

United Nuclear Corp - *Contractor*

White Plains N.Y.

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In reply please refer to:
UNC MTL-3722
March 16, 1964

Aeronautical Systems Division
Air Force Systems Command
U.S. Air Force
Wright-Patterson Air Force Base
Ohio

Attention: Mr. Richard H. Herald, APFT

Re: Bimonthly Status Letter No. 4
Contract No. AF 33(615)-1039
UNC Project No. 2199
Electrochemical Device for Oxygen Removal

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This letter covers the period January 1 through February 29 1964. DDC-IFA-A

SUMMARY *Abstract*

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The first thoria-yttria cell tested in sodium cracked at 140 hr. Its current efficiency and current density were low, but it apparently did remove some oxygen from sodium. The second such test encountered rising cell resistance, a new development. The rise is tentatively ascribed to depletion of oxygen from a stagnant sodium layer around the cell. Electrolysis of a zirconia-calcia cell in sodium was interrupted by overheating of the O-ring seal. A revised seal using forced air cooling, ~~has~~ eliminated this problem.

A zirconia-yttria cell electrolyzed in oxygen ~~has~~ ^{ed} shown encouragingly high conductivity and current efficiency at 1000° F. It also showed current efficiency increasing with current density up to a maximum before decreasing. This unexpected behavior has not been explained. Electroly- (A)

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ysis of zirconia-calcia plates in oxygen indicated that this material will not be as useful as zirconia-yttria at temperatures below 1400°F ?

~~In the large view, the results to date cannot be called encouraging. Loss of ionic conduction is the major concern. The electronic conduction created by reduction of the electrolyte tends to short circuit ionic conduction, eliminating oxygen transfer. The same behavior has now been reported in the course of related studies in London, England. It seems clear that operation with a partially reduced electrolyte will be necessary. Testing in the remaining period will be aimed at determining the feasibility of such operation.~~

1. ACTIVITIES DURING JANUARY AND FEBRUARY

1.1 TASK 200 - COMPATIBILITY TESTS

No additional compatibility tests were run in sodium. Efforts to obtain small samples of additional solid electrolyte materials are in progress.

Because of interest in graphite powder as an anode contact material a simple graphite-thoria compatibility test was run. A short length of thoria-15 w/o Y_2O_3 tube was tightly packed with graphite powder, out-gassed, sealed in a pyrex glass tube under a hard vacuum, and heated to 1000°F. After 140 hr the brown color of the as-received material had turned a partially translucent white through the entire wall thickness. Metallographic examination of a cross section showed no surface reaction between the graphite and ceramic. Additional tests showed that the color change could be obtained in vacuum in the absence of graphite.

1.2 TASK 300 - CELL EVALUATION AND DESIGN CRITERIA

1.2.1 Thoria-Yttria Tests

The first test of a gastight thoria-15 w/o yttria cell in sodium was run at 1000°F using graphite powder to provide electronic contact at the anode.

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For this test the current density was held at 0.1 milliamperes per square centimeter, a value chosen as representing about the minimum for a useful device. The oxygen content of the sodium was held at about 200 ppm in this and the subsequent tests. The apparent resistivity of the cell remained fairly steady at 6×10^{-4} ohm-cm. The voltage required was low, ranging from 2.6 to 4.9 volts. This reduced the possibility of electrolytic decomposition of the thoria. The test was terminated at 140 hr by circumferential fracture of the cell wall at the sodium-gas interface. The fracture was not due to any unusual mechanical shock. Smaller cracks were subsequently observed in the submerged portion of the cell.

