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Lawrence Livermore Laboratory

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

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

Laboratory investigations were initiated this month to identify the controlling factors in the dissolution kinetics of the lithium electrode in aqueous lithium hydroxide solutions. Electrode potential was measured upon application of a galvanostatic or triangular wave current. Solution concentration, temperature, and flow rate were held constant during each experiment and treated as experimental parameters.

Apparatus and Experimental Design. The experimental system, shown schematically in Figure 1, features a rectangular duct flow channel with cross section dimensions, 3.16 mm by 10.3 mm, and length, 650 mm. Electrodes of lithium and platinum, 10 mm by 10 mm square, were positioned opposite each other, flush with the horizontal walls of the channel, and near to the downstream end. Lithium electrodes[1] were prepared by extrusion of lithium metal into a 2-mm deep cavity in a removable section of the channel floor. A "Luggin capillary" for lithium electrode potential measurement was provided by drilling a 0.25-mm diameter hole into the electrode holder just 0.1 mm upstream of the electrode's leading edge (Figure 2). Constant flow rates of lithium hydroxide[2] solution were provided by a single-stroke piston pump, with a capacity of 2.3 l and velocity range of 3-60 ml/s. The flow channel and pump were constructed of Lucite, Epoxy resin, and Teflon. No metal or glass parts were allowed to contact the electrolyte. The electronic equipment consisted of a Princeton Applied Research galvanostat/potentiostat and programmer[3] and a Moseley recorder.[4]

The 130-hydraulic diameter long entrance provided by the flow channel assures fully developed laminar flow profiles in the vicinity of the electrodes.[5] The cell geometry allows accurate calculation of the primary current distribution.[6] Finally, the capillary position and dimensions allow electrode potential measurements to be made with an IR error of less than 10 mV at a current density of 1000 A/m^2.

Results. A typical voltammetric trace for the Li/3M-LiOH(aq) electrode is shown in Figure 3. The plot was obtained by imposing a triangular current wave form, with slopes of 0.20 A/s and -0.20 A/s, across the cell. The curve shows a linear polarization region of low electrode overpotential extending to an anodic current density of about 5500 A/m^2. Above this level, the anode potential rises sharply to over 15 V, indicating the formation of a highly resistive layer of reaction products on the lithium surface. For the low potential region of the curve, no differences were found between the results for scanning voltammetry (for 0.005 - 0.5 A/s) and steady-state galvanostatic polarization. The open circuit electrode potential of lithium in 3M-LiOH was in all cases -2.875 ± 0.01 V vs. Hg/HgO, 1M-LiOH. (This corresponds to about -2.75 vs. SHE).[9]

The anodic limiting current density, i_{lim}, increases with electrolyte flow rate. (See Figure 4). The plot of i_{lim} against flow rate is linear on a double logarithmic plot, with a slope of 0.22.

The slope of the potential-current plot in the linear region, however, is independent of flow rate for 3M-LiOH. (Figure 5). The resistance is 0.7 x (10^{-4}) ohm-m^2.

In quantitative measurements of electrode potential using our experimental setup, consideration must be given to the effects of current distribution within the cell. The reference capillary is located near the leading edge of the electrode, which is highly accessible to current flow. As a consequence, the potential measured at a given average anode current density (i_{ave}) is actually the potential of the electrode at the locally enhanced density (i_o) near the leading edge. Thus the resistance plotted in Figure 5 is greater than the actual resistance, $dE(i_{ave})/di_{ave}$, of the lithium/electrolyte interface. A correction factor, indicating the effects of secondary current distribution for an electrode showing a linear polarization behavior, may be easily calculated, using a regression method derived from Wagner's work.[6] When this is done, we find that the local current density near the capillary is equal to 1.4 times the average current density. Thus the actual electrode resistance is 0.5×10^{-4} ohm-m^2. Furthermore, the IR error resulting from capillary position (0.1×10^{-4} ohm-m^2) suggests that a reasonable estimation of electrode resistance is 0.4×10^{-4} ohm-m^2.

