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

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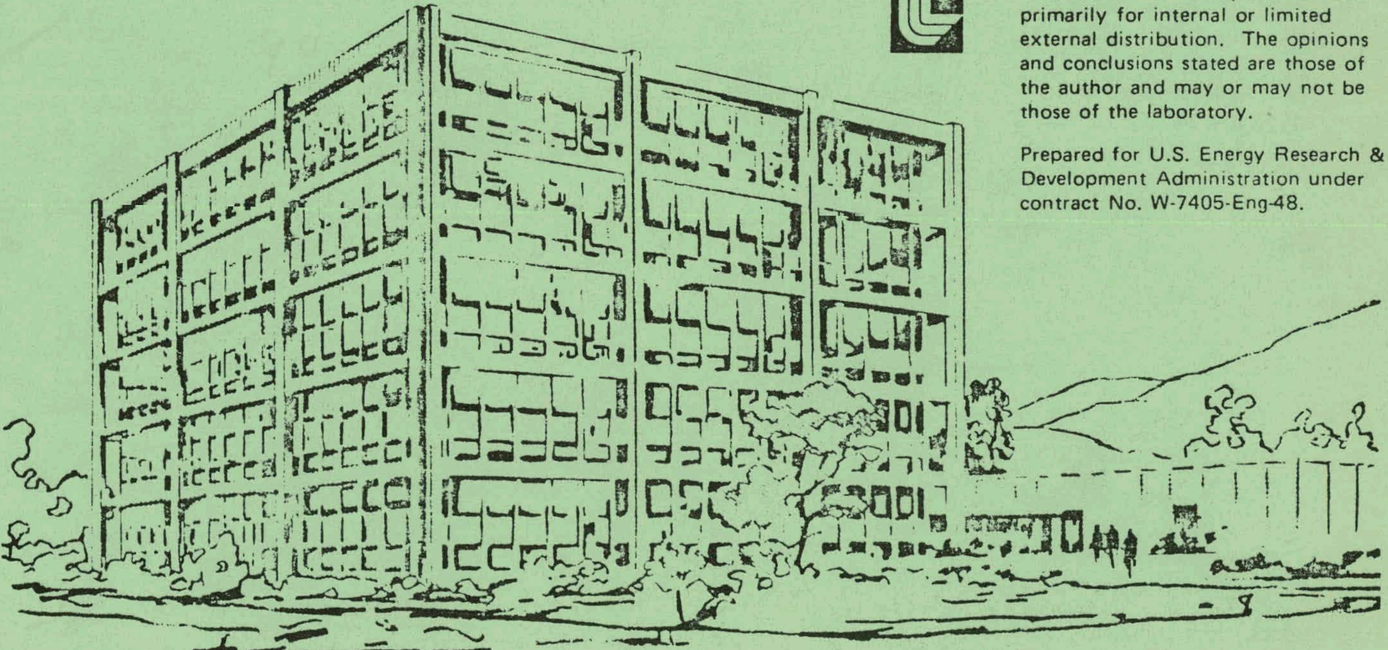

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I. INVESTIGATIONS OF THE KINETICS OF THE Li/LiOH(aq) ELECTRODE

Laboratory investigations of the kinetics of the lithium electrode continued this month. Electrode polarization was measured by voltammetric techniques, using a current ramp (di/dt at fixed values between +0.005 and +1 A/s). A matrix of data was obtained for different values of bulk electrolyte concentration and for electrolyte flow rates providing laminar flow. Details of the experimental apparatus and techniques were described in the March 1976 progress letter.

Results. Tracings of typical polarization curves are shown in Figure 1. The current scan rate was +0.01 A/s. Over a wide range of flow rates (corresponding to Re = 230 to 2300) the curves show a linear polarization region with a slope h_c on the order of $0.5 - 1 \times 10^{4}$-ohm-m^2 (see Figure 4). At a certain critical current density, which increases with flow rate and with dilution of the electrolyte, the potential rises rapidly to over +10 V.

In order to develop a quantitative description of the dependence of this critical current density on system parameters, a somewhat arbitrary but consistent definition of "limiting current density" was chosen. The limiting current density, i_{lim} is the current density such that

$$E(i_{lim}) = E(i = 0) + 1.3\ h_c\ (i_{lim})$$

(In general, the electrode potential at the limiting current density exceeds that extrapolated from the linear portion by only 20 - 60 mV.

