UCID- 17426-76-8

Lawrence Livermore Laboratory

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

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

September 17, 1976

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

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

I. LITHIUM PRODUCTION PROCESSES

Technical literature from 1962 to the present has been searched for methods of producing lithium metal from its compounds and for operating conditions of existing industrial plants. Results of this work have been reported recently.[1] Electrolysis of a molten mixture of LiCl and KCl is the only process by which metallic lithium is now produced on an industrial scale. Current efficiency is near 80% for the lithium reduction reaction, while total voltage efficiency of lithium reduction passes through a maximum of 50% at a cathode current density of 0.4 A/cm^2. For processes reported in the literature, the overall energy efficiency ranges from 9-41%. Main causes of the inefficiency are: (1) ohmic potential drop in the interelectrode gap, and (2) heating energy losses due to poor thermal insulation in the electrolysis cells. It should be mentioned that the most current production techniques, operating parameters, and efficiency data are proprietary and hence not available for our study.

We are now evaluating a promising alternative to present industrial production methods, which has been described already.[2] In a continuous process, lithium amalgam would first be formed by reduction of aqueous LiOH or Li_2CO_3 (battery endproduct). (See Figure 1). Lithium would then be electrochemically separated from the amalgam to form the pure liquid metal. The latter process requires a relatively low-melting (c. 180°C), chemically stable (in the presence of lithium), high conductivity, fused-salt electrolyte. An investigation is now underway for a suitable salt mixture. This far, promising candidates are the binary and ternary mixtures of LiI, LiOH, and $LiNH_2$. In particular, the eutectic mixture, LiOH(45.5%)-LiI(54.5 mol-%), melts at 180°C.

In addition to the analysis of the fused salt cell, the literature is being searched for polarization and efficiency data appropriate to the Li(Hg)/LiOH(aq) electrode at high temperatures and current densities.

The process described above is similar in concept to the charge cycle used in the Atomics International Na/air cell, where liquid sodium was electrochemically formed from concentrated sodium hydroxide (at 135°C) with an overall energy efficiency in excess of 80%.[3,4]

Results of the evaluation of the Li-amalgam production process will be reported shortly.

II. ELECTRODE KINETICS OF LITHIUM METAL IN AQUEOUS SOLUTION

Laboratory determination of the coulombic efficiency for the reaction,

$$Li + OH^- = LIOH(aq) + e^-,$$

was continued this month. In all cases studied, the coulombic efficiency was found to approach 1.0 as the anodic diffusion limited current density was approached. (Typical results shown in Figure 2). The anomalous coulombic efficiencies reported previously[2] (exceeding 1.0) were found to be the consequence of failure to reach a steady state, where the net rate of accumulation of hydrogen bubbles in the electrolyte reached zero.

Results of the kinetic study will be presented as a paper in the Fall Meeting of the Electrochemical Society.[5]