Significance of Results and Conclusions. Further data is required before any comprehensive picture of the electrode kinetics can be advanced. Tentative conclusions are: (1) The anodic dissolution of lithium is controlled by activation polarization below a certain critical current density -- the limiting current density, i_{lim}. (2) Above i_{lim}, the concentration of LiOH in the diffusion layer exceeds the saturation concentration by an amount sufficient to cause the precipitation of LiOH on the electrode surface, causing the electrode potential to rise. (3) The electrode resistance of the activation controlled region (0.4×10^{-4} ohm-m^2) is lower by a factor of about three than that obtained for the Lockheed cell configuration (direct anode-to-cathode contact), indicating that the plane-parallel electrode configuration used in our experiments may be more appropriate for batteries of the lithium-water type.[8]

II. ALTERNATIVE CELLS OF THE LITHIUM-WATER TYPE

Dry-box facilities are currently being updated for the casting of lithium and non-lithium base alloys. The first series of alloys will contain lithium metal doped with small quantities (0.001 - 1.0 at.-%) of metals forming divalent or trivalent oxides. The purpose of experiments to determine the electrochemical properties of these alloys is heuristic. If the dissolution of the lithium electrode is controlled by the migration of cation vacancies through a non-porous film at the lithium/electrolyte interface, the effect of such dopents would be to inject additional vacancies into the lattice and thereby to increase film conductivity. A procedure for casting lithium alloys with low-level metal additives is currently being developed.

III. PROCESSES FOR THE RECYCLING OF LITHIUM.

The first steps in the lithium reprocessing study has been initiated by a search of the literature for methods of electroreduction of lithium compounds. A detailed search from 1962 has been completed; prior work will be examined through abstracts and the review literature. Negotiations with Lockheed and Hooker Chemical Company for release to LLL of the SRI study on traditional methods of production of lithium are underway.

Some interest has been generated here in recent patented processes for production of lithium directly from fused mixtures of LiOH and Li_2CO_3, and from low temperature solution of lithium salts in liquid ammonia.

References and Notes

1. Lithium metal, 99.9%; supplied by D. F. Goldsmith Chemical & Metal Corp., Evanston, Ill.
2. Lithium Hydroxide Monohydrate (Reagent grade); supplied by G. Frederick Smith Chemical Company, Columbus, Ohio.
3. Model 173 Potentiostat/galvanostat; Model 175 Universal Programmer; Princeton Applied Research Corporation; Princeton, New Jersey.
4. Model 202 x-y Recorder; F. L. Mosely Co.; Pasadena, California.
5. R. Bird, W. Stewart, E. Lightfoot, Transport Phenomena (John Wiley & Sons, Inc., New York, 1960; p. 47).
6. C. Wagner, "Theoretical Analysis of the Current Density Distribution in Electrolytic Cells," J. E.ectrochem. Soc., 98, 116 (1951).
7. John S. Newman, Electrochemical Systems (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1973; p. 316).
8. E. L. Littauer and K. C. Tsai, "Anodic Behavior of Lithium in Aqueous Electrolytes," J. Electrochem. Soc., to be published.
9. The standard state electrode potential for the Li/1m-LiOH electrode is -3.05 V vs. SHE; the corrosion potential of the lithium electrode is thus 0.3 V noble of the standard electrode potential.

