

Lawrence Livermore Laboratory

Lithium-Water-Air Battery Project:
Progress During the Month of March 1977

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MASTER



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Abstract

The electrode behavior of the system, Ca/aq.-NaOH, NaCl, has been investigated at ambient temperatures. Limiting currents have been noted for intermediate concentrations of NaOH and NaCl, while rapid passivation at high ratios of NaOH to NaCl occurred. Low ratios of NaOH/NaCl yielded uncontrollable hydrogen evolution and rapid calcium dissolution.

A model of the aqueous cell of the proposed system for the production of lithium has been completed. The apparatus allows simultaneous determination of current efficiency and electrode polarization for the Li(Hg)/aq.-LiOH electrode upon cathodic polarization.

Cooling curves indicate the existence of a LiI-KI-LiCl eutectic with a melting point of approximately 230⁰C; possible errors are being considered arising from artifacts of the system and possible impurities in the salts.

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I. Publication of Kinetic Study Results

A paper¹ summarizing results of the kinetic study of lithium dissolution was accepted pending minor revisions by the Journal of the Electrochemical Society.

II. The Anodic Behavior of Calcium in Aqueous Electrolytes

The study of the polarization characteristics of the calcium electrode in aqueous electrolytes was continued this month. A rotating disk electrode of surface area 0.25 cm^2 was used in this work. As noted in last month's report, no limiting currents were obtained (at currents up to 4 A/cm^2) for the CaCl_2 electrolyte (4.76, 5.15, and 5.24 M). Indications of a possibly diffusion-limited current were obtained in LiOH/LiCl solutions, where the OH^-/Cl^- ratio is substantially higher than in $\text{CaCl}_2\text{-Ca(OH)}_2$ solutions. A detailed mapping of electrode behavior was made for the system, NaOH/NaCl . The investigated compositions are shown in Figure 1-a. High OH^-/Cl^- ratios yielded passivated electrode behavior upon closing the galvanostatic circuit. Low OH^-/Cl^- ratios yielded no limiting current. With intermediate ratios and with low (1-3M) concentrations of NaOH , there was evidence of a possible diffusion-limited current density. The polarization curves in pure sodium hydroxide solutions resemble those obtained with the Li/LiOH electrode. With the calcium electrode, however, limiting current densities were difficult to reproduce--a possible artifact of the experimental system which allowed hydrogen gas to accumulate on the surface of the anode.

In terms of electrode polarization behavior, the calcium electrode more closely resembles lithium than magnesium. At a current density of 2 mA/cm^2 , commercially pure magnesium (in 2M Mg(Br)_2 , $\text{pH}=10.5$) shows an electrode potential of 1.33 V (vs. NHE) ²; the thermodynamic value is 2.46 V .³ This high polarization loss (1.13 V) limits the energy efficiency of the magnesium electrode. For calcium, in the CaCl_2 solutions, the electrode potential is approximately -2.5 V (vs. NHE) --only 0.25 V above the standard electrode potential of -2.76 V . In the NaOH electrolyte, the open circuit potential is about -2.7 V , again only $0.2\text{-}0.3 \text{ V}$ noble of the standard electrode potential of -3.02 V .

Further experiments are planned or underway to determine the mass-transfer dependence of the limiting current and to determine the coulombic efficiency of calcium dissolution under well-defined experimental conditions.

III. Recycling of Lithium--Experimental Study of the Mercury-Amalgam/Aqueous Electrolyte Cell

An experimental cell has been constructed to measure simultaneously the current efficiency and electrode polarization of the Li(Hg)/saturated-LiOH electrode upon cathodic polarization. The cell, shown schematically in Figure 2, utilizes a Ni counterelectrode for the evolution of oxygen. Current efficiency is measured from the rate of gas evolution and from the rate of displacement of electrolyte from the cell. A port for amalgam extraction is also provided to allow separate determination of amalgam concentration.

