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

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Abstract

The energy efficiency of the aqueous electrolysis step in the proposed lithium production cell has been experimentally determined. Coulombic efficiencies approach 100% above 0.7 kA/m^2, for amalgam concentrations of 1.0-1.2 at-% Li, and for $T = 21^\circ C$. Under these operating conditions, cell voltage is 3.1 V, and the overall energy efficiency is 82 ± 1%.

The anodic dissolution of calcium in mixed NaOH-NaCl electrolytes has been studied in the concentration region near (1.6 M NaOH, 0.05 M NaCl). It was found that passivation could be effectively prevented by additions of water-glass, $Na_2O \cdot x(SiO_2)$, x = 3-5. An oscillatory phenomenon has been discovered where the potential of the calcium fluctuates with an amplitude of 0.4 V and a period of about 25 s.

Under investigation are several new concepts for the high-energy-efficiency production of lithium and calcium metals.

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PROGRESS DURING THE MONTH OF APRIL

I. Intent to Publish Results of Calcium Electrode Kinetics Study

A short abstract has been submitted to the Electrochemical Society; the paper will be presented to the Fall Meeting of the Society in Atlanta. The paper, coauthored by J. F. Cooper and P. K. Hosmer, is entitled, "The Behavior of the Calcium Electrode in Aqueous Electrolytes,"[1] A patent disclosure relevant to the work in this area was filed by LLL prior to the submission of the abstract.

II. The Anodic Dissolution of Calcium in Aqueous Electrolytes

A study of the dissolution of the calcium electrode in mixed NaOH-NaCl solutions was continued this month with emphasis on the transition region between passive and active behavior which occurs near the composition, (NaOH) = 1.5 M, (NaCl) = 0.1 M. It is anticipated that the most favorable balance between low electrode polarization and high coulombic efficiency will be found in this region of compositions. (See Figure 1.a, reference 2).

The long term stability of the open circuit potentials were also studied for two electrolytes, 4.2 M NaOH and 4.3 M NaCl. On newly prepared electrodes, the potential increased from an initial -3.1 V (vs SCE) to a stable -2.2 V, for the NaOH electrolyte. For the NaCl electrolyte, the initial and final corrosion potentials were respectively, -2.7 and -2.6 V. A similar time dependence was inferred from the current scans obtained with the high NaOH/NaCl ratio electrolytes.

The addition of water-glass ($Na_2O \cdot x\, SiO_2$, $x = 3\text{-}5$) to the mixed electrolyte, (NaOH) = 1.6 M, (NaCl) = 0.05 M, resulted in prolonged active dissolution. Figure 1.b shows the steady-state dissolution potentials for calcium in this electrolyte, i.e., for dissolution times approximately 1 - 2 minutes. At low current densities oscillatory phenomena was discovered. Potential or current oscillations are a common occurence during the anodic polarization of a variety of metal/electrolyte combinations. In many cases, periodic transitions between active and passive states are brought about by changes in the local anolyte composition brought about by the ongoing reactions and diffusion of reactants to and from the bulk.[3,4]

III. The Recycling of Lithium: Experimental Study of the Mercury Amalgam Fused Salt Cell

The lithium production concept being investigated by LLL is schematically shown in Figure 4. This month, voltage and coulombic efficiencies were determined for the aqueous step of the process, in which a lithium-amalgam is formed from the aqueous electrolyte. The experimental set-up was described in the previous monthly report.[2]

The experimental cell was operated at current densities from 0.07 to 0.7 kA/m^2. Current efficiency was determined from the total rate of gas evolution from the cell (anode plus cathode). In preliminary experiments, the cell was tested by evolving hydrogen at nickel cathode and oxygen at the nickel anode of the cell. The theoretical gas evolution rate, determined from the equation,

$$dV/dt = \frac{R\ T\ I}{(P_{atm} - P_{H_2O})n\ F} \tag{1}$$

was experimentally confirmed within ± 1.0%. In equation (1), V is volume of gas; R is the gas constant; T, absolute temperature; I, current; P_{atm} and P_{H_2O} are ambient and water vapor pressures; F is the Faraday constant; and n is the ratio of equivalents of charge to moles of gas produced (equal to 4/3 for the splitting of water).