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

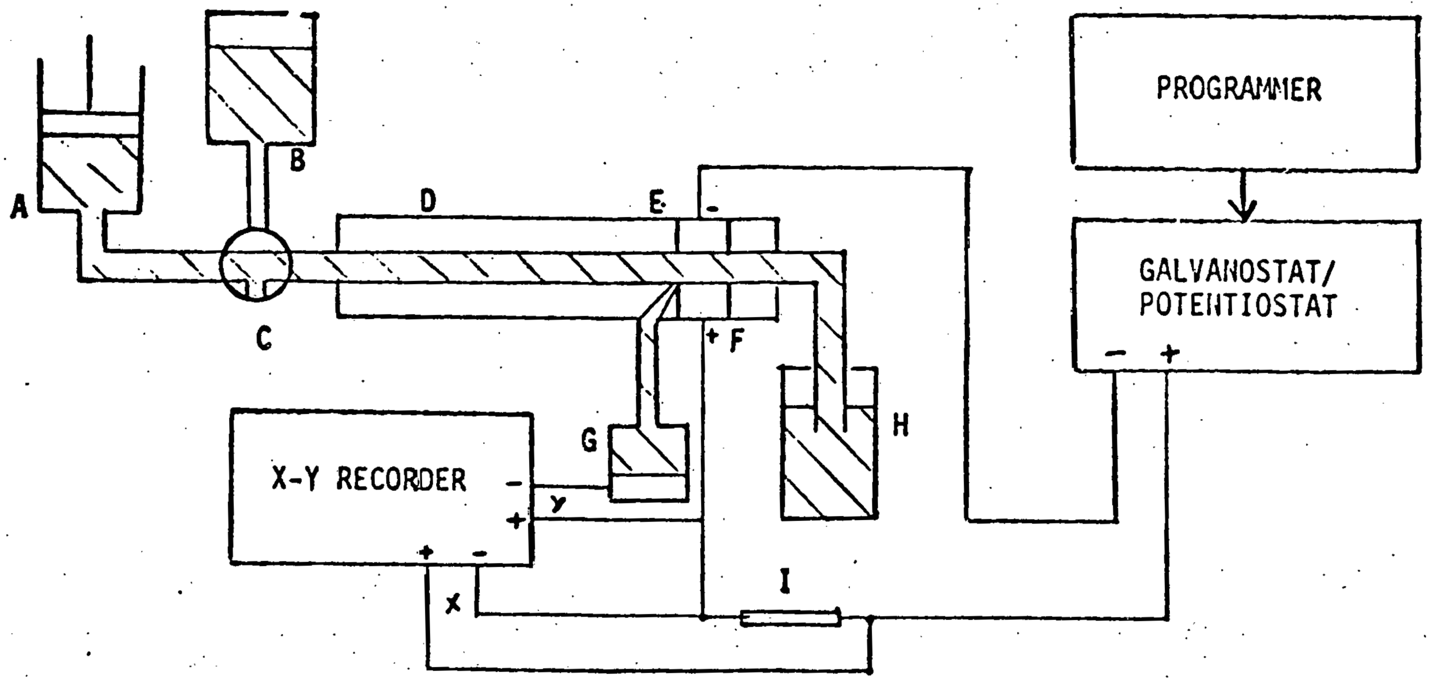

Figure 1. Schematic of Flow Channel and Electrical System. A. Piston pump; B. Electrolyte reservoir; C. Three-way valve; D. Flow channel; E. Platinum counter electrode; F. Lithium working electrode; G. Hg/HgO, 1M LiOH reference electrode; H. Electrolyte reservoir; I. 0.01 ohm current measuring resistor.

