DOE/PC/93219--T11

Third Quarter 1995 Technical Progress Report

For the Department of Energy Advanced Coal Research Program Grant:

Novel Carbon-Ion Fuel Cells

By the 93219

Duke University Department of Mechanical Engineering and Material Science

Principal Investigator: Dr. F. H. Cocks

Telephone: 919 660 5301

Assistant Investigator: Henry LaViers

Telephone: 919 660 5303

Fax: 919 660 8963

October 3, 1995

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED.

MASTER

RECEIVED
USDOE/PETC
95 OCT -6 AM 8:09
ACQUISITION & ASSISTANCE DIV.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DOE/AC/93219--T11

Overview of Work Proposed in Original Grant Application for the Third Quarter of 1995.

In the original grant proposal submitted to the Department of Energy, months 10 through 21 of the research were allotted to Task #2. The description of Task #2 was:

Task #2: "Measurements on Carbides with the Fluorite Structure," states:

"There are twelve known carbides of the fluorite structure with transition temperatures from 350-1450 C. Small quantities of these carbides in powder form will be purchased when commercially available. Pellets pressed from powder within an inert atmosphere will be made, CVI treated, and tested as described in Task #1. Pure carbides will be tested first, followed by carbides doped with impurities of different electrical valences whose atomic radii are favorable for solubility in the carbide lattice structure. Dopants will be introduced either during the chemical formation of the carbide, by mix and sinter diffusion, or by high energy ion bombardment of the powder prior to pelletization. The approximate time period for completion of Task #2 is twelve months."

Report of Work Completed to Date

The research project is proceeding on schedule with the creation of carbides in the form of castings of CeC_2 , LaC_2 and Al_4C_3 , to test the carbides for their phase transformation temperatures, for the ionic conduction of carbon-ions across the carbides when used as an electrolyte, and the attendant, but undesirable, parasitic conduction of electrons across the carbides when used as an electrolyte.

Laboratory Investigations to Date

Four significant laboratory results have taken place in a highly productive seventh quarter of this research project:

1. A natural carbon (98.9% C-12 and 1.1% C-13) sputter target has been acquired.
2. LaC_2 and Al_4C_3 have been made on site in the laboratory using the Arc Melt Furnace, and their room temperature crystal structures were confirmed using X-ray powder diffraction.
3. A method for producing in the laboratory carbon sputter targets of either natural or C-13 isotope has been found.
4. Final approval by Oak Ridge National Laboratories' High Temperature Materials Laboratory has been given for researcher Henry LaViers to use their High Temperature X-Ray Diffraction equipment in the month of October.

Each of the above four results will now be discussed in more detail.

Result No. 1: A natural carbon sputter target was acquired from the Johnson Matthey special products division. This natural carbon sputter target is of a 99.99% purity of the natural composition of 98.9% carbon-12 isotope and 1.1% carbon-13 isotope. It is of the standard size of 25.4 mm in diameter and 3 mm in thickness, and can be used in the sputter gun of the ultra high vacuum chamber fixture available at Duke University's Thin Films Development Laboratory. This natural carbon sputter target makes possible an alternative method of doing tracer diffusion studies of carbon in carbides. If the carbides could be made of the elemental metal and carbon-13 isotope exclusively, (see Result No. 3 described below) then a layer of natural carbon could be sputter deposited onto the carbide and the diffusion of carbon-12 studied.

Result No. 2: By melting the approximate stoichiometric amounts of the elemental metal and carbon together in an Arc Melt Furnace, aluminum carbide and lanthanum dicarbide have been made. In the case of aluminum, the stoichiometric amount plus 10% by weight of finely ground carbon powder was weighed out onto a 3 gram sheet of aluminum foil. The aluminum foil was then folded numerous times so as to enclose the carbon powder and form a "packet" that would not be blown about by the force of the electric arc inside the Arc Melt Furnace. The packet was then melted under an atmosphere

of 20 mm Hg of Ultra High Purity (99.999%) Argon gas using 200 amps of electric current. The melted sample was then hand crushed to a fine powder under oil in a cast iron crucible. The oil-protected powder was then analysed by Powder X-Ray Diffraction in a balsa wood sample holder that held a flat surface of the sample to the x-ray beam, but absorbed any excess oil so that the sample remained rigid and non-flowing during the test. The x-ray pattern produced showed all the expected peaks, but also showed two extra peaks of low amplitude that appear to be correlated with those of aluminum oxide.