The oxygen transferred by the electrolyte was presumed to have reacted with the graphite anode to form CO_2 with no change in volume (i.e., negligible CO formation). The total gas volume generated by the cell during the run was 2.15 cc. This is equivalent to an average current efficiency of 13% or an ionic transport number of 0.13. Short term current efficiency values ranging from 4 to 67% were observed with no pattern detectable in the variations. The low average efficiency is discouraging from a practical standpoint because the current density was already low. The total oxygen transferred by the cell represented about 0.2% of that present in the active length of thoria-yttria. Loss of smaller amounts has been shown to sharply reduce the ionic transport number in zirconia-4 w/o calcia (see page 5, UNC MTL-3468). Since no trend toward decreasing resistance was observed in this run, it seems probable that at least some of the oxygen released at the anode came from the sodium.

The original brown color of the cell was lightened for about 1 in. above the sodium level and darkened below it. The inner ceramic surface exposed to graphite powder was scalloped and glazed as though subjected to shallow slagging attack. The cause of this attack is not understood but it is believed to have occurred after sodium leaked in through the fracture since the graphite alone caused no attack in control tests (see Section 1.1). The mixture of sodium and graphite should not have been

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more corrosive to ceramics than either alone, as the solubility of carbon in sodium is very low. The appearance of the ceramic suggests attack by a molten salt or hydroxide. Metallographic examination of the cell wall revealed no penetration or microstructural changes below the attacked surface.

Testing of a second thoria-15 w/o yttria cell in sodium at 1000 F has begun. It is identical to the first except that the graphite column is reduced in height from 2 in. to 3/4 in., the depth of immersion in sodium is reduced from 1 3/4 in. to 1 in., and radiation shields and forced air cooling are used to reduce the temperature at the top end of the cell. The initial apparent resistivity of this cell was only 1.6×10^5 ohm-cm, but this rose in two days to the order of 6×10^6 ohm-cm. This has made it impossible to run the cell at the intended current density of 1 ma/cm^2 without going to voltages so high as to threaten decomposition of the thoria. Only small currents have been attained and no detectable oxygen has been produced to date. The cause of the rise in apparent resistance is still under investigation. Pressure-vacuum cycling of the anode space produced no change in resistance, so contact there is probably not the difficulty. Increasing the flow velocity past the cell reduced the apparent resistivity by a factor of 2. This tends to confirm some recent calculations indicating that diffusion of oxygen through sodium could limit the current density when the stagnant film thickness exceeds a few mils. Further investigation of this question is planned.

1.2.2 Zirconia-Yttria Test

The first zirconia-8 w/o yttria cell has been under fairly continuous test in oxygen for a total of 8 weeks. Graphite powder is used to obtain contact at the anode (inner) surface and a silver film is used at the cathode. The oxygen produced is led through hypodermic tubing to a gas burette and measured volumetrically. The cell current efficiency is being determined as a function of temperature and current density. Results to date

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show a maximum in the current efficiency vs current density curve at both 1200 and 1000°F. At 1200°F the current efficiency is close to 100% at 5 ma/cm², and drops to 36% at 0.1 ma/cm². This result is unexpected and no mechanism for it has yet been advanced. It encourages the use of higher current densities in tests in sodium.

At lower temperatures the maximum current efficiency apparently drops to lower values and occurs at lower current densities. These tests are continuing. Several hundred cubic centimeters of oxygen have been transferred through the cell by now. The apparent resistivity of the zirconia-yttria is low even at 100% ionic conduction (typically 6×10^5 ohm-cm at 1000°F). The low resistance permits higher current density before reaching the decomposition voltage of the zirconia. The graphite powder has provided more consistent anode contact than the previous silver films, but still leaves room for improvement. Tapping the cell has at times increased the current by a factor of 6.

1.2.3 Zirconia-Calcia Tests

A third zirconia-4 w/o calcia cell was constructed and tested in sodium at 1000°F. The inner surface of the cell was coated with silver to a calculated average thickness of 0.03 mils for a depth of 1¹/₈ in. Graphite powder was used to provide electronic contact to the silver film. The initial current density was 0.05 ma/cm², but this dropped as the apparent resistivity rose in three days from 4×10^5 to 1.2×10^7 ohm-cm. The cause of this rise was not known at the time, but it is now suspected to have been depletion of oxygen from a thick film of stagnant sodium. Electrolysis was discontinued after 72 hr because overheating of the O-rings resulted in gas leakage. Up to this time the cell transferred 2.0 cc of oxygen at an average current efficiency of 17%. The bottom inch of the cell was dark gray in color. Electrolysis will be resumed with provisions for cooling the O-rings.