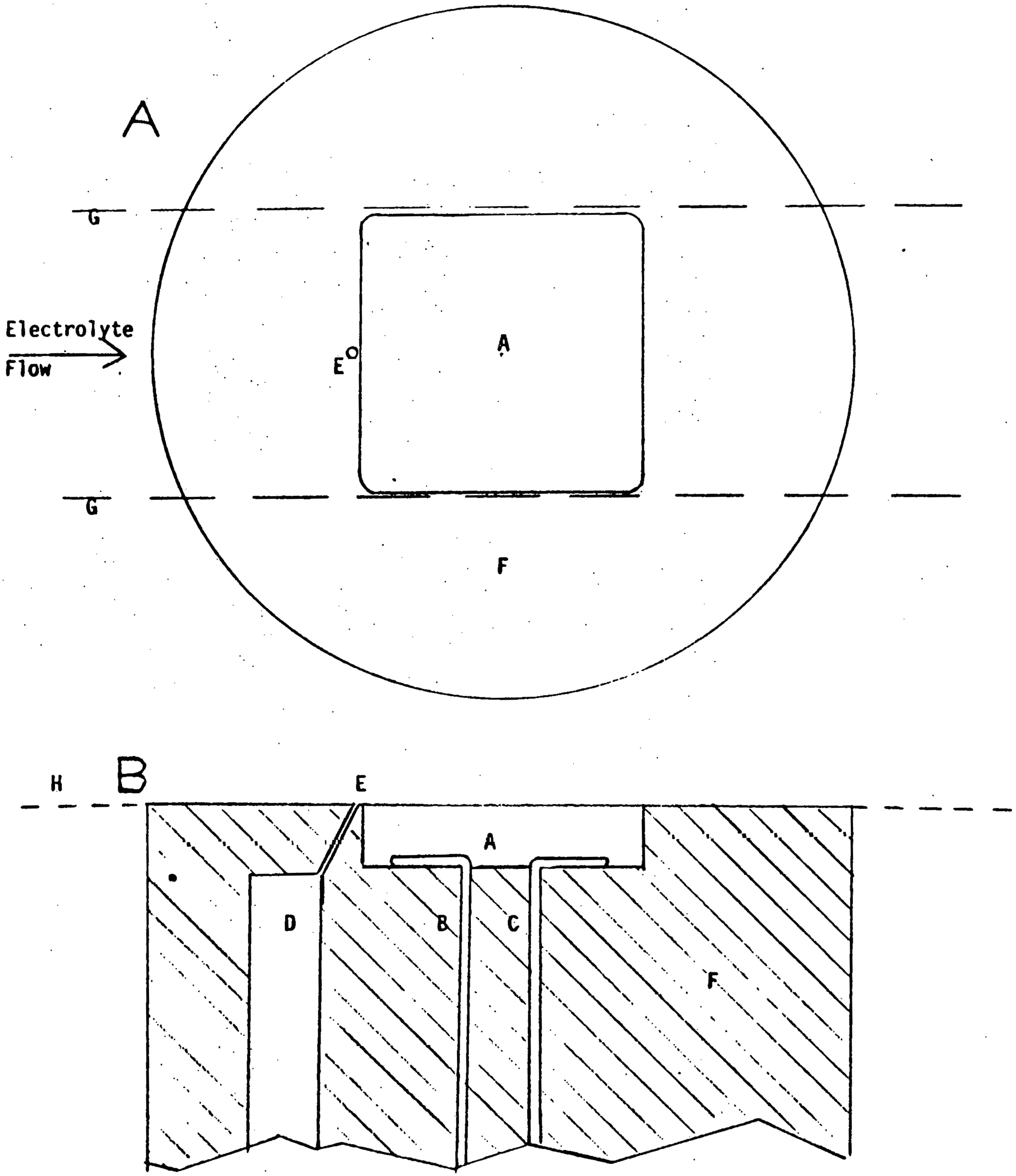

Figure 2. Lithium electrode and holder. A. Top view; B. Side view. A. Lithium electrode; B. Current carrying lead, C. Potential measuring lead. D. Reference electrode connecting tube; E. Reference capillary opening; F. Epoxy resin lithium electrode holder; G. Position of vertical walls of flow channel; H. Position of horizontal floor of flow channel.