Results are shown in Figures 2 and 3. In Figure 2.a, the coulombic efficiency is plotted against current density for amalgam concentrations of approximately 1.1 ± 0.1 at. % lithium. Coulombic efficiencies are defined by the equation,

$$e = \frac{\text{equivalents of Li(Hg) produced}}{\text{equivalents of charge passed}} = 5/4 - \frac{(P_{atm}-P_{H_2O})\ F\ \ (dV/dt)}{R\ T\ I} \tag{2}$$

The derivation of equation (2) takes into account the possible liberation of hydrogen at the mercury electrode but neglects the possibility of oxygen oxidation of the amalgam, which is expected to be relatively slow and diffusion-controlled. As seen in Figures 2.a and 2.b, coulombic efficiencies are above 95% in all but the most severe experimental conditions (i.e., high amalgam concentrations, low current densities). In general, the coulombic efficiency approaches 100% at current densities above 0.7 kA/m^2 for amalgam concentrations of 1 at. %.

In Figure 3, cell voltage is plotted against current density. In the experimental set-up, the mercury and nickel electrodes were spaced 11 mm apart to allow room for a magnetic stirring bar. The solid lines show the experimental cell voltage with the electrolyte IR drop corrected to a spacing of 3 mm. The line labeled "treated Ni anode" shows the approximate cell voltage obtainable with a specially annealed nickel anode according to published polarization data.[5] The total energy efficiency of the lithium amalgam production process at 21 °C is approximately 82%. Higher efficiencies are expected at more elevated temperatures.

IV. Approaches to the Production of Lithium and Calcium at High Energy Efficiencies.

For a transportation system based on calcium or lithium fuels to be economically feasible, the energy efficiency of production of the metals must exceed about 70%. This level may be easily reached with the proposed lithium-mercury cell, although the scarcity and toxicity of mercury may present difficulties which would increase the actual cost of production significantly beyond that indicated by the cost of the process energy. Upon the suggestion of our collegues at Lockheed, we are jointly considering alternative processes. In general, the processes considered involve two-step reductions of the metal. The first step brings the starting material (for example $Ca(OH)_2$ or LiOH) to the level of reduction of a metallic solution (in mercury, in NH_3, or in low melting tin or lead-based solders). The second stage produces the pure metal (calcium or lithium). The first stage may be electrochemical in nature, or (see below) a thermal-chemical reduction.

In the case of calcium, a two-stage electrolysis of CaO dissolved in $CaCl_2$ is now proposed by LLL:

Inert anode / fused CaO-$CaCl_2$ / molten tin or lead based
solder / fused $CaCl_2$ / Ca

The system may operate isothermally or at different temperatures; the tin may be circulated between the two fused-salt cells, or held in a stationary, thin porous material which separates the electrolytes of the two cells. For the intermediate $CaSn_3$, the cell voltages are 2.16 V and 1.19 V.

A thermal-chemical reduction of CaO to a calcium alloy is possible, using carbon as a reducing agent. Suitably stable alloy are currently being sought. Thermal-chemical processes are more efficient in the use of primary energy resources, as they rely partly on direct thermal energy and avoid the exclusive use of the more costly electricity.

References:

1. John F. Cooper, Pamela K. Hosmer, "The Behavior of the Calcium Electrode in Aqueous Electrolytes," paper to be presented in the Fall Meeting of the Electrochemical Society, Atlanta; October 1977; UCRL-79547.
2. John F. Cooper, et al., "Progress During the Month of March," UCID-17426; April 11, 1977.
3. John F. Cooper, "Periodic Phenomena in the High Current Density Anodic Dissolution of Copper," (Ph.D. Thesis, University of California, Berkeley, April 1975).
4. J. Wojtowicz, "Oscillatory Behavior in Electrochemical Systems," (Modern Aspects of Electrochemistry, ed. J. Bockris; Plenum Press, New York; Vol. 8; 1972).
5. B. E. Conway, et al., "The Electrochemistry of the Nickel-Oxide Electrode. V.," Electrochimica Acta 14, 677 (1969).

