ELECTROCHEMISTRY OF ACETYLIDES, NITRIDES
AND CARBON CATHODES IN MOLTEN HALIDES

Progress Report
to

Division of Materials Sciences
Office of Basic Energy Sciences
U.S. Department of Energy

MASTER

April, 1980

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1. Purchase and Installation of Inert-Atmosphere Facility.

Following authorization of the budget contained in the 1979-1980 renewal proposal, a complete glove-box system was ordered from Vacuum/Atmospheres Inc., Hawthorne, CA. The system, consisting of:

- Glove-box and furnace well
- Vacuum furnace/Transfer Chamber
- Oxygen Removal Unit
- Water Removal Unit
- Nitrogen Removal Unit
- Atmospheric Temperature Control
- Pressure Control
- Water and Oxygen Monitor

was originally promised for December, 1979, but did not arrive until March, 1980.

In January, 1980, the IIT administration announced plans to convert one of the two laboratories presently used by the P.I. (Perlstein Hall 127) to office space. In return, a presently unused part of the second floor of the building will be remodeled for use as a laboratory by the P.I. The exchange is advantageous since it will consolidate the P.I.'s laboratories in one large, completely equipped, laboratory with air conditioning, separate exhaust, and vacuum connections. The switch-over is expected to be completed during the summer of 1980.

2. Overview of Activities.

Meanwhile, the glove-box at the Institute of Gas Technology, used for the work reported in the 1978-1979 Progress Report, had to be cleared at the end of August, 1979. Thus, only a few additional EMF data on acetylide containing melts could be gathered; these are incorporated in the publication and presen-

tations described in Part 3.

During the 7-month period without an inert-atmosphere box, a beginning was made with two experiments simple enough to allow the use of a small glove-bag with once-through purging of helium. These experiments are described in Part 4; one of them is in progress, the other is to start soon.

In addition the P.I. was involved as a co-author in the preparation of two extensive reviews. Both of these furnished ideas for the application of relaxation techniques used in this work to problems originating in other molten-salt systems (molten carbonate fuel cell, lithium/metalsulfide battery). This will be discussed in Part 5.

3. EMF Measurements in Acetylide Containing Melts: Intercalation of Lithium and Calcium.

A few additional data points were obtained for acetylide solutions in contact with graphite and carbon. These data agreed reasonably well with the results obtained earlier (Progress Report 1979-1980) and reinforced the conclusion that intercalation takes place not only in Li^+ containing melts but also in Ca^{2+} melts.

No calcium-graphite intercalation compounds have been reported in the literature, although barium-graphite intercalates have been reported (1,2,3) and strontium intercalates are also known (4,5). Thus, it is important to corroborate our conclusion that calcium forms intercalation compounds with graphite, particular-

ly since direct combination of calcium and carbon (the method used by Herold and co-workers to produce intercalation compounds) reputedly yields only calcium carbide.

To confirm the conclusions drawn from our emf measurements, we are planning to synthesize calcium-graphite compounds using the method of Herold (elementary combination) and to determine the degree of conversion to carbide, by chemical analysis.

From discussions with Dr. W.E. Haupin (Alcoa) at the recent 1980 Conference on Ionic Liquids (Dead Sea, Israel) we learned that sodium and lithium intercalate not only in graphite, but also in other types of carbon (e.g., that used as a lining of aluminum reduction cells), according to the (mostly unpublished) experience of aluminum companies. This is a welcome confirmation of one of our conclusions and encourages us to continue our work using not only graphite, but also amorphous carbons.

The emf measurements have been presented at the Gordon Research Conference on Molten Salts and Metals (Wolfeboro, NH, August 1979) and at the 1980 Conference on Ionic Liquids (Dead Sea, Israel). A presentation of this work will also be made at the Electrochemical Society meeting in St. Louis, MO., May, 1980; the Extended Abstract is attached.