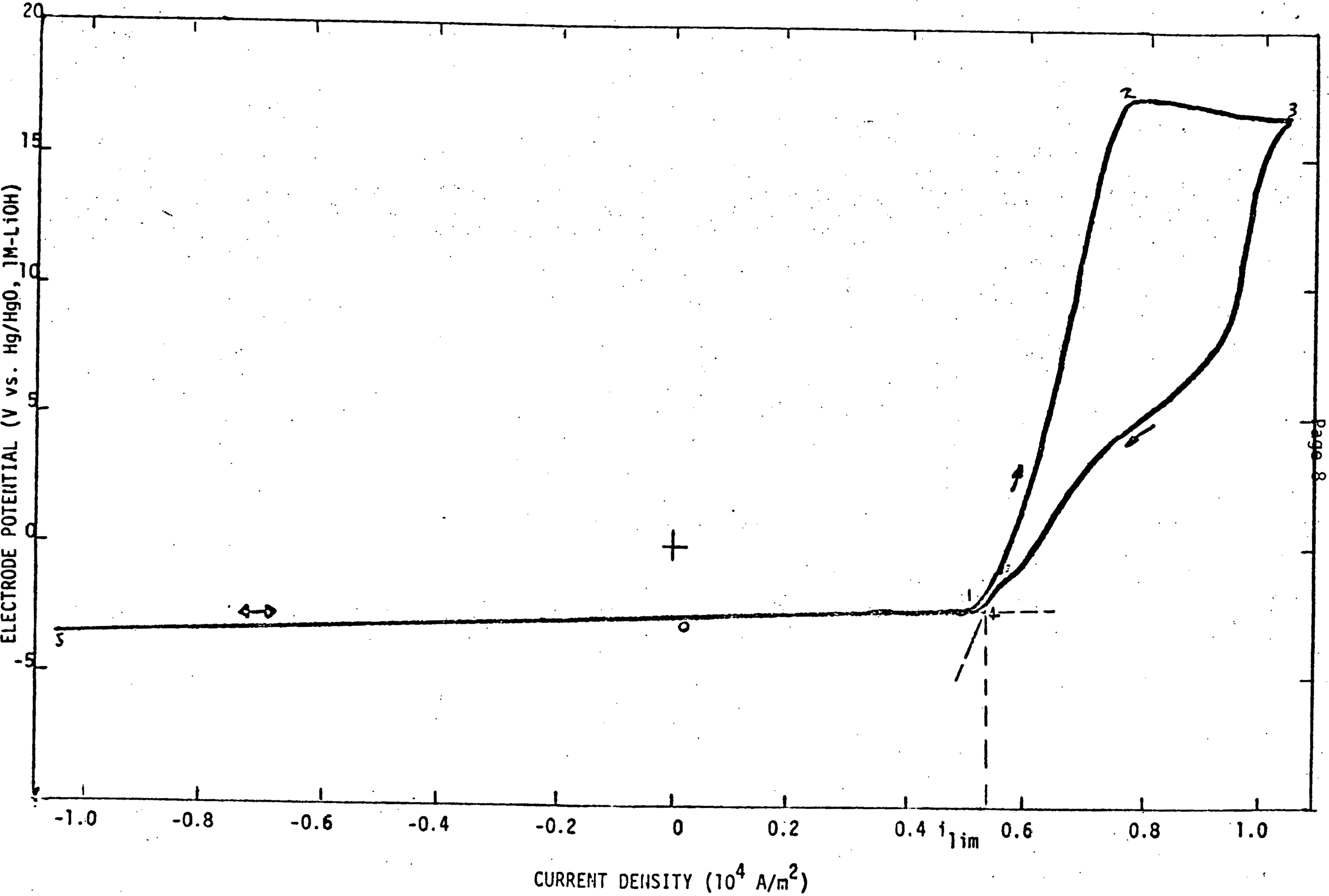

Figure 3. Triangular Wave Voltammetry. Li/3M LiOH; Scan rate = ± 0.2 A/s; Flow rate = 550 mm/s; Re = 1300; Current scan proceeds, 0123450; Anodic limiting current density, i_{lim}, obtained by extrapolation

