Lawrence Livermore Laboratory

Lithium-water-air Battery Project:
Progress During the Month of May 1976

John F. Cooper, Pamela K. Hosmer, and Robert V. Homsy

June 3, 1976

This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the laboratory.

Prepared for U.S. Energy Research & Development Administration under contract No. W-7405-Eng-48.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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.

DISCLAIMER

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

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or 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.

MEMORANDUM -- June 3, 1976

TO: Albert Landgrebe and Kurt Klunder
FROM: John F. Cooper, Pamela Hosmer, and Robert Homsy
SUBJECT: Lithium-water-air Battery Project: Progress During the Month of May, 1976.

John F. Cooper
Program Manager
Lithium-water-air
Battery Project

8b
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

I. INVESTIGATION OF THE KINETICS OF THE Li/LiOH(aq) ELECTRODE

A. Current Efficiency Measurements

The current efficiency for lithium dissolution is a parameter of fundamental importance both in the design of a lithium-water-air battery and in the interpretation of electrode polarization data. Current efficiency is defined as the ratio of the current in the external circuit to the rate (expressed as an electrical current) of lithium dissolution:

Mathematically,

$$e = IF/R \quad (2)$$

where e is the current efficiency, F is Faraday's constant, and I is the current in the circuit external to the cell. The rate of lithium dissolution is the sum of the external circuit current and the corrosion current, I_{corr} :

$$R/F = I + I_{\text{corr}} \quad (3)$$

Hence:
$$e = 1/(1 + I_{\text{corr}}/I) \quad (4)$$

The functional dependence of e on experimental parameters (external current, electrolyte concentration, and temperature) has not yet been determined with acceptable accuracy (i.e., $\pm 2\%$). This month, a technique was developed for the rapid and accurate determination of current efficiency through the measurement of the steady-state, nonequilibrium hydrogen gas evolution rate from closed lithium-water cells. In the apparatus shown schematically in Figure 1, the electrodes are contained in a closed cell connected to a two-cylinder burette filled with water. By the controlled draining of liquid from the burettes, the water head may be kept to a minimum and experimental conditions maintained at a constant pressure to within 1 mm water. (At constant pressure, Henry's Law corrections to the measured gas volume are not necessary.) Temperature is held constant with the use of a large water-bath heat sink. Current efficiency is given by the equation,

$$e = \frac{IR_g T}{nF(P - P_{H_2O}) (\Delta V / \Delta t)} \quad (5)$$

The stagnation point flow system employed allows (1) a uniform primary current distribution; (2) an anode surface which is at all points equally accessible to the solution from the standpoint of diffusion; and (3) a liquid-phase mass-transport rate comparable to that obtained with the rectangular duct flow channel.¹ The system was tested by the evolution of hydrogen and oxygen gas from stainless steel electrodes, where the current efficiency for gas evolution reactions was assumed to be 100%. Equation (5) obtained to within a few percent.

B. Electrochemical Properties of Lithium-based Alloys

The ionic conductivity of metal oxide films can be altered drastically in many cases by the controlled introduction of foreign cations of dissimilar valence.² A study of the electrochemical behavior of lithium metal alloyed with small quantities (less than 5 atomic percent) of metals forming di- or trivalent cations has been undertaken as a means of inferring the conduction mechanism within the film.

This month, a technique for preparation of alloys of lithium through arc melting has been developed. The results of the polarization studies on the first set of samples shows no marked effect of Ca or Al dopants on film conductivity. Chemical and metallographic analysis of the alloys and controls is planned.

II. ALTERNATIVE CELLS OF THE LITHIUM-WATER TYPE

A lithium-bromine analogue of the lithium-water battery has been discovered this month:

The lithium electrode showed an open circuit potential of -2.85 V (vs. SCE), a linear polarization behavior (slope, $1.8 \times 10^{-4} \text{ ohm m}^2$) and a limiting current density of about 6000 A/m^2 in stirred electrolyte. No gas evolution

was observed at the anode or cathode. Testing of this system over a matrix of compositions is planned, and carbon and graphite cathodes will be tested in single cells.