The cell is, in effect, a breadboard model of the aqueous cell proposed for the production of a Li(Hg) amalgam as part of a process for lithium production at high current efficiencies. The process has been described elsewhere.⁴

IV. Recycling of Lithium--Experimental Study of the Mercury-Amalgam/Fused Salt Cell

Experimentation continued on the low-melting fused salt intended for use in the fused salt cell of the proposed lithium production process.⁴ Several cooling curves were run on the LiI-LiCl-KI mixture to make a preliminary estimate of the eutectic temperature in this system. The cooling curves did not show a completely flat eutectic halt, but a range of about 14-20°C. The lowest eutectic measured was at 232-250°C for a sample of molar composition: 51% LiI- 8%LiCl-42%KI. For the binary LiI-KI eutectic, we obtained 270-290°C; and for pure LiI we obtained 451-467°C.

Whether this temperature range effect is due to impurities in the LiI starting material (LiCl and KI are specified "reagent grade" and appear to be pure) or due to an artifact in our experimental system is

not yet clear. Nonetheless, the work indicates a $\sim 40^{\circ}\text{C}$ lowering of the eutectic melting temperature in going from the LiI-KI binary reported in the literature⁵ to the LiI-LiCl-LiI ternary system. It is anticipated that a more careful investigation of the eutectic composition and the use of other additives such as LiBr should lower the melting point of the fused electrolyte even further. (For the process, a melting point in the range of $200\text{-}225^{\circ}\text{C}$ is optimal).

V. Summary

The calcium electrode yields limiting currents below 4 A/cm^2 in the cases of intermediate concentrations of NaOH and NaCl and at intermediate (1-3M) concentrations of NaOH alone. High ratios of NaOH to NaCl produced rapid passivation at current densities below 10 mA/cm^2 , while low ratios produced uncontrolled dissolution and hydrogen evolution.

A cell has been constructed for simultaneous current efficiency and polarization measurements of the Li(Hg) electrode upon cathodic polarization. A lowering of the melting point of KI-LiI eutectic by the addition of LiCl has been confirmed. Results obtained in these studies will be used to construct a breadboard model of the lithium recycling process at this laboratory.

1. John F. Cooper, Pamela K. Hosmer, and Robert V. Homsy, "The Anodic Behavior of Lithium in Aqueous Lithium Hydroxide Solutions," Preprint UCRL-78156 Rev. 1, January 10, 1977.
2. R. Glicksman, "Anodic Dissolution of Magnesium Alloys in Aqueous Salt Solutions," J. Electrochem. Soc., 106, 83 (1959).
3. Handbook of Chemistry and Physics (Chemical Rubber Company Press, ed. Weast, 1976-77).
4. John F. Cooper, "Summary of the Lithium-Air Battery Research Program," Lawrence Livermore Laboratory, UCID-17425; March 17, 1977.
5. D. B. Leiser and O. J. Whittemore, "The System LiI-KI," J. Am. Cer. Soc., 50, 60 (1967).