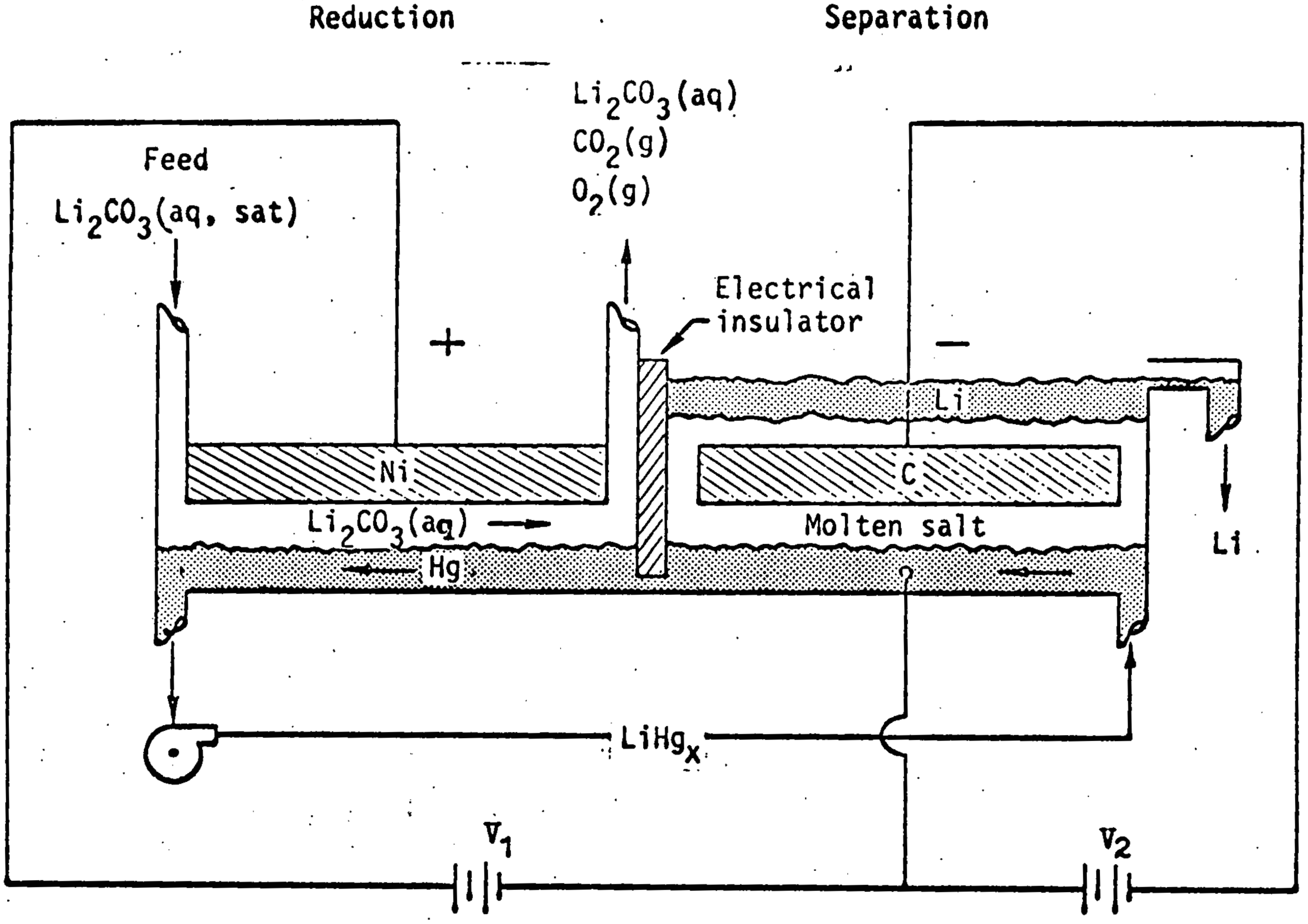

Figure 1. Mercury Amalgam Process for the Production of Lithium (Schematic). The molten-salt cell would operate at a temperature just above the melting point of lithium (186°C). The aqueous electrolyte cell would operate at a high temperature maintained by heat losses from the molten-salt cell.