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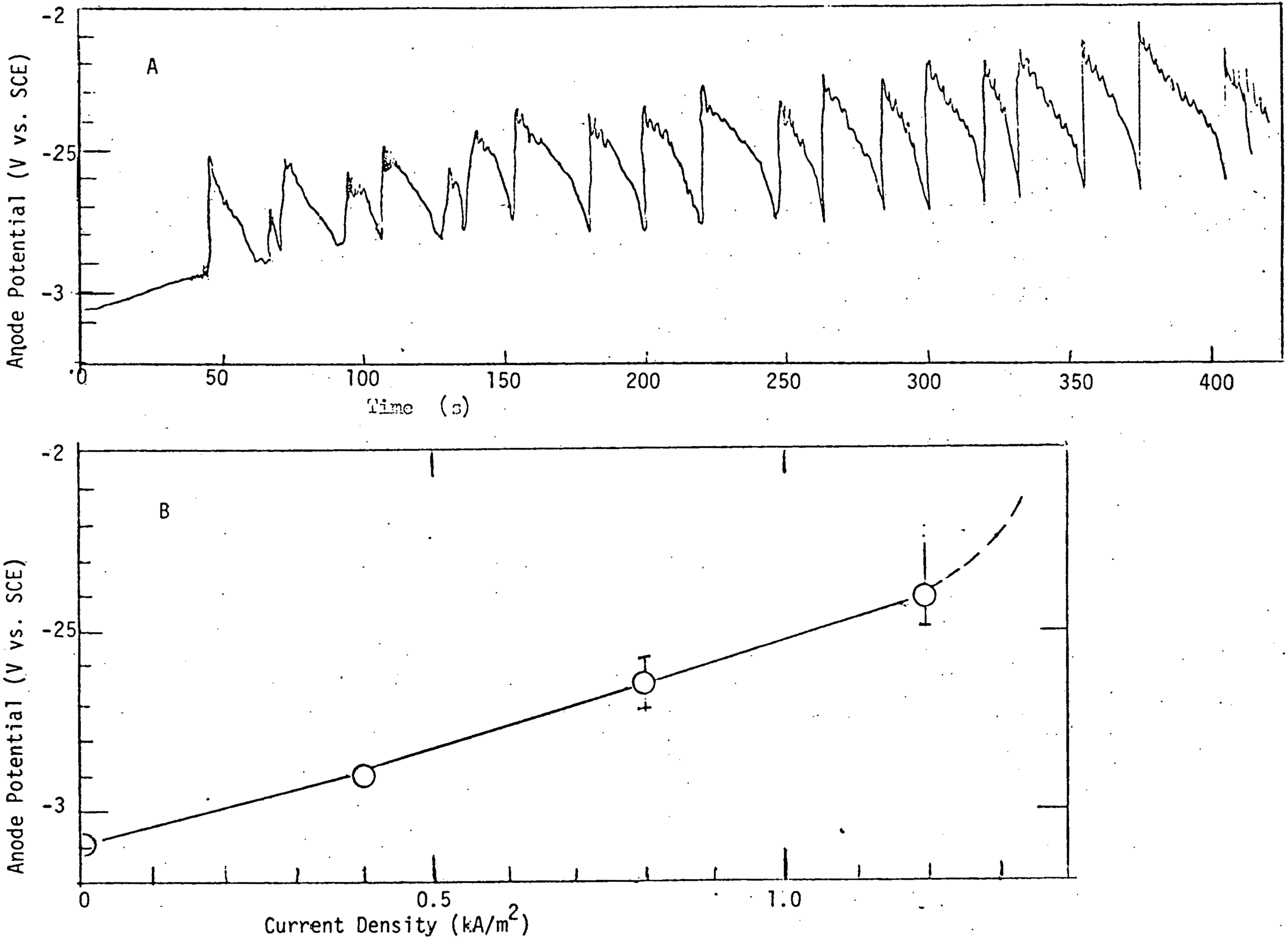
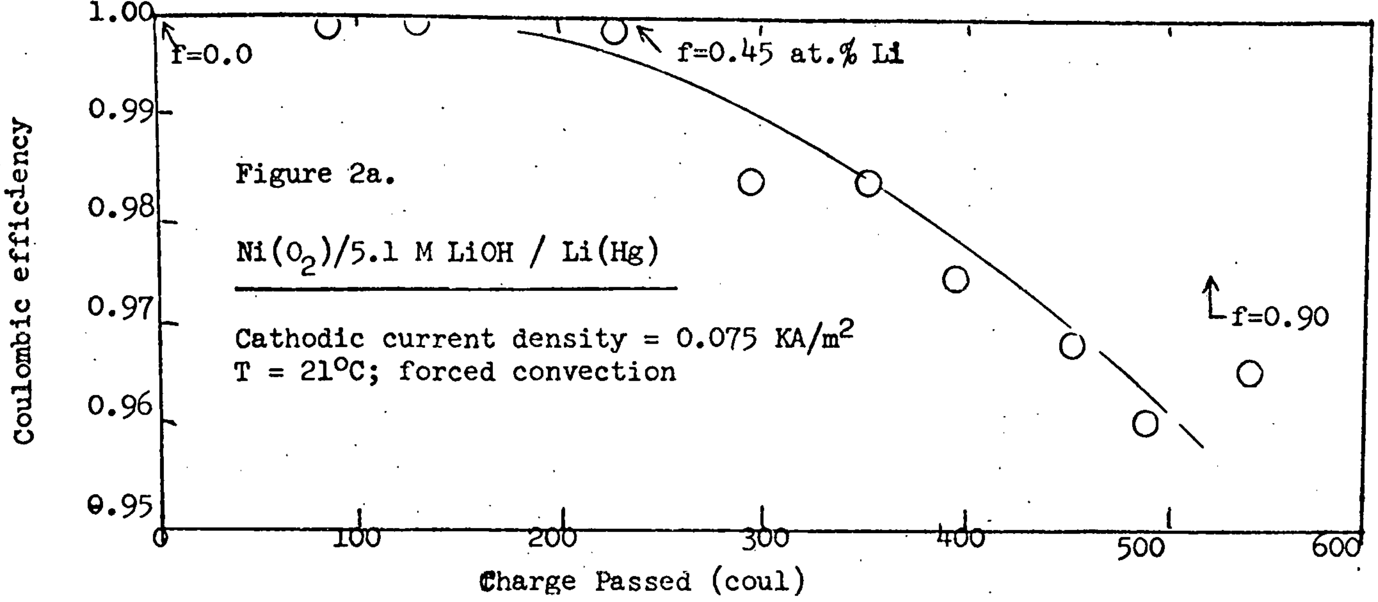


