 63 were soaked for 470 hours in molten Na_2S_4 at 350°C. The samples were then removed, washed and examined. Electrical conduction tests of the film were performed using a soft copper wire as the probe in order to avoid abrasion and penetration of the thin surface films whose properties are to be determined. Two test runs were made.

Sample 62 had an as-deposited initial dark gold color and a net tensile stress in the film. It's thickness, calculated from the known sputtering parameters and time, was 3 micrometers. It showed the insulating aluminum sulfide layer wherever clean aluminum was exposed to the melt, and a conducting dark brown/gold surface film on the TiN covered surfaces. The TiN layer survived in a few areas but flaked off in others. This was confirmed by the electrical conductivity measurements. Large flakes of this film had also been observed to spall off the glass witness slides.

Sample 63 had an as-deposited dark gold color with better adhesion than #62, was neutral in film stress and was 3 micrometers thick. This film had substantially larger areas of the brown/gold film remaining and these areas were conducting. Quantitative surface resistance measurements were not attempted in these samples and the resistivity was determined qualitatively by point to point measurements.

Run 2. Samples 60 and 61 were partially immersed in the Na_2S_4 melt for 500 hours at a temperature of 350°C. They were then removed from the test cell and washed with water to remove excess sulfide.

Sample 60 exhibited modest compressive stress, only slight peeling of the film from the glass witness slide, a dark gold color and was 3 micrometers thick. This sample appears to have been essentially unaffected by the sodium sulfide exposure. Approximately 98% of the original film area appears to be intact. The resistance of the film, as measured between points spaced from 1 cm to 3 cm apart on its surface is in the range of 1.5 Ω to 5 Ω. Exposed aluminum areas have corresponding resistances of 5 kΩ to 150 kΩ. Unexposed, uncoated, aluminum coupons show corresponding resistance values far lower and their values are very sensitive to surface abrasion even by the soft copper wires. This sample showed high resistance to surface abrasion during the resistance measurements.

Sample 61 exhibited neutral stress, a dark gold color and good adhesion to the glass witness test slide. Sample thickness was 3 micrometers measured using a profilometer. Most of this coating was lost during the test. Approximately 75% of the film area flaked off, exposing the bright aluminum substrate. The surface pattern in the remaining film suggests that it cracked during exposure rather than reacting chemically with the sodium sulfide melt.

Tentative Conclusions Coatings in compressive stress appear better able to stand exposure to a sodium sulfide melt at 350°C than films in neutral or tensile stress. Coating #60 showed little if any observable corrosion over the test period. The few areas in which the film may have been lost could have been the result of faulty local surface cleanliness before deposition, and in any case would not have reduced the useful electrode area significantly.

April - June 1993

Run #3 This run tested two sample coupons with sputtered TiN coatings for 500 hours in the Na_2S_4 bath at a temperature of 353°C. The samples were lowered into the sulfide melt during the test and removed following the test period, washed in water and examined visually and electrically for coating resistance.

Sample 55 had an initial light gold color and a net compressive stress as measured by deflection of the glass cover slip on which the corresponding witness film was deposited. This coupon lost most of the film from its 'front' surface while the 'back' side film was completely intact visually. The electrical resistance of the film was unchanged for portions of the film lying above the melt on both sides and a factor of 2 higher for portions of the coupon from which the film had been removed by the melt. Both sides of the coupon were coated at the same time using a rotating sample holder.

Sample 56 This sample had an as deposited dark gold color and a net neutral to slight tensile stress. The TiN film appeared completely intact on both sides of the coupon and the film resistance was unchanged from the values measured prior to the exposure test. This sample appears to have successfully resisted the corrosion of the melt.

Run 4 In this test the two coupons used were coated with TiN by Balzer's Tool Coatings Inc. using the standard approach by which they apply wear resistant coatings to machine tool bits, drills etc. The coatings were light gold in color and had a matte finish in spite of the high polish on one of the coupons as presented to them for coating. The coupons were coated on one side only. The initial electrical sheet resistance of the coatings was very low compared to the sputtered films. Following a brief, inadvertent, exposure to air at 350°C the samples were immersed in the standard sulfide melt for 600 hours. These sample coatings did not survive this exposure. Virtually all of the original film area (80%) flaked off leaving bare aluminum surfaces with the expected high resistance Al sulfide film comparable to that found on the uncoated side of the coupons.

Conclusions Sputtered TiN coatings on aluminum substrates appear able to survive exposure to sodium sulfide for periods up to 500 hours at 350°C with essentially no change in their initial condition. The failure of some sputtered films appears likely to be related to differences in the substrate surface preparation rather than their state of compression or tension as deposited.

July - September 1993

During this period testing of container electrode coatings was continued using static sodium sulfide corrosion test cells and the arrangements were made to conduct tests of the TiN coatings in a complete Na/S cell in collaboration with the Salt Lake City office of SPI. The results of the static tests all of which showed good corrosion resistance are highlighted below.

Because previous experiments had shown both good and poor adhesion of the TiN films to the Al coupons, particular attention was given to the cleaning procedures for the tests during this period. Two sample coupons with sputtered TiN coatings were soaked for 500 hours in a Na_2S_4 bath at a temperature of 391 °C. The samples were lowered into the sulfide melt during the test and following the test period were removed, washed in water and examined visually and for electrical sheet resistance. The positioning of the samples was arranged so that the coupons were half immersed in the melt so that any difference between the sample as immersed in the liquid and vapor could be readily determined.

Sample 9-15/P had an initial dark brown/gold color and a net neutral stress. Both sides and edges of the aluminum sample coupon had been coated at the same time using a rotating sample holder. Prior to coating, this coupon was polished and etched briefly in HF. The coupon was partially immersed in Na_2S_4 at 390°C for 500 hours. This coupon emerged from the melt with the coating intact and essentially no observable change in either its appearance or electrical properties.

Sample 9-15 This sample had an as-deposited dark brown/gold color and a net neutral stress but was not polished. Following exposure the TiN film appeared completely intact on both sides of the coupon and the film resistance was unchanged from the values measured prior to the exposure test. This sample appears to have very successfully resisted corrosion in the melt.

Run 5 In this test the two coupons used were coated with TiN by Balzer's Tool Coatings Inc. using their standard reactive ion plating (IP) approach for putting wear resistant coatings on machine tool bits, drills etc. The coatings were light gold in color and were delivered to ERIM with a matte finish in spite of the high polish on one of the coupons as presented to Balzers for coating. The coupons were coated on one side only. As with the first set of ion-plated coatings in the previous quarter, the initial electrical sheet resistance of the coatings was very low (0.2 Ω) compared to the sputtered films (2-3 Ω). Both of these samples were soaked for 500 hours at 350°C in molten Na_2S_4. When removed and washed in distilled water, the appearance and electrical resistance of both samples appeared unchanged.

Conclusions When the aluminum substrate is properly cleaned prior to deposition of a TiN coating, the coatings appear to be durable up to at least 500 hours in static tests at or above realistic temperatures for Na/S cells. These results tend to confirm the previous conclusion that adhesion failure was related to differences in substrate surface preparation rather than the state of surface stress in the as-deposited coatings.

October - December 1993

Plans to complete the TiN coatings for Na/S cell tests could not be completed in this period since the Al electrode bodies for the sulfur core Na/S cells at SPI were not received from SPI until January and the deposition of coatings was therefore not possible during this period. The deposition of the TiN coatings proceeded both with sputtering of samples at ERIM and with the commercial ion plating at Balzers to prepare the battery cores.

During this period, testing of container electrode coatings was continued using static sodium sulfide corrosion test cells and the arrangements to conduct tests of the TiN coatings in a complete Na/S cell in collaboration with the Salt Lake City office of SPI were finally completed. The results of the additional static tests during this period, all of which showed good corrosion resistance, are highlighted below.

Aluminum Film Samples Two glass microscope slides were cleaned and Al films deposited on them as substrates for the sputtered TiN coatings to be tested. The TiN coatings were approximately 3 microns thick. Following deposition there were many, very small pin holes visible. This is probably due to the relatively large strains that can be seen in both the Al and the TiN films. Following immersion in the sulfide for 519 hours at 330 - 350°C, the pinhole density was worse and the holes larger. Over the time period of the test, however, original but unexposed samples also developed blisters indicating that the stresses in the films were too severe for a proper test. Some portions of the Al films under the TiN remained intact, implying that additional/better cleaning might have been required. Because significant areas of the combined films were left intact, it appears that with an appropriate approach to ensuring stress free films and clean aluminum, the corrosion could be controlled. In this particular case, however, those areas in which the TiN peeled off and exposed the Al film, the Al film was also attacked sufficiently to enlarge the clear area and expose the glass substrate. It is possible that the self-limiting aluminum sulfide layer thickness may consume the thickness of the films deposited here while the layer can still be useful for bulk substrates.