We have prepared a manuscript for publication but, before submitting it, are awaiting the first results of the calcium-graphite intercalation experiments, to remove any remaining uncertainty about the interpretation of the data.

4. Current Work.

A. Calcium activity and diffusion coefficient in calcium-aluminum alloys.

As reported in the 1978-1979 Progress Report, emfs of Ca-C couples were measured between 540 and 700 °C. Unfortunately, as pointed out there, the activity coefficient of calcium in the reference electrode, $\text{CaAl}(\alpha)\text{-CaAl}_4$, is known only at one temperature (500°C). Moreover, the range of temperatures over which the $\alpha\text{-phase/CaAl}_4$ two-phase region exists, is limited (up to 616°C); the calcium activity above this temperature is unknown (Figure 1).

Consequently, it was decided to measure the calcium activity in the alloy between pure Al and CaAl_2 , over a 500-800°C temperature range. The measurements are carried out by standard emf techniques. In the initial measurements coulometry is used to vary composition at constant temperature. Later measurements will cover temperature dependence at constant composition. Some 20 experiments are planned, in total.

We intend to utilize the potential-time (relaxation) curves obtained by current interruption during coulometric charging or discharging not only to determine calcium activity but also to extract information about the diffusivity of calcium in the various alloy phases. Calcium diffusivity in the α (solid solution), CaAl_4 , and CaAl_2 phases are unknown; yet they are of great interest in connection with rate limitations occurring in high-temperature calcium/metalsulfide cells, at high current density. In lithium-aluminum alloy the difference between lithium diffusivities in the α (solid solution) and β (intermetallic compound) phases is 3 to 4 orders of magnitude (6,7).

Figure 1 Calcium-Aluminum Phase Diagram

The technique used to measure activity and diffusivity simultaneously is similar to the "GITTT" technique (galvanostatic intermittent titration technique) employed by Huggins and co-workers (7,8) to measure these quantities in lithium-aluminum alloys. However, we feel that in their approach the existence of a moving boundary (alpha-beta in lithium-aluminum; more complicated in calcium-aluminum) is not properly accounted for; the moving-boundary effect cannot be neglected a priori in an unknown situation such as in calcium-alloy.

Therefore, we are at present modeling mass transfer in a cylindrical geometry with moving boundaries between two or three phases. A computer program is being developed which will interpret the current-interruption transients on-line, using the storage capacity of the Explorer digital oscilloscope (purchased in 1979-1980) as a buffer. In the proposed budget for 1980-1981 we request funds for a computer terminal and coupler to our interactive "Prime" computer at IIT (to be cost-shared by IIT).

The emf measurements on the calcium-aluminum alloys require an inert atmosphere; since a glove-box was not available during most of the past year (see Part 1), we have constructed a small system involving a glove-bag (Figure 2) in combination with the silica reaction tube fabricated earlier (Progress Report 1978-1979). Its use is awkward, but adequate for the present transition period. The alloying of calcium and aluminum and the weighing of samples must still be done in a high-purity atmosphere, i.e., in a properly functioning glove-box, and here we have had generous assistance from Dr M.F. Roche's group in the Chemical Engineer-

Figure 2. Experimental set-up for calcium-alloy emf measurements (glove-bag, reaction tube, furnace, recorder)

ing Division of Argonne National Laboratory, who have shown much interest in the calcium activity measurements.

B. Synthesis of calcium intercalation compounds with graphite.

We have recently designed a sealable tube of refractory metal (essentially a small autoclave) in which lithium and/or calcium can be heated with carbon or graphite, with or without molten salt as an intermediary to accelerate the reaction, under an inert atmosphere. This tube is now being fabricated and will be used for synthesis experiments. The immediate objective is to determine the degree of conversion of calcium-graphite intercalates to carbides, as a function of time at reaction temperature. (See also Objective 2 in Renewal Proposal).