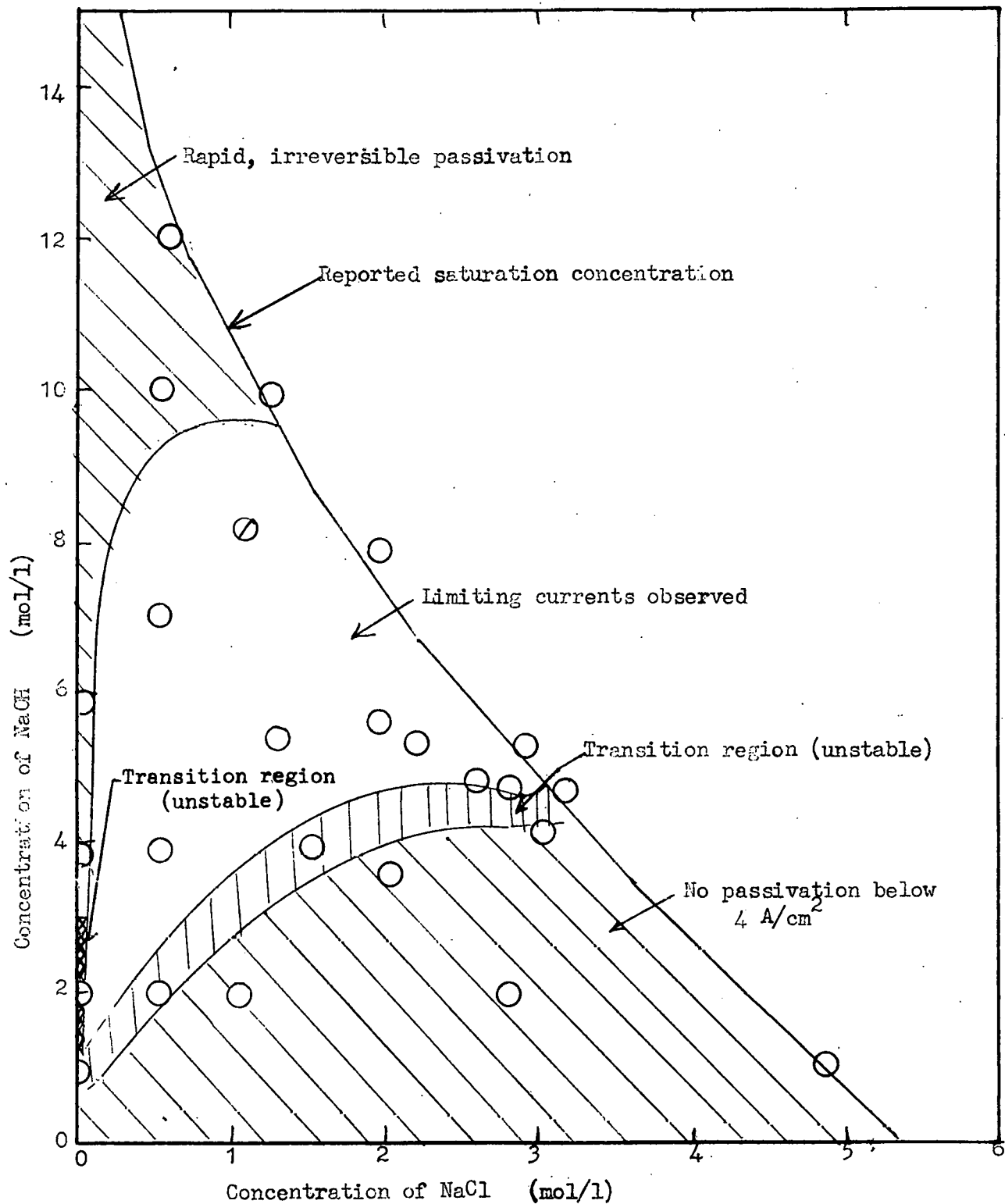


Figure 1-a. Compositions of electrolytes investigated in conjunction with the calcium electrode. Ca/NaOH, NaCl, H₂O; ambient temperature. Boundaries of regions are approximate

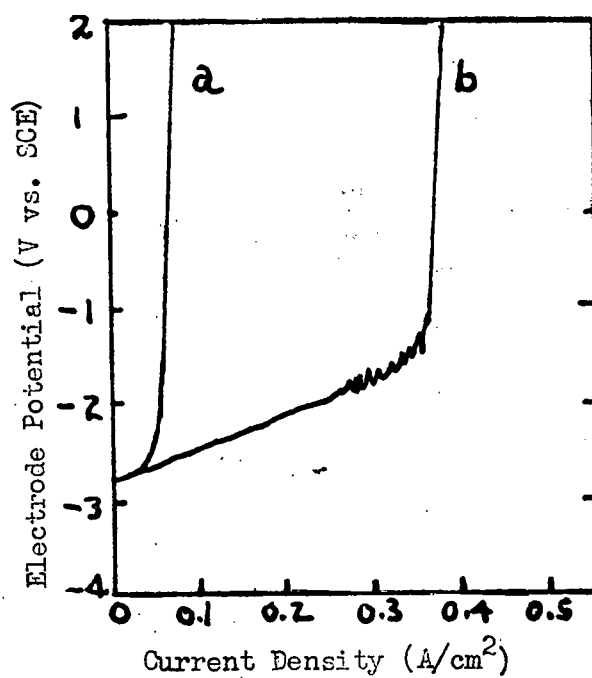


Figure 1-b. Behavior of the calcium electrode in 1 M NaOH
a. anodic scan (20 mA/cm²-s) following cathodic polarization;
b. initial scan (20 mA/cm²-s).