Samples 10/28 These TiN films were sputtered onto 6061 aluminum coupons in a 60 minute sputtering run. The Al coupons were prepared by buffing with rouge, wiping with methanol, ultrasonically cleaned in acetone and etched for 30 seconds in a 3% solution of HF. They were then partially immersed in the sulfide melt and soaked for 495 hours at 355°C. Upon removal from the melt, the lines showing the melt level was visible on the films, but the films appear to be almost entirely intact. A few very small peeled areas, of approximately 0.3 mm dimensions appeared on one surface of one of the coupons.

Samples 12/7 These two coupons were sputtered with TiN following ultrasonic cleaning in acetone and then glow discharge cleaning in the sputtering rig for 45 minutes at 50 millitorr and 3.5 kV. They were then partially immersed in the standard melt and heated for 492 hours at 345°C. When removed from the melt, these films appear to be completely unaffected by the sulfide exposure. The line of demarcation is not visible after careful cleaning and when abraded with Kimwipe tissues under alcohol, the films do not show scratches. These are the best films seen to date in terms of their non reaction with the sulfide melt. This verifies the importance of proper substrate cleaning prior to deposition.

7. Cell Tests

SPI's laboratory group in Salt Lake City agreed to incorporate ERIM TiN coated samples in several of its standard sodium sulfur test cells. Because of their interest in the possibilities of using the TiN coatings in their commercialization work, they were willing to carry out these tests at no cost to the DOE program. For ease of fabrication of the coatings, the sulfur-core cell configuration was chosen. Such cells use a central electrode to collect current from the sulfur/sulfide chamber. For this configuration, the sulfur electrode rod may be coated its outer surface. While coating of the inside surface of a cylindrical container electrode is feasible by both sputtering and by ion-plating, for test purposes the coating of a rod is much simpler. While most Na/S cells currently in use are sodium-core, there appear to be a number of reasons for considering the sulfur-core geometry in the future.

The geometry of the central core body for the SPI test cells is shown in Figure 5. The electrode body is fabricated from 6061 aluminum stock. The original set of 6 cores on which TiN sputtered coatings were deposited was fabricated by brazing the weld flange and mounting stud to the solid bar shown in the figure. A specialized, low melting aluminum solder was used to join the pieces. The main shaft diameter is 1.25 cm and the length is ~ 10 cm. This assembly method was adequate for the sputtering deposition approach and 4 TiN sputter coated samples were prepared and shipped to SPI for testing.

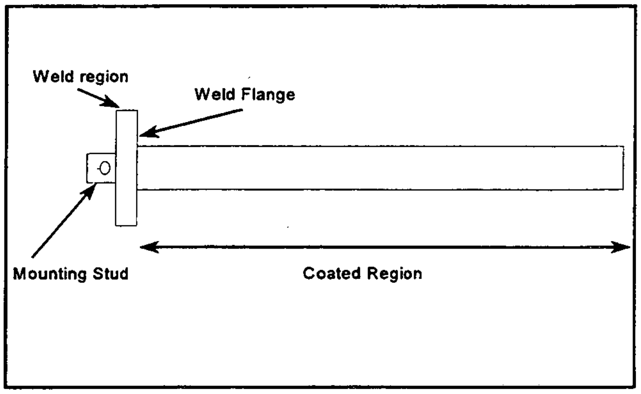


Figure 4 Aluminum Electrode for Sulfur Core Sodium Sulfur Battery. Shaft Length = 10 cm, Diam. 1.25 cm.

Sputtered Coating Tests

The following section contains the text of the SPI report on the tests they ran on these 4 electrode samples. Three of the samples were prepared in a single sputtering run and had thicknesses of 1 μ. The fourth sample was sputtered in an earlier run and had a thickness of $\sim 3\ \mu$. The data for the cells is plotted on the graphs shown.

While there were difficulties with the initiation of the tests on these films at SP that might cast doubt on the detailed results, it nevertheless appears that these particular sputtered coatings are not suitable for long term Na/S service. There is considerable evidence that the Interface preparation may have been inadequate in these cases. The use of an alternative deposition method, ion-plating, appears to hold promise of less expensive coatings and probably superior performance. The ion plating deposition process occurs in a glow discharge regime in which sputter cleaning of the substrate of the substrate at elevated temperature is a natural part of the coating operation.

Test Summary SES Cells 096 - 099 (Silent Power Report)

General

Four cells (SPI numbers -096 through -099) with TiN current collectors were assembled and placed on test. Cell -098 was assembled with a 3 μm thick sputtered coating on the current collector and the other cells used a 1 μm thick coating. In cells -098 and -099, three segments of glazed nickel/chromium wire were added to the sulfur electrode assemblies. These were included to allow full recharge of the cell in the event that the TiN electrodes exhibited the same "single-phase only" operation as has been observed in cells using pure molybdenum electrodes.

During the sodium filling procedure for these cells, some difficulty was experienced and the effort required multiple evacuations and backfills before a proper fill level was achieved. Experience has shown that this sometimes results in a cell that is sodium starved (under filled), and in such cases an increased cell resistance is typically observed.

Testing

All cells were instrumented with voltage sense leads, K type thermocouples and placed in a common furnace. After heating to 330° C at a rate of 15°C/Hr each cell was subjected to standard initialization and break-in cycles. After break-in, the cells were cycled discharged at 4 amps and recharged at 2 amps.

Cell -096 failed near the top charge. A temperature excursion of 450°C was reached during the failure period. After cooling it was clear that the sodium side compression seal had failed and likely caused subsequent fracture of the electrolyte. A post-test analysis (PTA) of the cell revealed corrosion of the TiN coating.

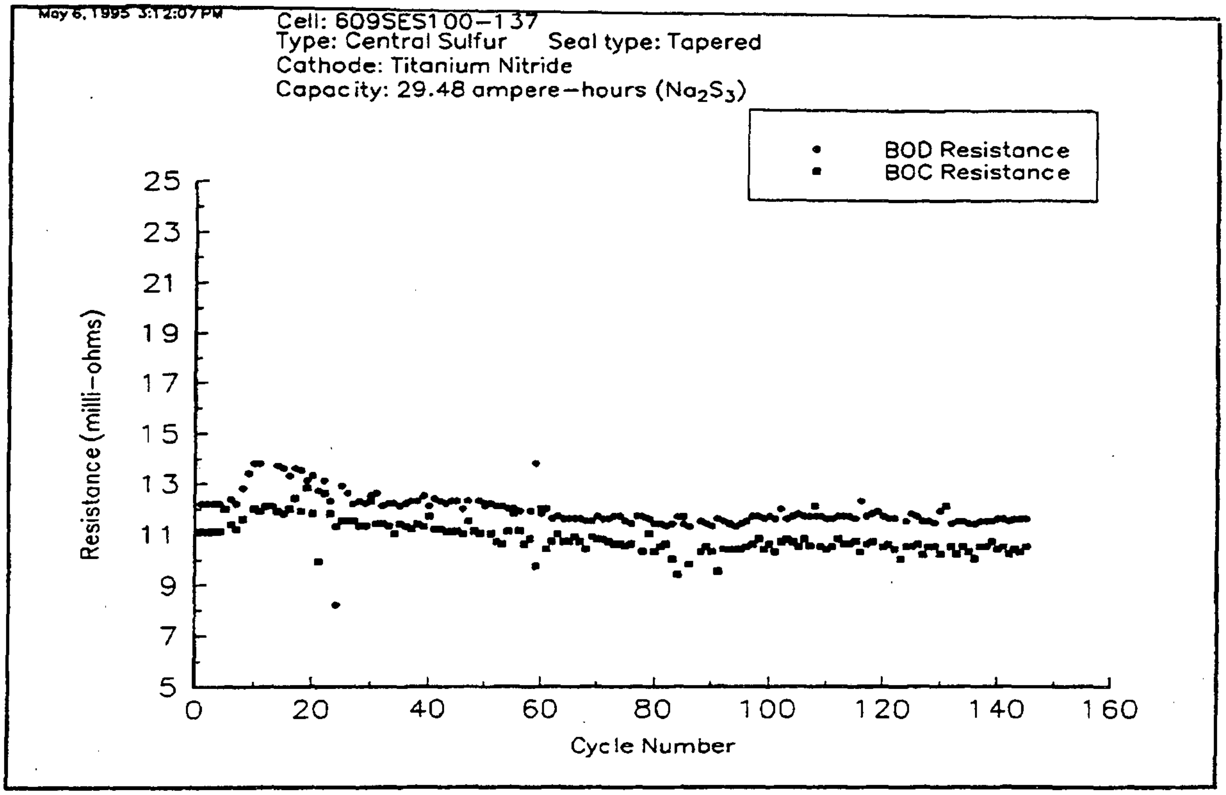
The sodium side seal of cell -098 failed before completing the break-in cycles. A PTA of the cell revealed corrosion of the TiN coating.