5. Reviews of the Electrochemistry of Two Major Molten-Salt Systems Related to Energy Conversion.

During the past year a lower level of experimental activity than originally planned, was forced by the delays in the delivery of the inert-atmosphere facility. This was compensated for by preparing two extensive reviews, both invited Chapters in books:

1. "Electrochemistry of sulfur in halide melts", co-authored with Dr. M.L. Saboungi (Argonne National Laboratory), to appear in "The Sulfur Electrode in Nonaqueous Media" (R.Tischer, Ed.), Academic Press, N.Y., during 1980.

2. "Physical Chemistry and Electrochemistry of Alkali Carbonate Melts, With Special Reference to the Molten Carbonate Fuel Cell", co-authored with Dr. H.C. Maru (Institute of Gas Technology), to appear in Volume 4 of "Advances in Molten Salt Chemistry" (G. Ma-

mantov and J. Braunstein, Eds), Plenum Press, N.Y., to appear in 1980.

Both Chapters will appear with acknowledgment of support by the U.S. Department of Energy, Office of Basic Energy Sciences.

During these review activities, two important problems were identified germane to the present work on acetylides and carbon cathodes. The electrochemical reduction of carbonates to acetylides (carbides) in molten-salt medium has been suggested and reported by several authors as an interesting route to acetylene production (pages 115-121 of Review 2); however, positive results have never been confirmed, presumably because of the poor stability of acetylides in all but a few halide melts (e.g., LiCl-CaCl_2). The present work on acetylides can be of essential help in this respect and would naturally lead to an exploration of carbonate reduction. This is therefore proposed as a follow-on effort in the continuation of this work (1982-1983).

Similarly, it was found during preparation of the review of sulfur electrochemistry in molten halides, that the corrosion resistance of refractory metals such as molybdenum (an important element in the development of lithium/metalsulfide batteries) is not clearly understood. Although MoS_2 layers have been identified as a corrosion-inhibiting factor by workers at Argonne National Laboratory, it is not clear whether their effect is a result of solid-conduction mechanisms or of slow kinetics of sulfur discharge at the substrate. Aspects of this question could be profitably studied by means of the electrochemical relaxation techniques used in the present work to study intercalation. There-

fore, an exploration of this question is proposed as an extension of the intercalation-deposition kinetics study. (1982-1983)

6. Publications; promotion.

Attached are three publications resulting from this year's effort:

- 6.1. "Cathodic Processes at Graphite and Carbon Electrodes in Chloride Melts Containing LiCl or CaCl₂", by J.R.Selman and J. Qafisheh, Extended Abstract of a presentation to be made at the Electrochemical Society Meeting in St. Louis, MO, May, 1980.
- 6.2. "Electrochemistry of Sulfur in Halide Melts", by J.R.Selman and M.L. Saboungi, Invited Chapter in "The Sulfur Electrode in Nonaqueous Media" (R. Tischer, Ed.), Academic Press, N.Y.
- 6.3. "Physical Chemistry and Electrochemistry of Alkali Carbonate Melts, With Special Reference to the Molten Carbonate Fuel Cell", by J.R.Selman and H.C. Maru, Invited Chapter in Vol. 4 of "Advances in Molten Salt Chemistry", (G. Mamantov and J. Braunstein, Eds), Plenum Press, N.Y.

Other publications during 1979-1980 are:

- 6.4. V. Sampath, A.F. Sammells, and J.R. Selman, "A Performance and Current Distribution Model for Scaled-Up Molten Carbonate Fuel Cells", J. Electrochemical Soc. 127 (1980) 80-85
- 6.5. J.R.Selman and J. Tavakoli-Attar, "Free-Convective Mass Transfer to a Rod-Shaped Vertical Electrode", J.Electrochemical Soc. 127 (1980) 1049-1055.
- 6.6. J.R.Selman and J.C. McClure, "Limiting Current to a Vertical Rotating Rod Electrode", to appear in June issue of J.Electroanal. Chem. (1980)

Per April 1, 1980, the P.I. was notified of promotion to the rank of Associate Professor, with tenure.

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