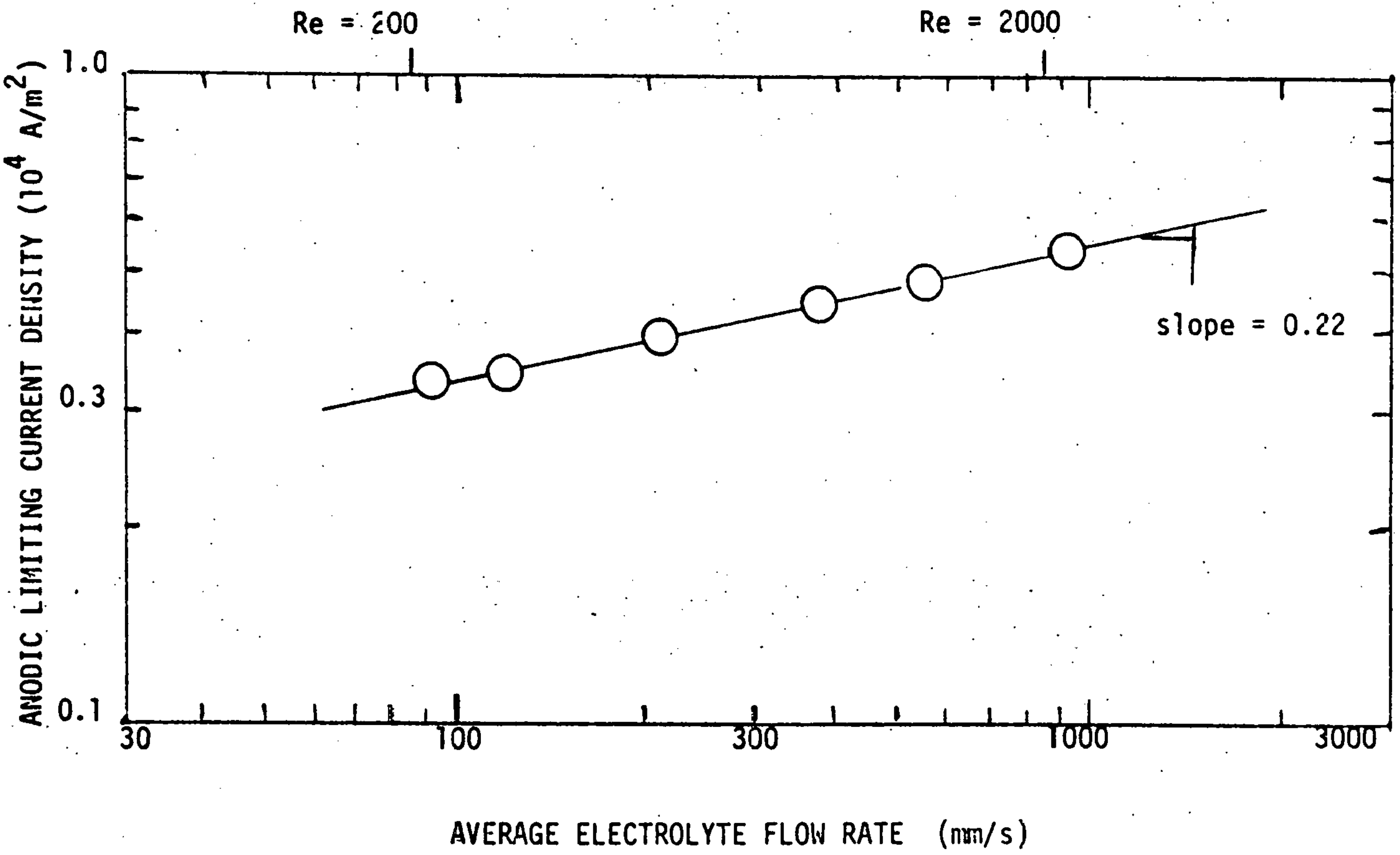

Figure 4. Limiting Anodic Current Density. Li/3M-LiOH; current scan rate = 0.01 A/s; Temperature = 18°C.