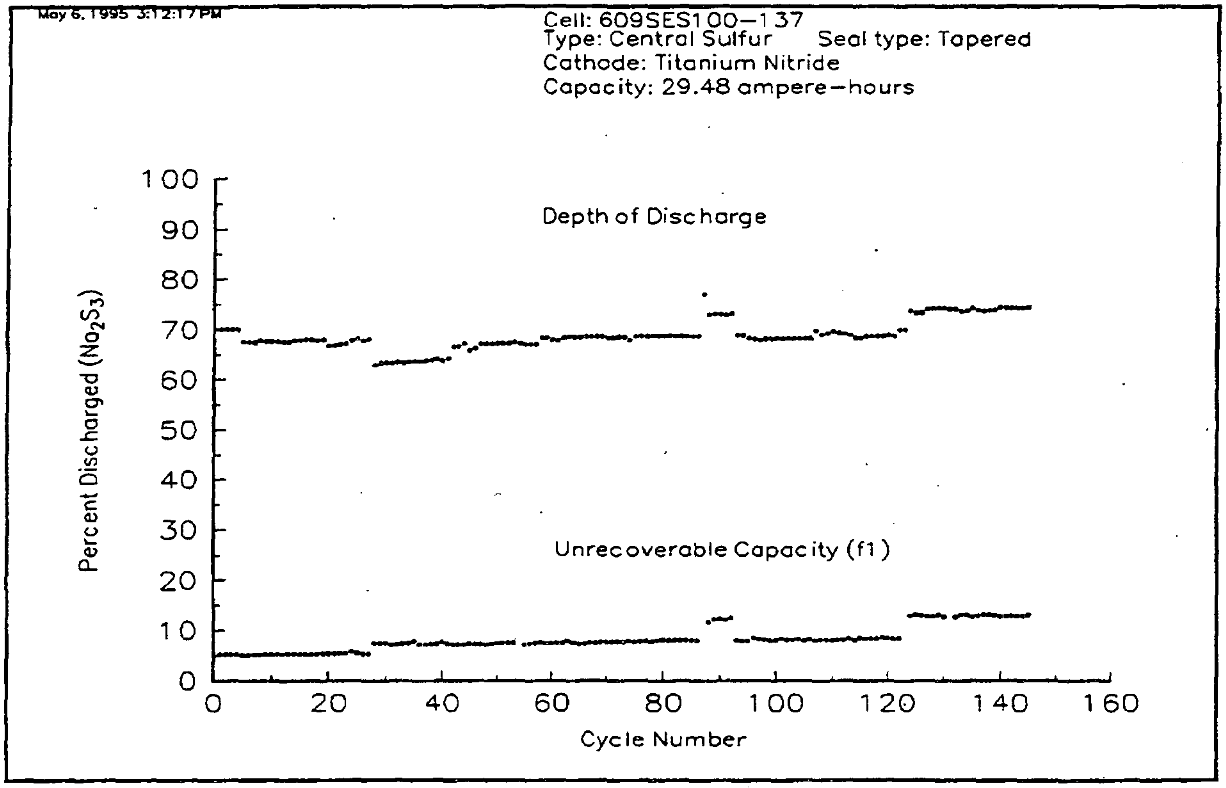
Cells -097 and -099 completed more than 120 cycles but performed poorly with high resistance and poor recharge characteristics. In both cases the resistance was initially high (50 mΩ) but decreasing until about cycle 115 where the resistance in both cells abruptly increased and cycling was no longer possible. Plots of cell resistance, DoD and f1 are shown over the life of testing in Figures 1 through 4 for cells -097 and -099. Cells of this design with Nichrome flame sprayed current collectors typically have stable internal resistances of around 12 mΩ and unrecoverable capacities o 10%.

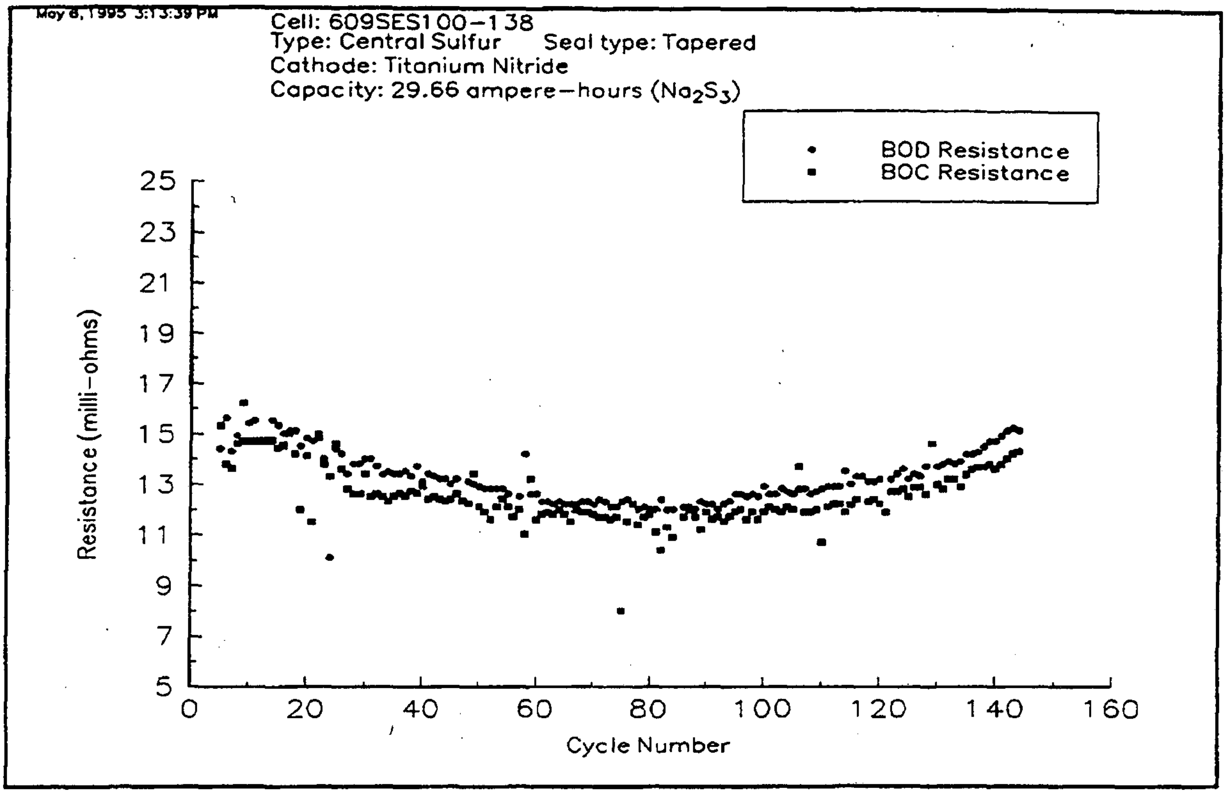
The PTA of both cells revealed that very little TiN coating remained on the aluminum pole. Further, there was no evidence that sodium under-filling had occurred in these cells.

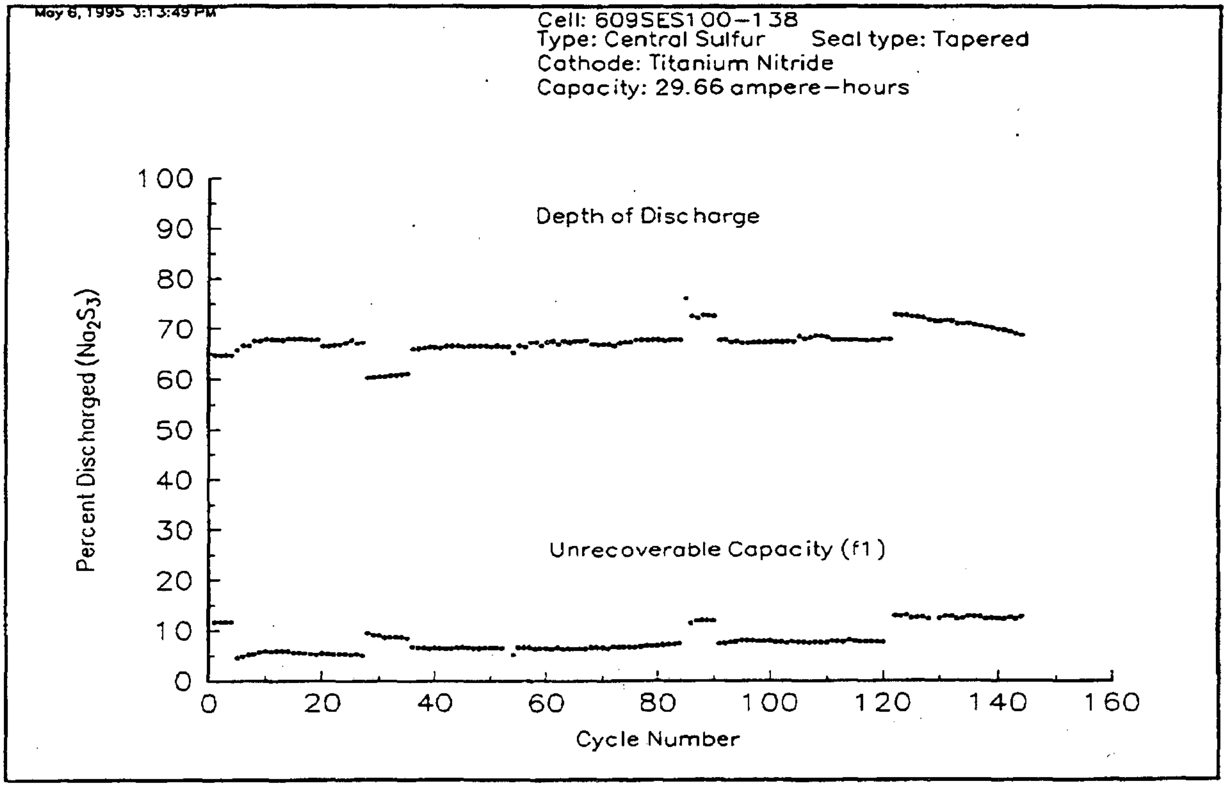
Summary

In all of the cells tested in this round, the TiN electrode (and/or the interface) was attacked and corroded by sodium polysulfide, and therefore these sputtered films appear to be a poor candidate as a sulfur-side current collector.