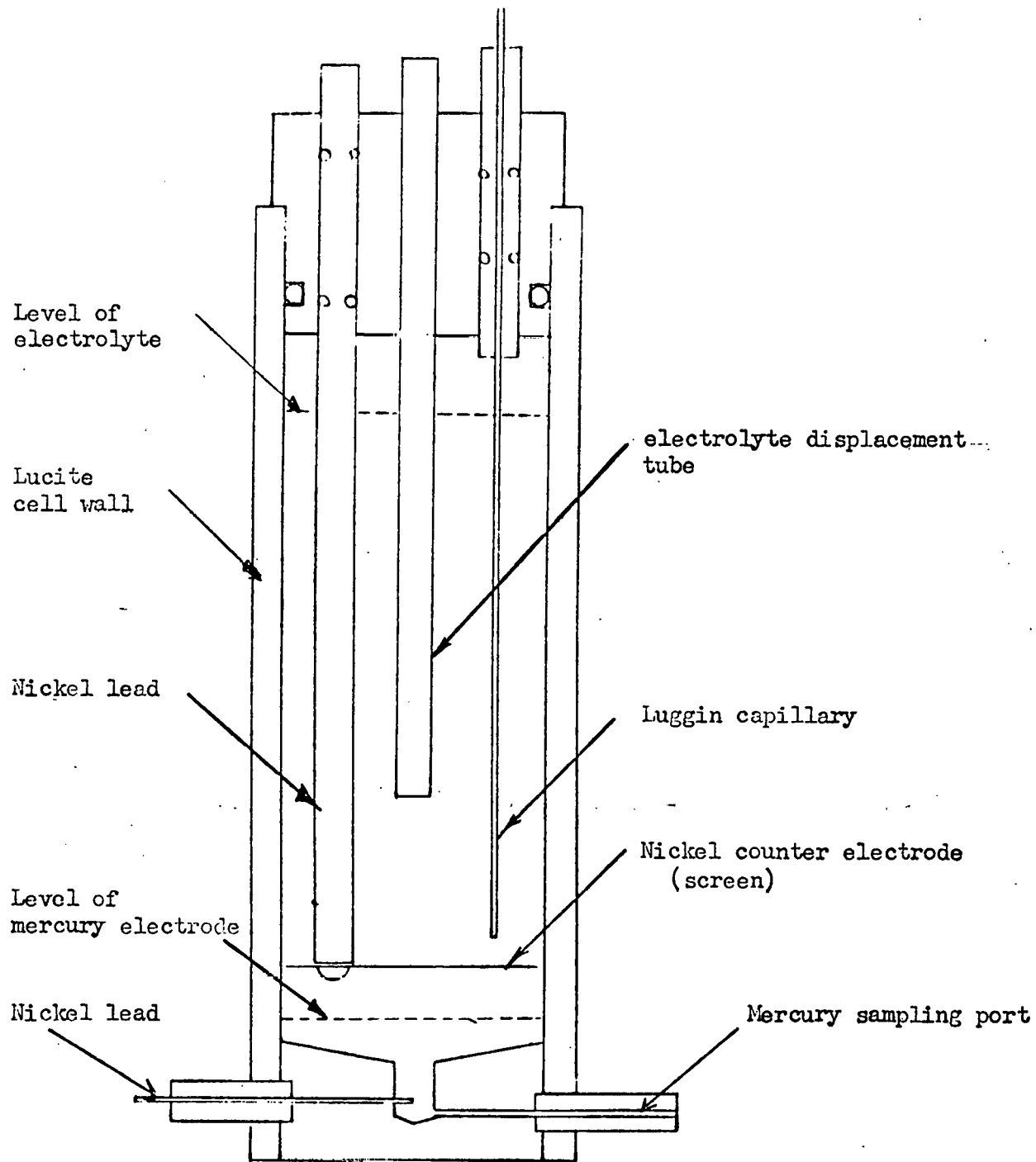


Figure 2. $\text{Li(Hg)/LiOH(aq)/O}_2(\text{Ni})$ Experimental Cell for Investigation of Lithium Recycling Process. Cell allows simultaneous measurements of mercury electrode potential and coulombic efficiency of lithium deposition reaction. A port is furnished for extraction of mercury samples for analysis. Luggin capillary is movable and may be positioned at any point between the Ni and Hg electrodes.

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