A series of small curved plates were cut from a zirconia-4 w/o calcia tube, silver coated on both faces, and electrolyzed in oxygen at several

temperatures and current densities. The objective of these tests was to determine the threshold temperature below which electrolysis caused a marked drop in resistance, signalling the onset of electronic conduction. At 1 ma/cm^2 this temperature was about 1400 F, although the threshold was not a sharp one. At 5 ma/cm^2 , the threshold temperature was not found but was above 1400 F. These tests took as long to complete as electrolysis of a gastight cell in oxygen. Since the latter produces more positive and quantitative results, it will be used in the future except when impervious tubes are not available.

1.2.4 Resistance Measurements

The apparent resistance of a solid electrolyte sample calculated as the ratio of impressed d-c voltage to current, differs from the true resistance due to voltages generated by the cell. A number of attempts were made to measure true resistance using 1000 cps alternating current and an a-c impedance bridge. To date, these have failed due to inability to obtain a good null point. It appears that pickup of extraneous signals by the cell assembly and its supporting equipment is the problem. Efforts to eliminate the pickup are continuing.

1.2.5 Visit by B.C.H. Steele

An informative discussion was held with Mr. B.C.H. Steele of the Imperial College, London, who visited United Nuclear Corporation after presenting a paper at the AIME annual meeting in New York. He has been working on solid electrolytes for 5 yr, concentrating on oxygen potential measurements in refractory metals. He has been able to measure ionic transport number as a function of equilibrium oxygen pressure for a number of solid electrolyte materials. Of these he found the thoria-yttria family best at low oxygen pressures. Members of this family retain an ionic transport number greater than 0.99 down to at least 10^{-4} atmospheres of oxygen at 1830 F. At pressures above 10^{-1} atmospheres they take in oxygen above the stoichiometric ratio. The excess oxygen

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produces positive hole conduction and changes the color from the translucent white to brown. This explains the color change observed in the graphite compatibility test (Section 1.1).

1.2.6 Interpretation of Results

It now appears unlikely that 100% ionic conduction can be maintained in solid electrolytes used for oxygen removal from sodium. Darkening and reduced current efficiency have been observed in every cell tested in sodium to date. The oxygen pressure in sodium containing 10 ppm of oxygen at 1000°F, calculated on the basis used by Steele, is on the order of 10^{-44} atmospheres. Fortunately, 100% ionic conduction is not essential to a useful device. A current efficiency as low as 10% would probably be acceptable so long as a useful ionic current density can be maintained. The results to date suggest that under some conditions, the current efficiency can level off above 10% and does not necessarily decrease with increasing current density.

2. WORK SCHEDULED FOR NEXT PERIOD

2.1 TASK 200 - COMPATIBILITY TESTS

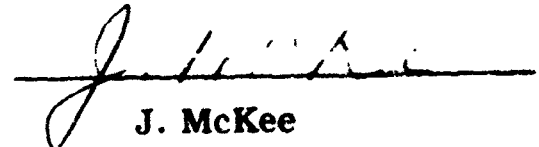
Control specimens of the electrolyte will be exposed to flowing sodium along with each cell tested in sodium.

2.2 TASK 300 - CELL EVALUATION AND DESIGN CRITERIA

Testing during the remainder of the program will explore the possibilities of removing oxygen from sodium at useful rates through partially reduced electrolytes. An ionic current density of 0.1 ma/cm², or 0.3 mg O/hr-cm², will be adopted as a minimum useful oxygen removal

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rate. Testing of zirconia-yttria cells in sodium will begin. Continuing efforts will be made to obtain longer runs with thoria-yttria and zirconia-calcia cells in sodium.


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