May 6, 1995 3:12:07 PM
Cell: 609SES100-137
Type: Central Sulfur Seal type: Tapered
Cathode: Titanium Nitride
Capacity: 29.48 ampere-hours (Na_2S_3)
● BOD Resistance
■ BOC Resistance
Resistance (milli-ohms)
25
23
21
19
17
15
13
11
9
7
5
0
20
40
60
80
100
120
140
160
Cycle Number


May 6, 1995 3:12:17 PM
Cell: 609SES100-137
Type: Central Sulfur Seal type: Tapered
Cathode: Titanium Nitride
Capacity: 29.48 ampere-hours
Depth of Discharge
Unrecoverable Capacity (f1)
Percent Discharged (Na_2S_3)
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
Cycle Number


May 8, 1995 3:13:39 PM
Cell: 609SES100-138
Type: Central Sulfur Seal type: Tapered
Cathode: Titanium Nitride
Capacity: 29.66 ampere-hours (Na_2S_3)
● BOD Resistance
■ BOC Resistance
Resistance (milli-ohms)
25
23
21
19
17
15
13
11
9
7
5
0
20
40
60
80
100
120
140
160
Cycle Number


May 6, 1995 3:13:49 PM
Cell: 609SES100-138
Type: Central Sulfur Seal type: Tapered
Cathode: Titanium Nitride
Capacity: 29.66 ampere-hours
Depth of Discharge
Unrecoverable Capacity (f1)
Percent Discharged (Na_2S_3)
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
Cycle Number

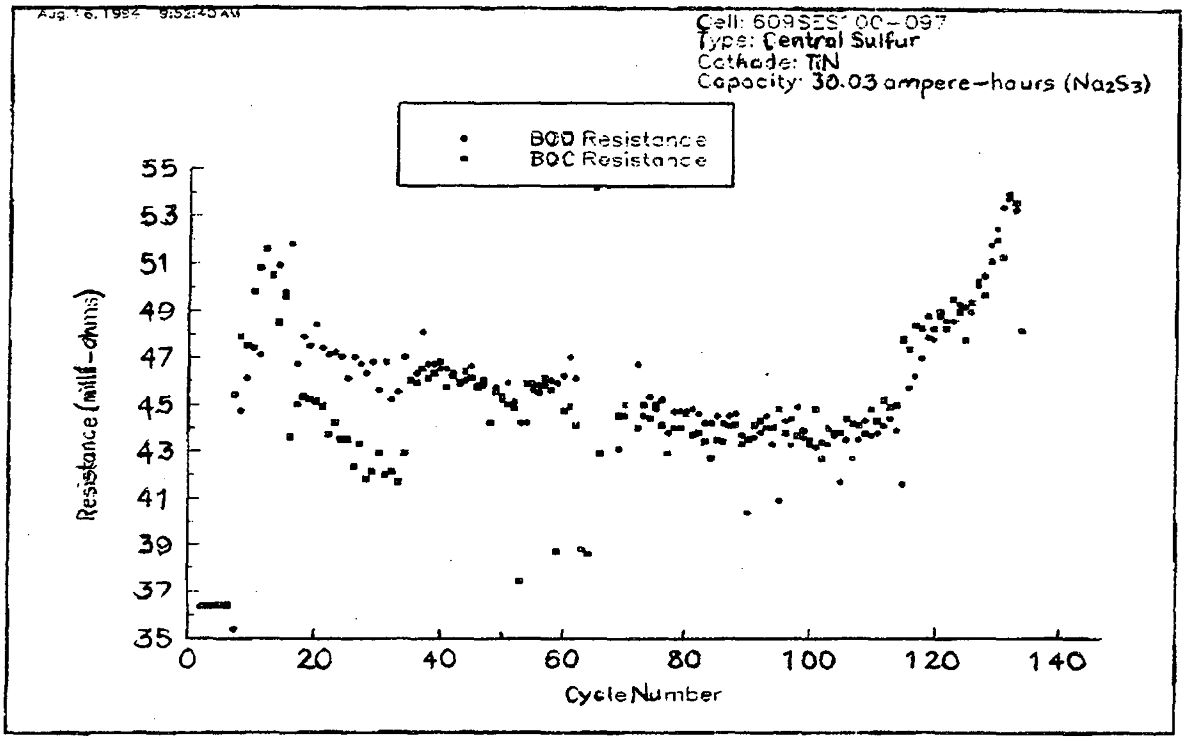


Figure 1 - Cell resistance for cell -097.

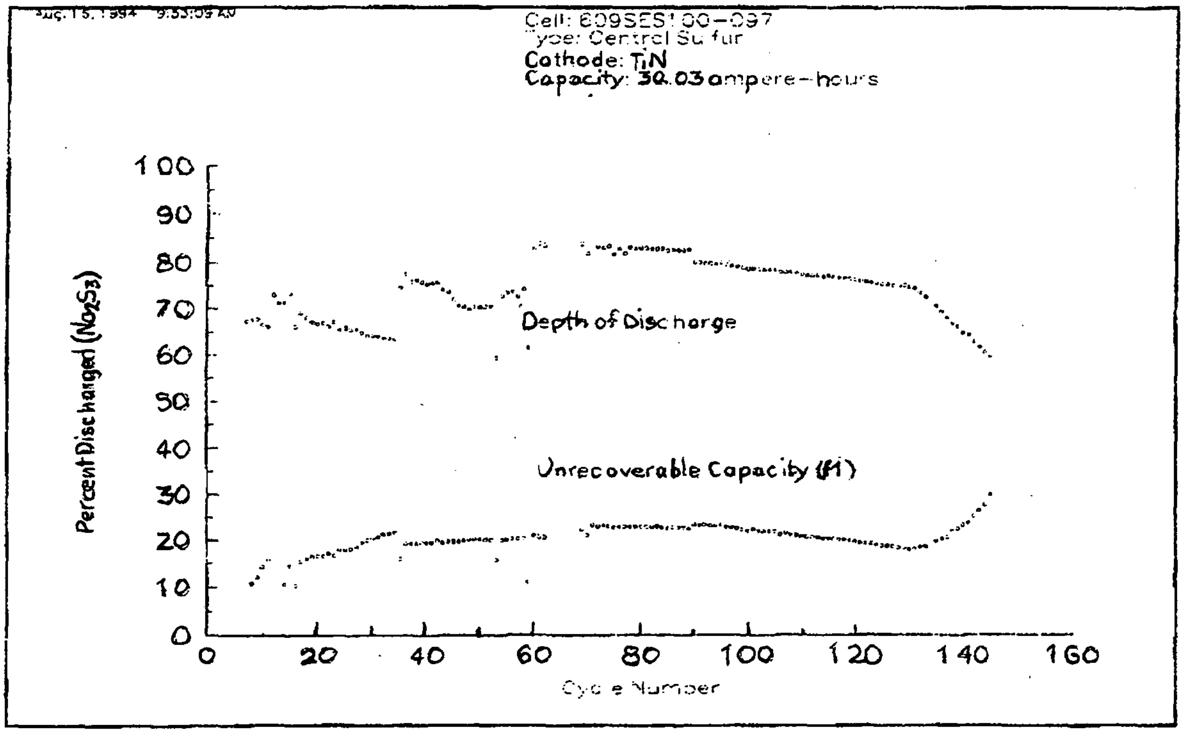


Figure 2 - Depth of discharge and unrecoverable capacity for cell -097.