Figure 1.a. Potential oscillations during the anodic dissolution of calcium. Ca/1.6 M NaOH, 0.05 M NaCl; i = 0.07 kA/m^2. Figure 2.b. Quasi-steady state electrode potential for anodic dissolution of calcium. Ca/1.6 M NaOH, 0.05 M NaCl; water glass additive, stirred electrolyte.



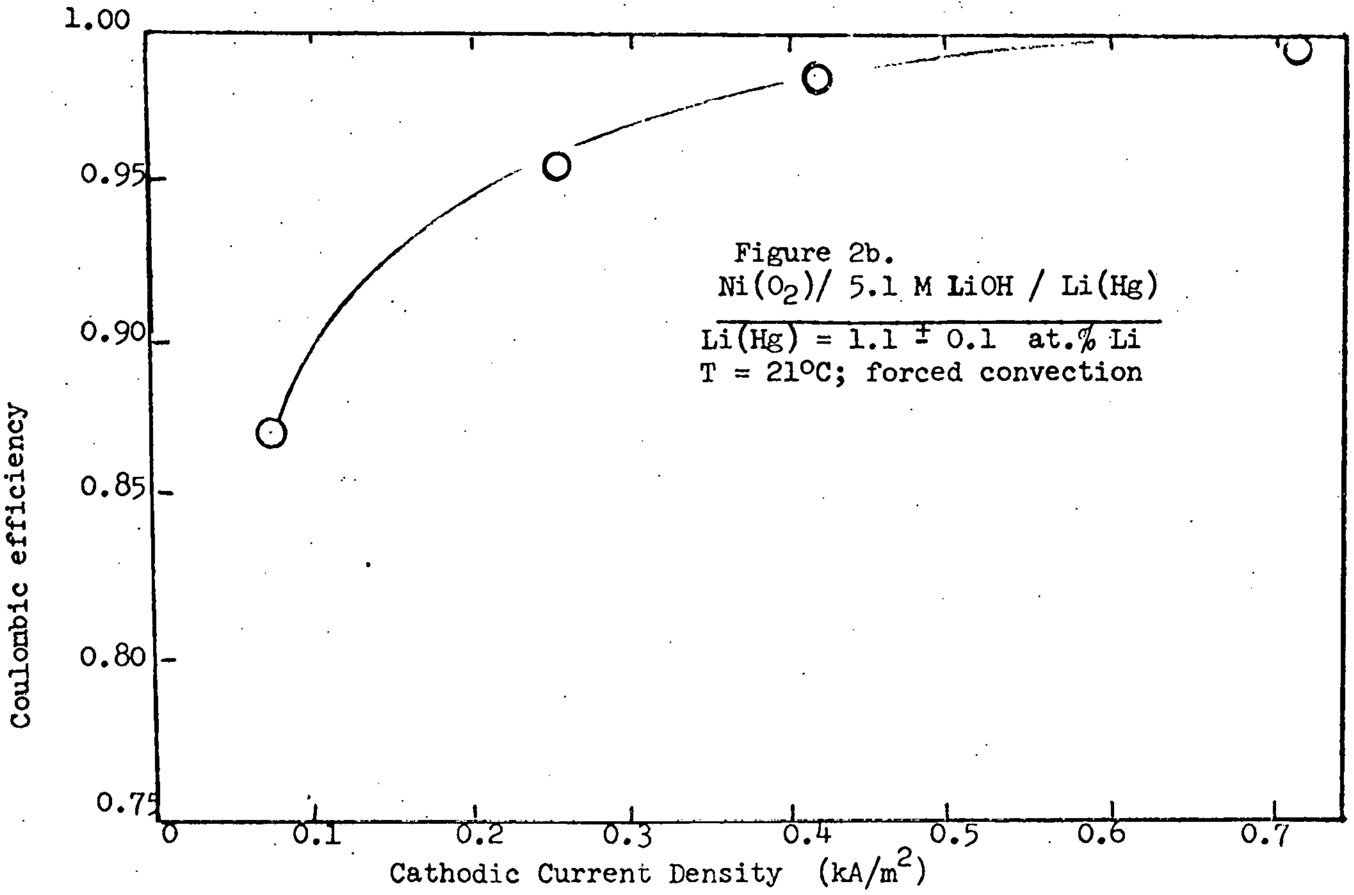


Figure 2a. Coulombic efficiency of lithium amalgam formation at amalgam concentrations frpm 0 to 0.90 at.% Li at low current densities (0.075 kA/m^2). T = 21°C.

Figure 2b. Coulombic efficiency of lithium amalgam formation as a function of current density at amalgam concentrations of 1.1 ± 0.1 at. % Li. T = 21°C.