The synthesis of lanthanum dicarbide was slightly different to that of the aluminum carbide. The elemental lanthanum available was in the form of 1 mm diameter by 3 mm long rods stored under oil. Attempts to react these rods with carbon powder were unsuccessful, but the rods did react with a short section of carbon rod. X-Ray powder diffraction spectra showed all the expected peaks with no discernable extra peaks.

Result No. 3: Prior to this quarterly report, previous reports have detailed efforts to create various pressed and sintered pellets or carbon sputter targets. These prior efforts used various techniques, such as low and high pressure binderless pressing, pressing with glucose, sucrose, B₂O₃, C₁₄, and Amyloid MEK binders and hot pressing at 500 degrees Centigrade with and without binders. All of these previous efforts were unsuccessful or marginal. On September 19th, 1995, Mr. Henry LaViers received an invitation, after a series of telephone calls, to visit the Morganton North Carolina plant of SGL Carbon Company Inc., an international company specializing in pressed carbon and graphite products. The Morganton plant of SGL Carbon was built during World War II as part of the Manhattan Project and produced most of the graphite for the atomic bomb efforts at Oak Ridge and Hanford. Today the plant produces a wide variety of carbon products ranging from nuclear applications to intricate one-time casting molds for the production of oil well drilling bits.

Mr Fred Miller of SGL Carbon gave Mr. LaViers a tour of the plant and related laboratories and examined the results of Mr. LaViers' past efforts to produce pellets and sputter targets. He also examined the Carbon-13 powder that a sputter target was desired to be made from. Mr. Miller recommended SGL Petroleum Tar with a softening point of 57 degrees Centigrade as a binder and provided a heat treatment schedule for its carbonization. Mr. Miller donated the tar and also provided graphite flakes to pack the pressed shapes in during carbonization. He also provided valuable advice on shrinkage and carbon yields.

Using the above described information, pressed carbon shapes, including trial 25.4 mm diameter sputter targets, have been successfully produced at the Duke laboratories virtually from the first attempts when the SGL procedures are followed to the letter. These

pressed shapes have required 20% by weight tar as the binder. The initial 20% tar is reduced to 12% by weight after carbonization. In the case of a Carbon-13 sputter target, this will mean that the ultimate purity of the finished target will be 88% Carbon-13 and 12% Carbon-12, where the Carbon-12 is an undesired but necessary addition from the tar binder.

Result No. 4: On October 2nd, 1995 Oak Ridge National Laboratories' High Temperature Materials Lab notified Duke University officially that Henry LaViers was approved to use the High Temperature X-Ray Diffraction Equipment there in the second week of October, 1995. Time permitting, twelve samples will be analysed for their carbon sub-lattice parameters and their phase transition temperatures. These twelve are:

Cerium dicarbide,

Cerium dicarbide doped with 15, 25, and 35 mole % Barium carbide

Lanthanum dicarbide,

Lanthanum dicarbide doped with 15, 20, and 25 mole % barium carbide

Aluminum carbide

Aluminum carbide doped with 5, 15 and 30 mole % magnesium carbide

Conclusion

The research project "Novel Carbon-Ion Fuel Cells" is entering its 8th quarter. Methods to successfully cast lanthanide carbides are being investigated. Dopants for the fluorite structure carbides have been selected. Sources and methods for making Carbon-13 sputter targets have been found with the help of SGL Carbon Co. of Morganton North Carolina.

References

1. Bottelberghs, P.H., "Low Frequency Measurements on Solid Electrolytes and Their Interpretations", in Solid Electrolytes, Van Gool ed., Academic Press, 1978,p154.
2. Gschneider, K.A. and L. Eyring, Handbook of the Physics and Chemistry of Rare Earths, Volume 15, Chapter 99, page 61, by G. Adachi, N. Imanaka and Z. Fuzhong.
3. Loe, I.R., I.J. McColm and T.A. Quigley, 1976, Journal of the Less Common Metals, Volume 46, page 217.
4. Ibid
5. McColm I.J., V. Kotrocz, T.W. Button, N.J. Clark and B. Bruer, 1986, Journal of the Less Common Metals, Volume 115, page 113.
6. Hajeck, B., P. Karen, 1986, Collect. Czech. Chem. Commun. Volume 51, page 1411.
7. Pialoux, A., 1988, Journal of the Less Common Metals, Volume 143, page 219.
8. Aldrich Chemical Company, catalog numbers 38,946-3 and 27,720-7, 1994 Catalog.