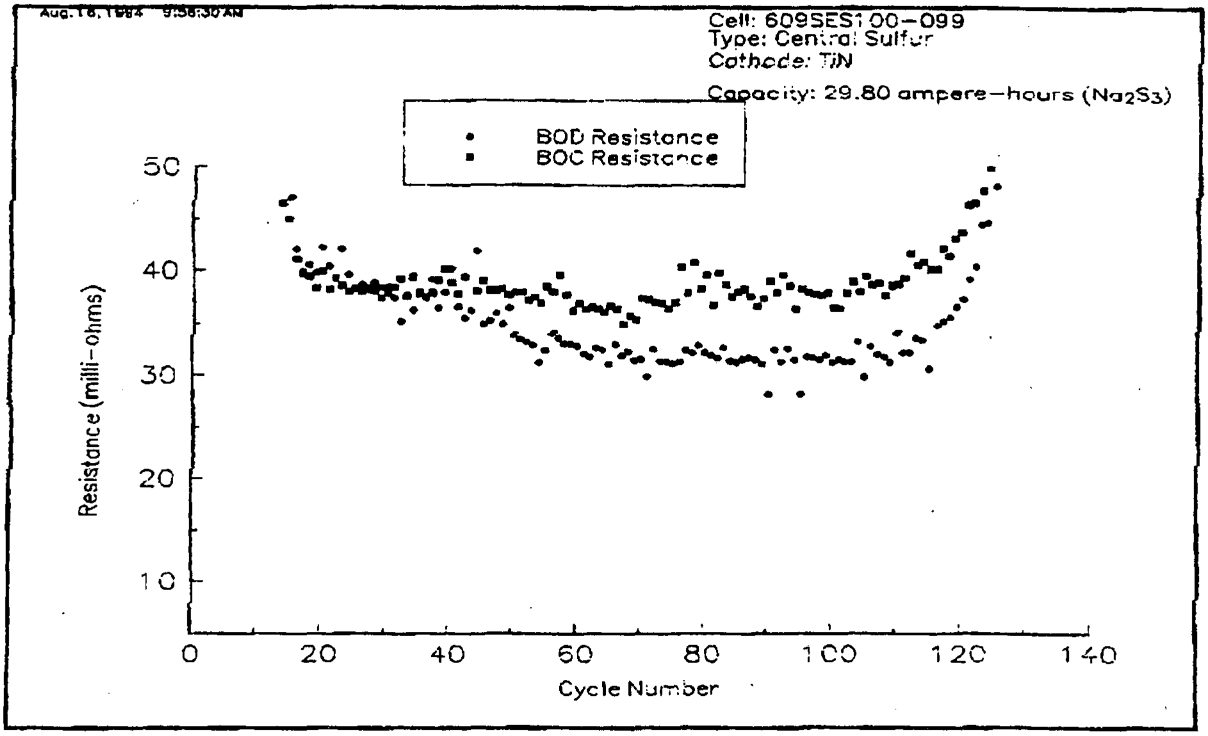


Figure 3 - Cell resistance for cell -099.

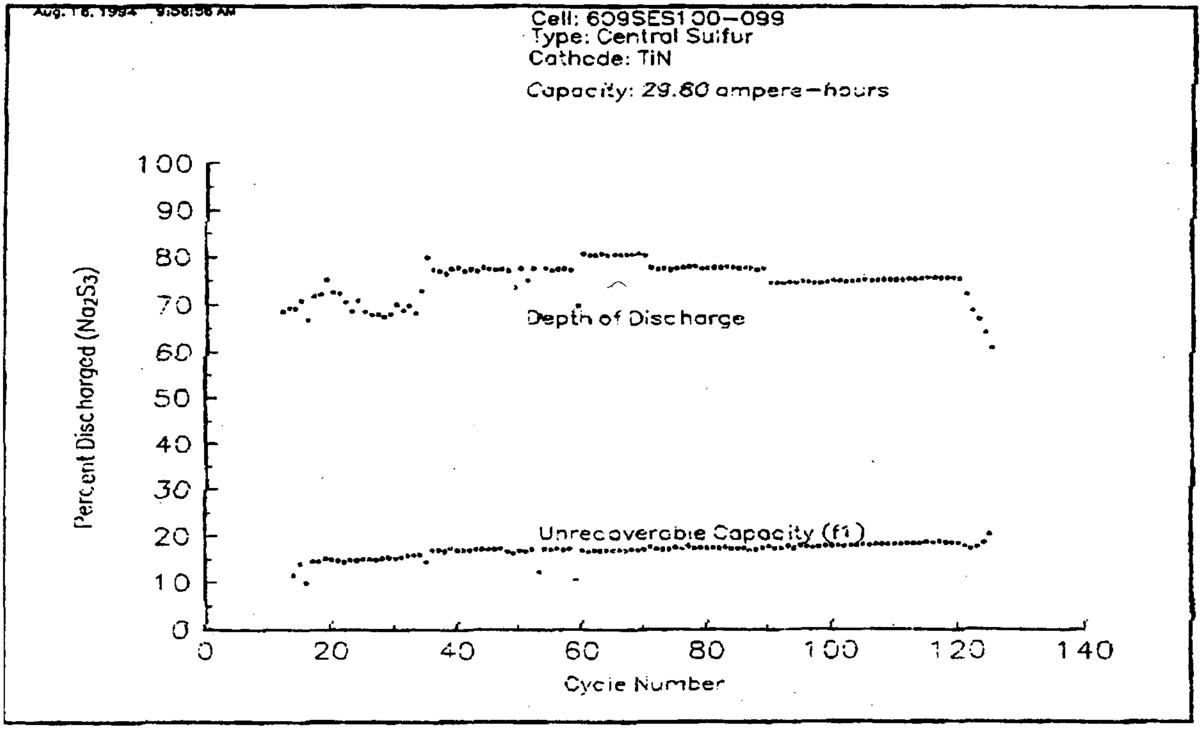


Figure 4 - Depth of discharge and unrecoverable capacity for cell -099.

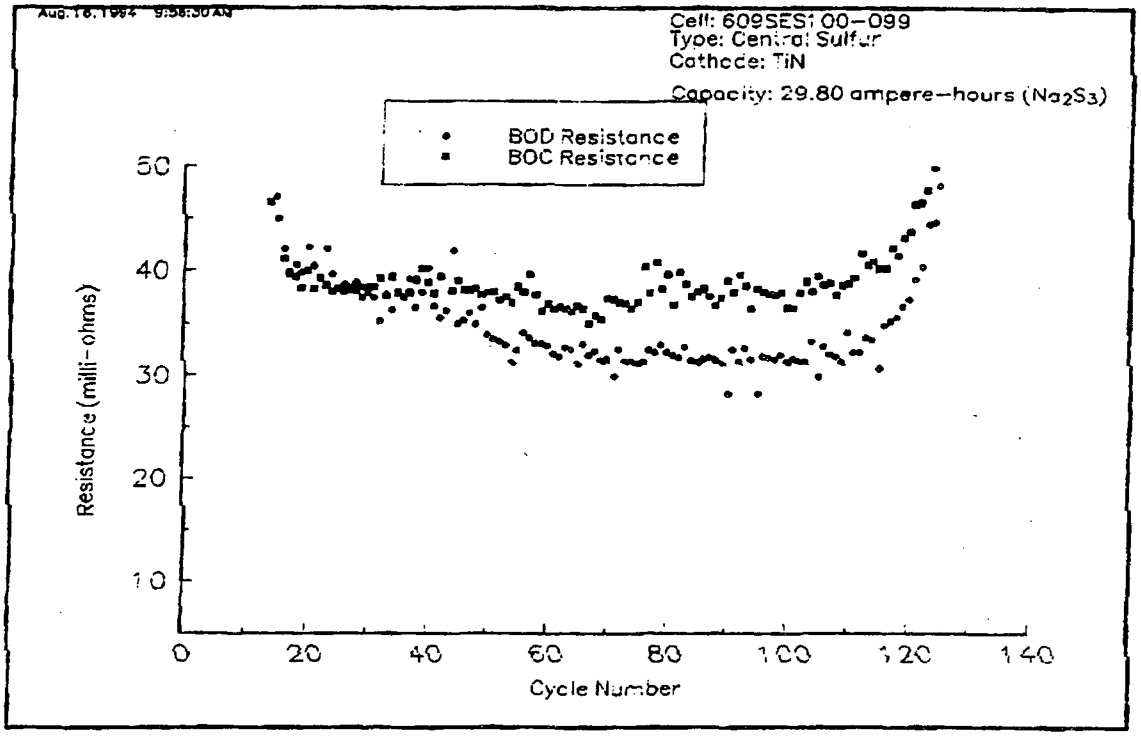


Figure 3 - Cell resistance for cell -099.