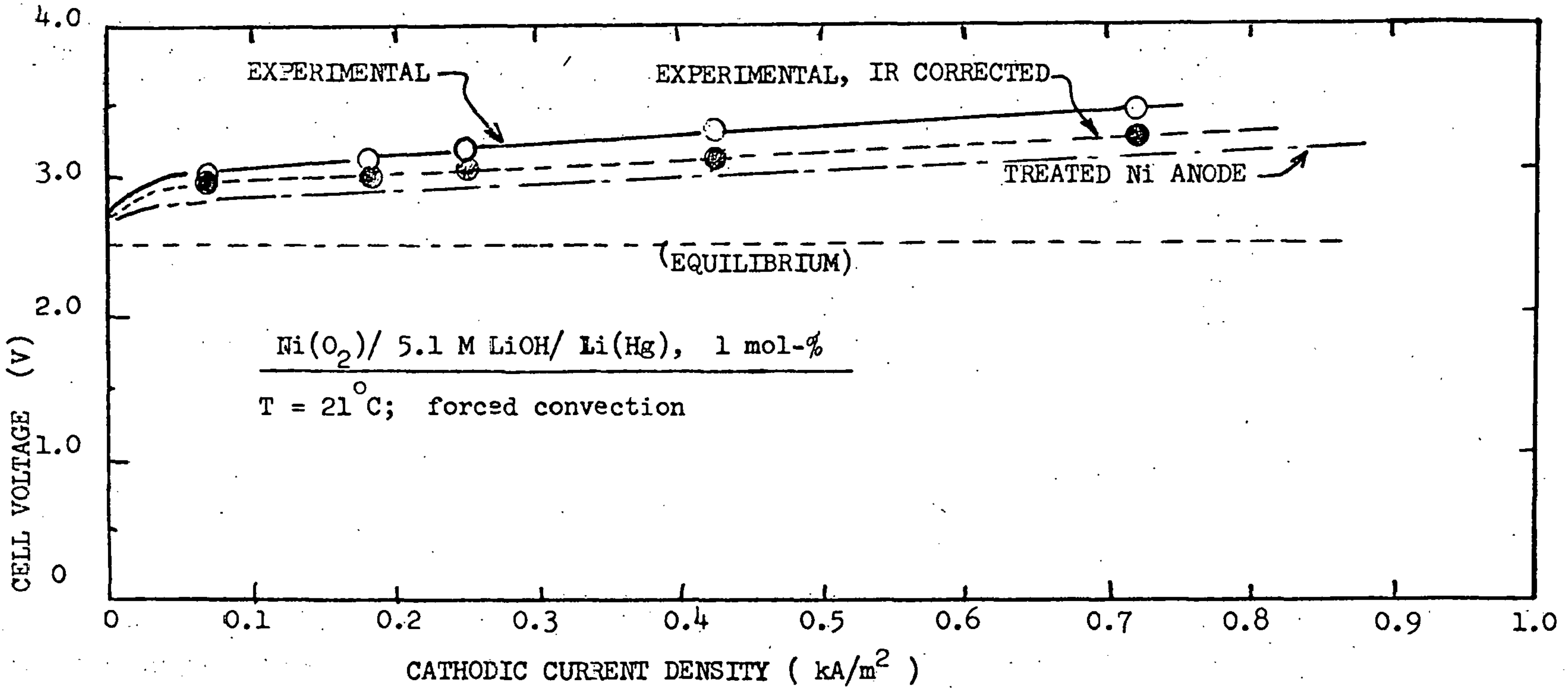


Figure 3. Experimental cell voltage of aqueous electrolyte, lithium amalgam cell. Experimental values refer to actual measurements. These values were corrected for the large IR drop due to the spacing of the electrode at 11 mm a part rather than at the preferred separation of 3 mm. The larger spacing was used in order to allow room for a magnetic stirring bar. The curve labeled "treated Ni anode" shows projection of the experimental data using polarization data for a purified, annealed Ni electrode reported in the literature.