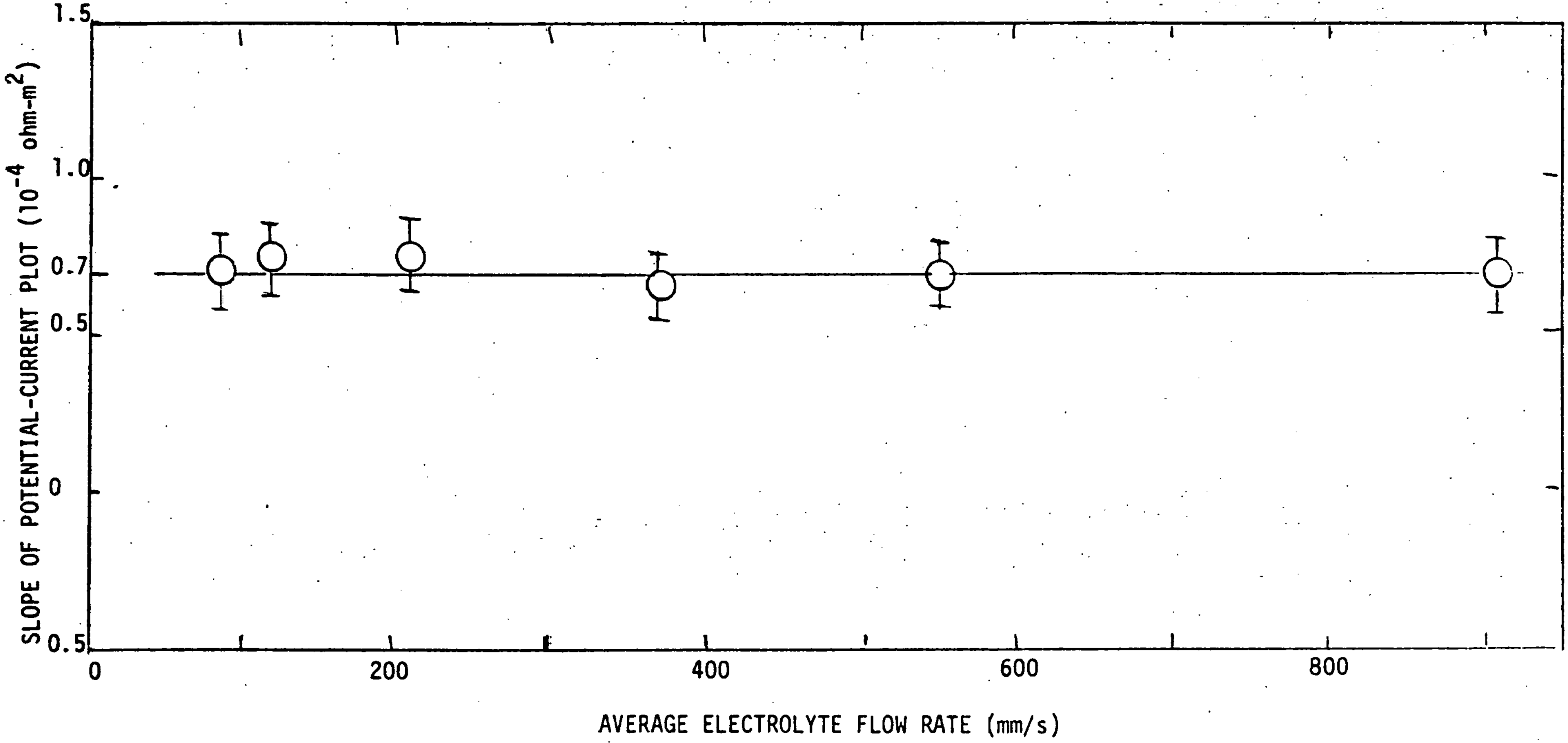

Figure 5. Electrode Resistance is Independent of Flow Rate. Li/3M-LiOH; scan rate = 0.01 A/s; Temperature = 18°C, slope refers to anodic branch of low polarization region of current-potential plot.

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