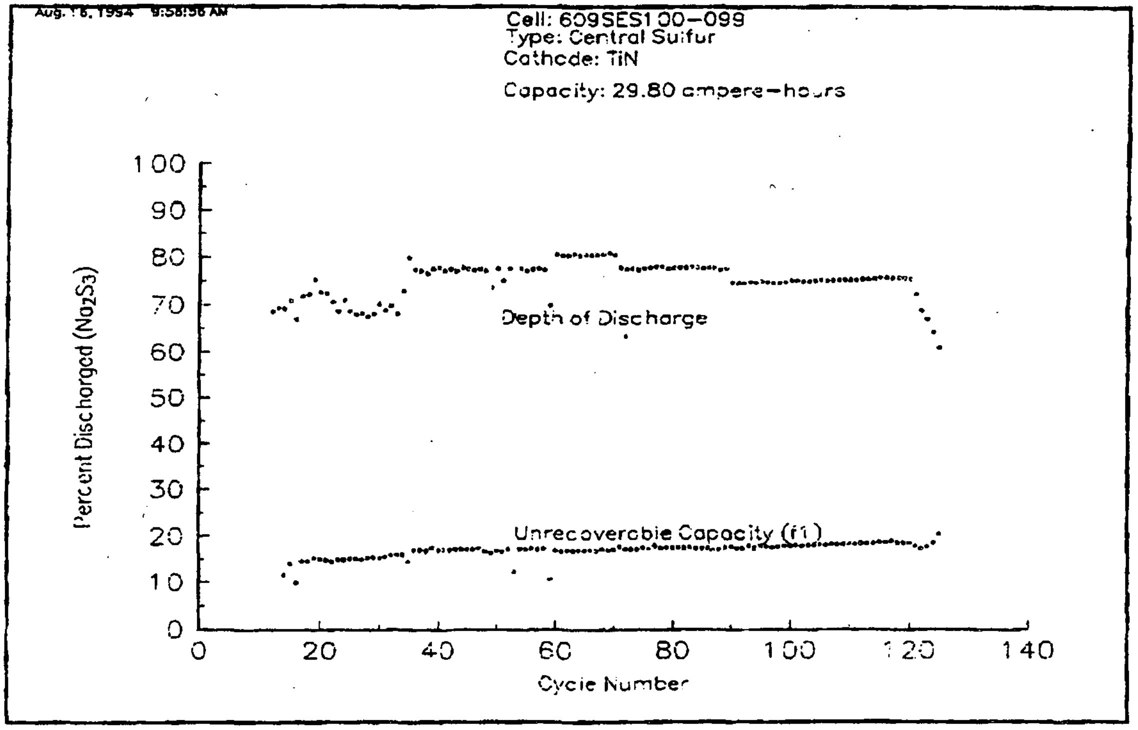


Figure 4 - Depth of discharge and unrecoverable capacity for cell -099.

Ion Plated Coating Cell Tests

Initial attempts to deposit ion-plated TiN coatings on the standard sulfur-core electrode bodies could not be completed because the standard electrode bodies, in the shape and size shown in Figure 4 were assembled with a low temperature Al solder which could not survive the 500°C temperatures that occur in both the pre-deposition cleaning and deposition processes. SPI arranged for the fabrication of one-piece cores (sidestepping the low-melting solder problem) of the proper size and the deposition by Balzers was then completed. The coatings were applied by the same commercial method used for the coupon tests described earlier. The new, coated cores were then shipped to SPI for assembly into the test cells. Cell tests on the ion-plated samples were performed at SPI in the same sulfur-core geometry used for the sputtered coatings described above. In contrast to the results of the sputtered coating tests, these trials appear to have been very successful, yielding durable films and consistent cell performance over many test cycles. A copy of the interim report submitted to ERIM by SPI is on the following pages. It shows the discharge data and internal cell impedance for a test period incorporating over 300 cycles. Two of the 3 cells are still on test undergoing approximately 2 complete charge/discharge cycles per day.

Testing Update - Central Sulfur Cells
Using
Titanium Nitride Coated Current Collectors

Scott L. Olsen
Manager of Testing

July 25, 1995

Silent Power, Inc.
Salt Lake City, Utah

Testing Update - Central Sulfur Cells
Using
Titanium Nitride Coated Current Collectors

General

Three Cells (SES build numbers 137, 138 and 140) were assembled using titanium nitride coated aluminum as the sulfur side current collector. Theoretical capacity for these cells was 29.48 ampere-hours for cell 137, 29.66 for cell 138 and 29.79 ampere-hours for cell 140. The sodium-side used a tapered, thermo-compression-bond (TCB) seal, with a conventional planar TCB seal used on the sulfur-side. All three cells were placed on test February 24, 1995.

Initial electrical performance was expected to match the "standard" SES cell performance then degrade as the TiN electrode corroded away. This prediction was based on behavior of cells tested earlier which used TiN coated electrodes. These cells were expected to initally show the following characteristics:

Resistance @ EOD (70 - 80% of theoretical) - 11 to 14mΩs

Unrecoverable Capacity (f1) - less than 10% of theoretical capacity (< 3 Ah)

Useable capacity - 21 ampere-hours

Testing

Following initialization and break-in cycling both cells were subjected to cycling with charge rates of 2 and 4 amperes (charge and discharge respectively) with 18 ampere-hours of charge removed, through about cycle 30. The charge and discharge currents were then increased to 3.6 and 9 amperes respectively, for the remainder of testing.

Observations

All three cells performed very well relative to earlier TiN cells and the "standard" cells with Ni/Cr coated current collectors. Cells 138 and 140 showed initial resistance values around 15 mΩs then decreased as cycling continued. While cells 137 and 140 have completed more than 300 electrical cycles and remain on test, cell 138 showed an upturn in resistance around cycle 90. General performance of this cell had degraded during further cycling as indicated in Figures 1 and 2 and the cell was removed from test after completing about 180 electrical cycles. A post test analysis has not been performed on this cell but initial visual inspection showed no evidence of seal failure.

A plot of cell resistance taken at BoD and BoC for cells 137 and 140 is shown in Figures 3 and 4. Cell 137 showed a slight "hump" in resistance which has been observed in varying degrees in other cells of this design. The cause of this anomaly is unknown. Cell 140 started with higher resistance but gradually decreased during cycling. Figures 5 and 6 show f1/DOD plots for both cells. Step changes in f1 and DOD are artifacts of the test system and not cell "behavior". Both cells have exhibited a gradual increase in f1 over the life of testing equivalent to about +5% per 1000 cycles. This rate is higher than observed with standard ses cells which tend to show "flatter" f1's during the first several hundred cycles.

Some instability is seen during the last 50 or so cycles. We believe this is due to perturbations caused by installation of new cells onto the test system.

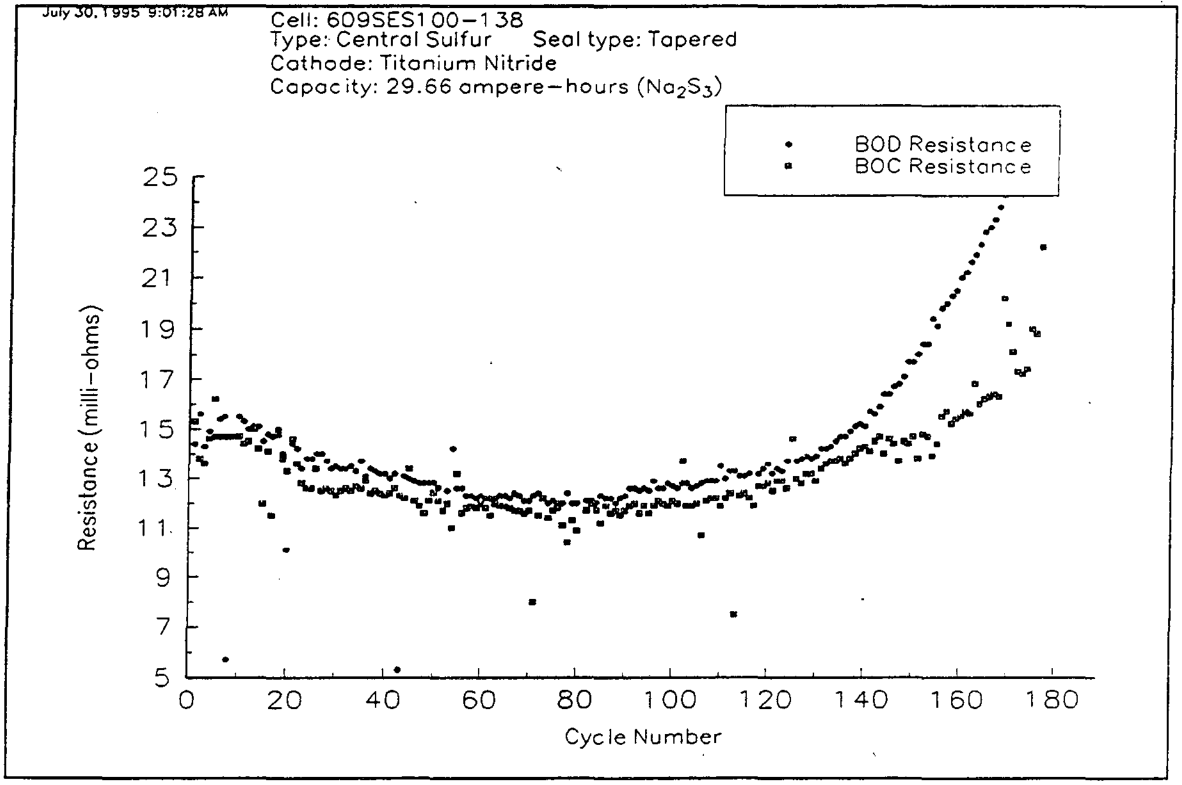


Figure 1 - Cell resistnace during cycling for cell 138.