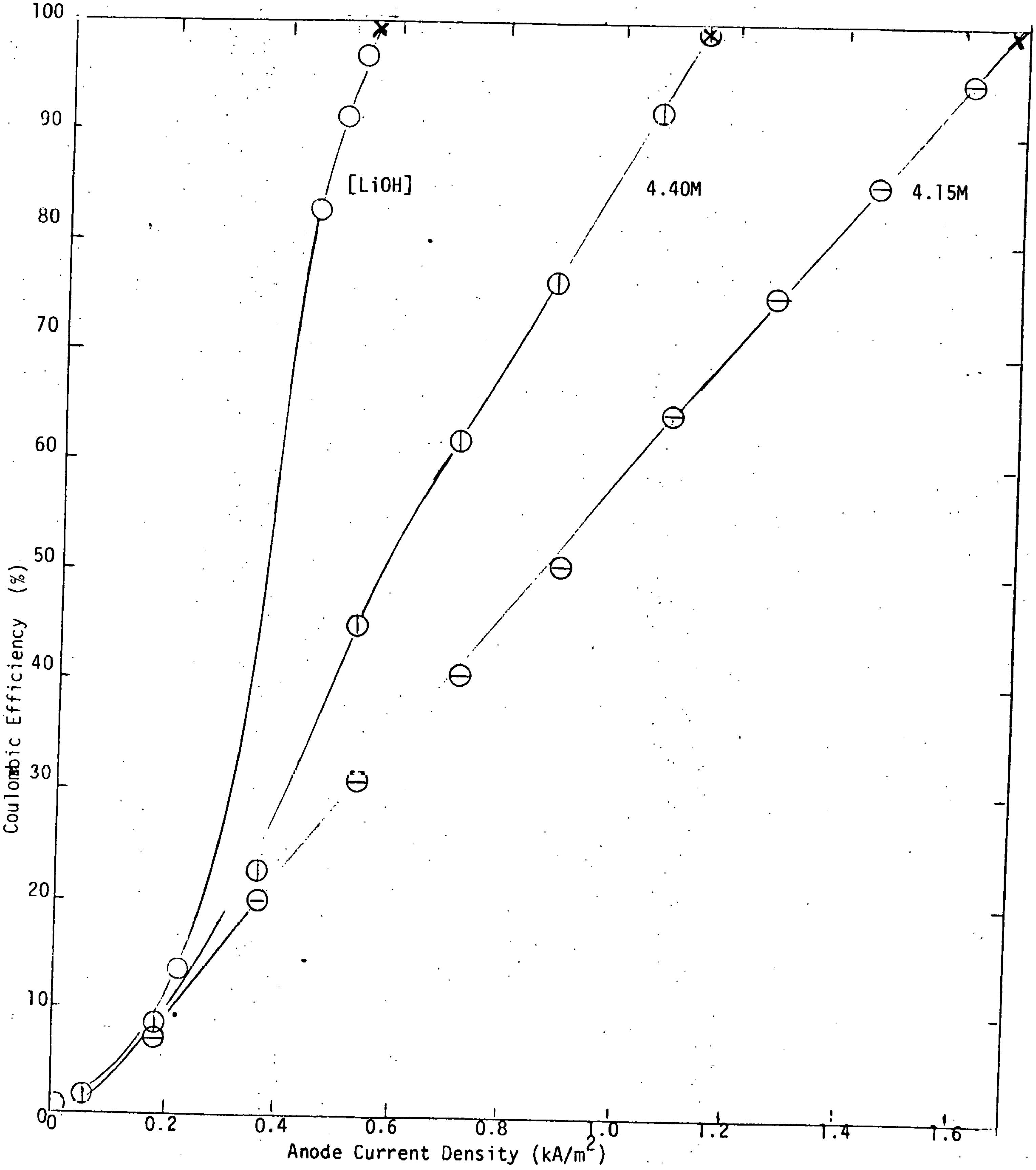

Figure 2. Current Efficiency Increases with Anodic Current Density. Cell, Li/LiOH(aq)/Pt galvanostatic dissolution of lithium; 23°C; forced convection. (x) Denotes anodic limiting current density.

References

1. Robert V. Homsy, "Industrial Production of Lithium Metal: Review of the Literature," Lawrence Livermore Laboratory, Report, UCRL-52124, September 2, 1976.
2. John F. Cooper, Pamela K. Hosmer, Robert V. Homsy, "Lithium-water-air Battery Project, Progress During the Month of May, 1976"; Memorandum, June 3, 1976.
3. L. A. Heredy, H. L. Recht, and D. E. McKenzie, "The Atomics International Sodium-air Cell, "Symp. on Power Systems for Electric Vehicles, Columbia University, N. Y., 1967.
4. L. A. Heredy, et al., "Sodium-air Secondary Battery," Proc. Advanced in Battery Technology, The Electrochemical Society; Dec. 1, 1967.
5. John F. Cooper, Pamela K. Hosmer, Robert V. Homsy, "The Anodic Behavior of Lithium in Aqueous Lithium Hydroxide Solutions," Lawrence Livermore Laboratory, UCRL 78156; to be presented at the Fall Meeting of the Electrochemical Society, Las Vegas; October 20, 1976.

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

Technical Information Department
LAWRENCE LIVERMORE LABORATORY
University of California | Livermore, California | 94550