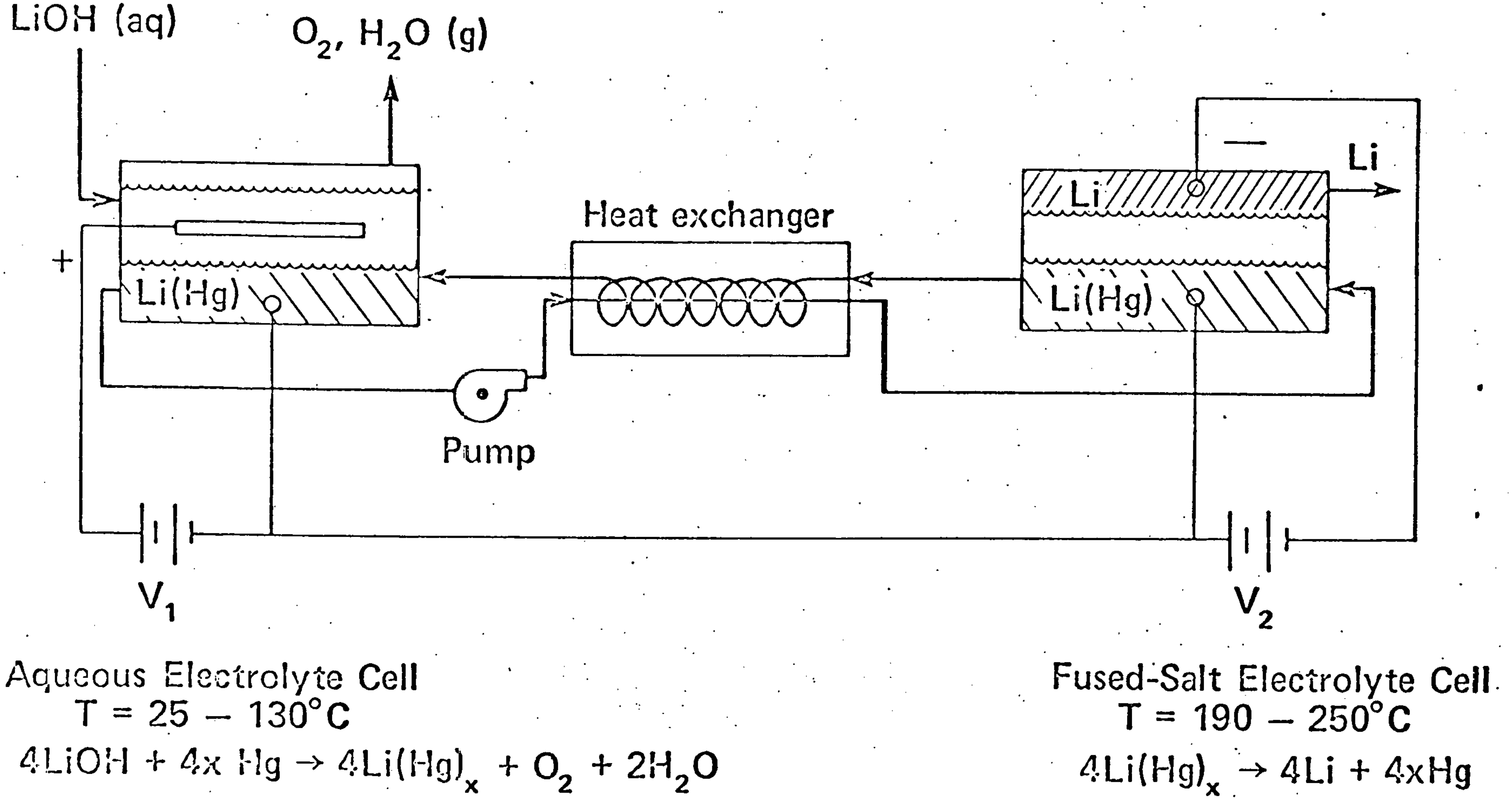


Figure 4. Lithium Production Cell--Schematic. In this concept, an aqueous solution of a lithium compound (in this case, LiOH) is reduced in an aqueous electrolyte cell to produce oxygen gas and a lithium-mercury amalgam (to a concentration of 1-10 at. %, depending on temperature). The amalgam is cycled between the left hand cell and a high temperature, fused-salt cell, where the lithium is electrochemically concentrated to form a pure melt. To conserve energy and avoid heat losses, the amalgam is circulated using a counter-current heat exchanger.

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