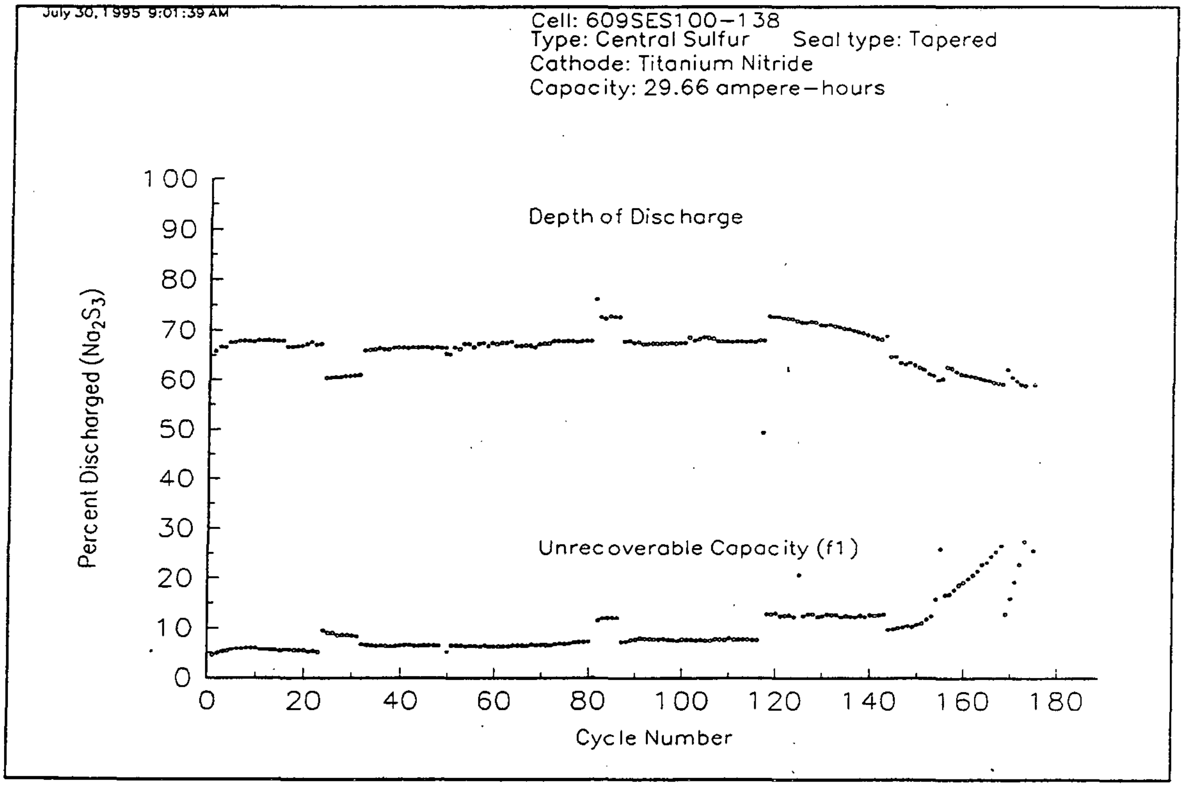


Figure 2 - DoD and F1 for cell 138.

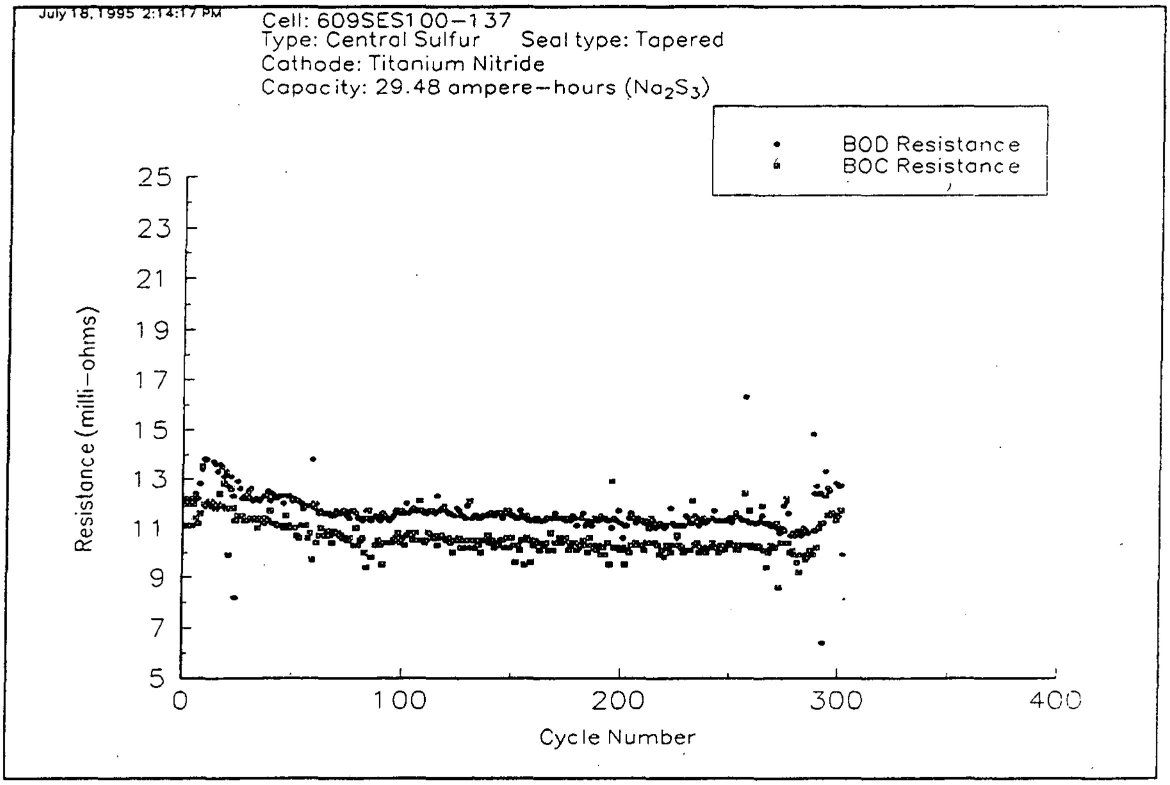


Figure 3 - Resistance versus cycle number for cell 137.

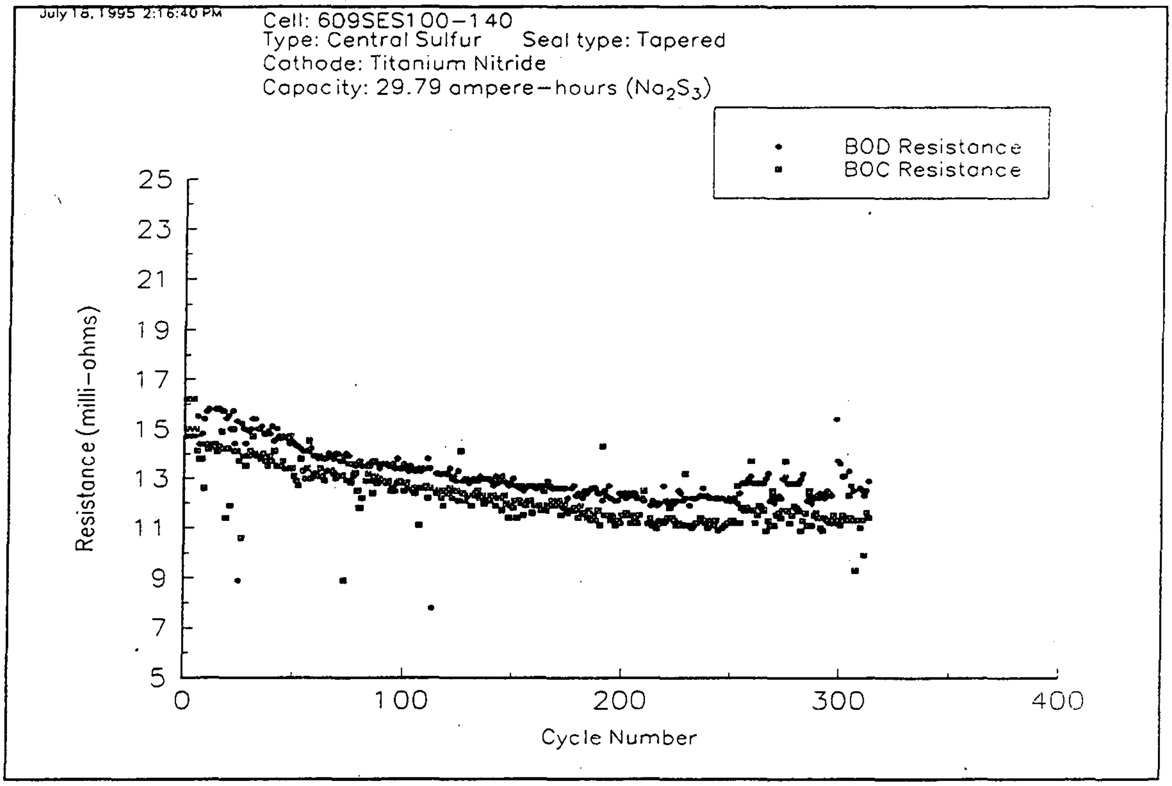


Figure 4 - Resistance versus cycle number for cell 140.