III. RECYCLING OF LITHIUM BATTERY REACTION PRODUCTS

A technique of lithium production is being evaluated which may offer efficiency and production cost advantages over the present day high temperature fused salt electrolysis techniques. The proposed technique is illustrated schematically in Figure 2. An aqueous solution of a lithium salt is electrolyzed to form a lithium-mercury amalgam and an oxidizer (e.g., oxygen, bromine, iodine, etc.) in the left-hand chamber. Temperature is held above 100°C and concentration of the electrolyte is allowed to occur by evaporation. The amalgam is continuously circulated between the left and the right-hand chambers. In the right-hand chamber, lithium is concentrated by electrolysis, using a low-temperature (about 200°C) fused-salt mixture and an inert cathode. Liquid lithium is tapped from the surface of the molten salt electrolyte and its heat of fusion is recovered and transferred to the left-hand chamber. The evaluation of this proposed process involves a survey of the polarization data of the four electrode systems and an estimation of IR losses in the two electrolytes for a number of promising electrode/electrolyte combinations.

We gratefully acknowledge the contribution of B. Earl Kelly, who designed and constructed the experimental apparatus used in this research.

TABLE 1. RESULTS OF INITIAL SURVEY OF ELECTROCHEMICAL BEHAVIOR OF LITHIUM-BASE ALLOYS

No.	Alloy Composition	Crucible	Corrosion Potential (V vs. HG/HgO, 1M-LiOH)	Limiting Current Density (10^{-4} A/m ²)	Resistance (10^{-4} ohm-m ²)	Comments
1.	Li*	304 Stainless steel	-2.38	0.180	1.1	Initial corrosion potential -2.86V; increased to -2.38 after anodic dissolution.
2.	Li	ARMCO Iron	-2.81	0.200	0.60	Corrosion potential is 0.06V noble of that of lithium not melted in ARMCO Iron crucibles.
3.	Li, 9.1 wt% Al (2.5 at% Al)	ARMCO Iron	-2.20	0.190	0.80	
4.	Li, 9.2 wt% Ca (1.7 at% Ca)	ARMCO Iron	-2.85	0.160	0.80	

-4-

* All Lithium used in alloy preparation was 99.9% Li, supplied by D. F. Goldsmith Chemical and Metal Corporation, Evanston, Ill.

Figure 1. Apparatus for Determination of Current Efficiency

A, cathode lead; B, anode lead; C, three-way stopcock; D, glass tubing (1 mm); E, two-cylinder burette; F, thermometer; G, lithium anode holder; H, lithium anode; I, stainless steel cathode; J, water bath heat sink; K, lithium hydroxide solution; L, flow channel tube; M, magnetic stirring bar; N, Lucite vessel; O, burette stopcock.

Figure 2. Proposed Technique for the Production of Lithium from Aqueous Solutions of Lithium Salts

A, reservoir for lithium salt solution; B, valve; C, pressure controlled valve for exhaust of evolved gases; D, exhaust; E, aqueous electrolyte, lithium compound slurry; F, inert grid anode; G, mercury amalgam primary cathode; H, thermal and electrical insulating barrier; I, fused-salt mixture; J, heating elements; K, molten lithium; L, tap for lithium removal; M, N, variable voltage sources (D.C.)

Symbols

e	current efficiency	n	equivalents of current per mole of hydrogen gas
F	Faraday's constant	P	pressure
I	external current	P_{H_2O}	partial pressure of water vapor
		R_g	gas law constant
		R	rate of lithium dissolution
		T	temperature
		V	gas volume
		t	time

REFERENCES

1. A. J. Arvia and S. L. Marchiano, "Transport Phenomena in Electrochemical Kinetics," (Modern Aspects of Electrochemistry, Plenum Press, New York, 1971; ed. by Bockris and Conway; Chapter 3).
2. Per Kofstad, (Nonstoichiometry, Diffusion, and Electrical Conductivity in Binary Metal Oxides, Wiley-Interscience, 1972).

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research & Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or 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.

NOTICE

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research & Development Administration to the exclusion of others that may be suitable.

Technical Information Department

LAWRENCE LIVERMORE LABORATORY

University of California | Livermore, California | 94550