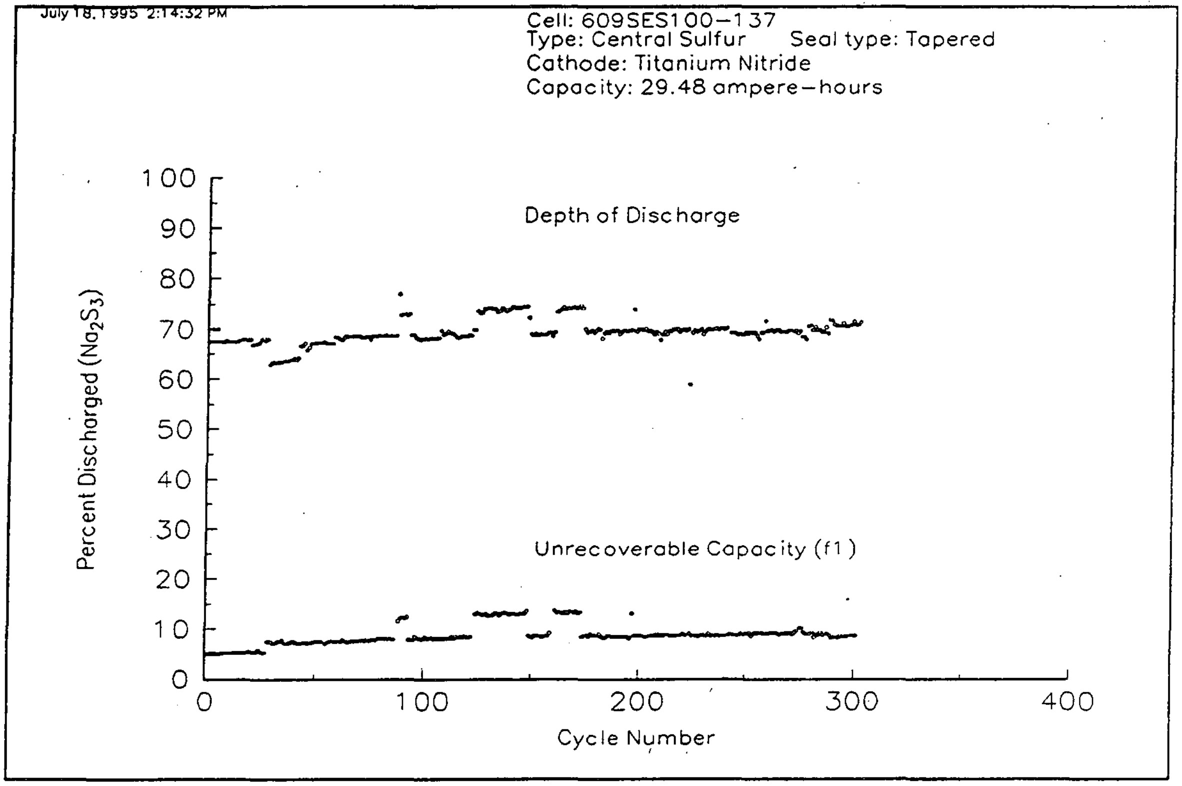


Figure 5 - DOD and f1 versus cycle number for cell 137.

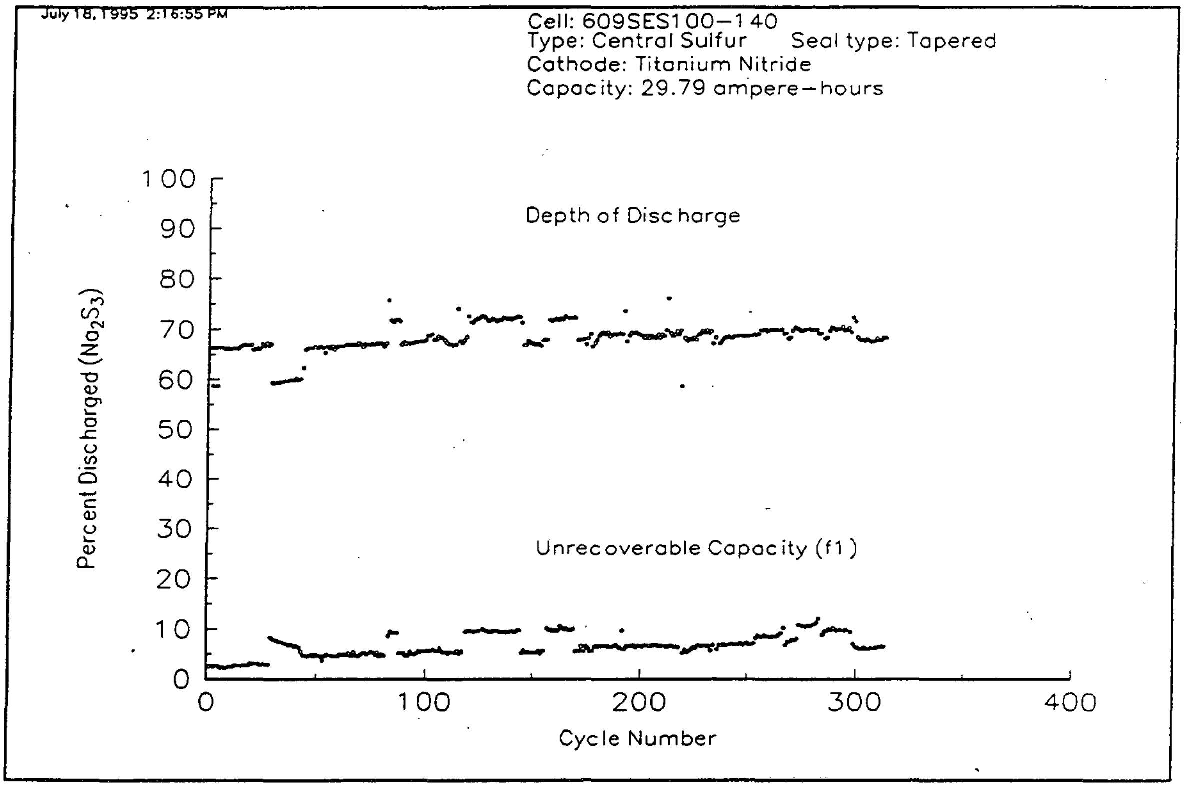


Figure 6 - Dod and f1 versus cycle number for cell 140.

8. Conclusions

Based on the data and reports from Silent Power, Inc. on the cell testing carried out thus far, the TiN electrode coatings as deposited by a commercial reactive ion-plating process appear to offer corrosion resistance and electrode interfacial resistance better than the 'standard' (Ni/Cr coated) container electrodes and comparable to the best of the Na/S cells they have previously tested. Silent Power has said that they expect to continue the testing this series of cells on their own funding, as they have done to date. They currently expect that testing will continue at least until December 1995. The relatively poorer performance of the reactively sputtered TiN electrodes which were the initial subject of the investigation appears to be related to the difficulty experienced in repeating consistently the substrate preparation conditions used in the earlier samples prepared at Ford. The commercial, high temperature, in-situ heating approach to substrate pretreatment used by Balzers appears to produce coatings with the excellent adherent qualities found in the Ford sputtered films. The ion-plating process is a fully commercialized process, permits substantially faster coating deposition than sputtering and is expected to provide a commercially affordable coating cost. Investigation of the prospective costs for such coatings was not possible during this program and will need to be carried out to permit a rational choice of direction in future Na/S cell design. While most vehicle batteries employ the sodium core design, it appears that for several applications, including utility load leveling, the sulfur core design used for testing these coatings may become the design of choice. It should be possible to produce the coatings on the interior surface of a cell wall if required.

9. References from Initial Ford Work

"Graphite Aluminum and Silicon Carbide-Coated Current Collectors for Sodium Sulfur Cells", M. Mikkor, Journal of the Electrochemical Society, 132, p 991 (1985).

"Candidate Materials for the Positive Current Collector in Sodium Sulfur Cells - I, Ceramic Oxides", H.S. Wroblowa, R.P. Tischer, G.M. Crosbie and G.J. Tennenhouse, Corrosion Science 26, p 193 (1986).

"Candidate Materials for the Sulfur Electrode Current Collector - II, Aluminum and its Alloys", R.P. Tischer and H.S. Wroblowa, Corrosion Science 26, p 371 (1986).

"Candidate Materials for the Sulfur Electrode Current Collector - III, Al/SiC Composite Materials", R.P. Tischer, W.L. Winterbottom and H.S. Wroblowa, Corrosion Science 26, p 377 (1986).

"Method of Making a Current Collector for a Sodium/Sulfur Battery", U.S. Patent # 4,649,002, by R.P. Tischer, W.L. Winterbottom and H.S. Wroblowa, Assigned to the Ford Motor Company (1987).

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