Two kinds of limiting currents were observed, depending on the concentration and flow rate. At low concentrations (3 and 4 M), plots of i_{lim} against v were linear on double logarithmic paper. At high concentrations (4.9 M to saturation), limiting current was independent of flow rate. (Fig. 2) At the lower concentrations, a marked dependence of limiting current on concentration was also observed (Figure 3). At an intermediate concentration, 4.44 M, both types were observed, with a transition at flow rate of about 300 mm/s.

Interpretation. Intuitively, one might expect that an upper limit to the rate of dissolution of the lithium electrode would be reached when the solution-side mass transfer limitations of the system were approached. At this limit, the rate of dissolution (i.e., the current density) would just equal the maximum rate of transport of dissolved lithium hydroxide away from the electrode surface by the combined actions of migration, diffusion, and fluid convection. The appropriate mass transfer correlation for this system is given by*

$$\mathrm{Nu(average)} = 1.84\ (\mathrm{Re\ Sc}\ 2w/L)^{1/3}$$

which, when evaluated in terms of our system, yields

$$i_{\mathrm{lim}}(\mathrm{average}) = \frac{1.46\ nF\ D^{2/3}\ (C_{\mathrm{sat}} - C_b)\ (v)^{1/3}}{(L\ w)^{1/3}(1 - t_-)}$$

Three observations strongly support our intuitive model of mass transport limited dissolution in the case of the first kind of limiting current (i.e., that observed at the higher flow rates or lower concentrations.) (1) Slopes of the least-square lines a, b, and c of Figure 2 have values of 0.23, 0.31, and 0.37 which are reasonably close to the theoretical 1/3 value. (2) With the same least-square lines, limiting current density is found proportional to bulk electrolyte concentration (Figure 3). (3) At various flow rates, the plots of i_{lim} against C_b extrapolate to approximately the saturation concentration of lithium hydroxide at $i_{\mathrm{lim}} = 0$. For reasonable (order of magnitude) values of D (1.5×10^{-6} cm^2/s) and t_- (0.5), equation (ii) is quantitatively predicted as well.

Conclusions and Further Work. Three tentative conclusions may be stated concerning the dissolution of lithium electrodes. First, an upper limit to the rate of discharge of a lithium-water battery anode will be set by the mass transfer limitations of the flow system, and not (it appears) by the kinetics of charge transport within any microscopic surface films on the anode. Second, the resistance of the anode surface film in the linear

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* J. Newman, Electrochemical Systems (Prentice-Hall, Englewood Cliffs, N.J.; 1973; p 318, p 223). (As an approximation, we have assumed binary electrolyte dilute solution behavior and the mass transport characteristics of the annular region between two concentric cylinders of large diameter.)

polarization region is quite low and essentially independent of flow rate. Third, the plane parallel electrode geometry used in these experiments results in as low an electrode resistance as in the traditional Lockheed battery design (anode/cathode contact under pressure); owing to its lower resistance to electrolyte flow, the plane parallel geometry should therefore be considered for the automotive battery design.

Considerable difficulty was encountered this month in attempting to obtain accurate apparent valence (or coulombic efficiency) data for lithium dissolution under well defined conditions of current distribution and hydrodynamics, using electrode weight loss measurements. An experimental design that appears to be suitable for such measurements incorporates large electrodes (5-cm^2 area) and stagnation point flow. Results of apparent valence determinations will be reported next month.

An abstract of a paper to be presented at the fall meeting of the Electrochemical Society concerning the lithium dissolution kinetics has been submitted.

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

LIST OF SYMBOLS

Symbol	Definition
a	current sweep rate
A	anode projected area
C_b	bulk electrolyte concentration
C_{sat}	concentration of saturated electrolyte
D	diffusion coefficient
E	Electrode potential
F	Faraday's constant
h_c	slope of linear portion of polarization curve
i	current density
I	current
i_{lim}	limiting current density
L	electrode length
Nu	Nusselt number
n	number of electrons transferred per unit reaction
Re	Reynolds number
S_c	Schmidt number
T	temperature
t_-	transference number
t	time
v	average flow velocity of electrolyte (volumetric flow divided by cross section area of channel)
w	characteristic dimension of electrolytic cell (i.e., electrode separation)
ν	kinematic viscosity of electrolyte (bulk)

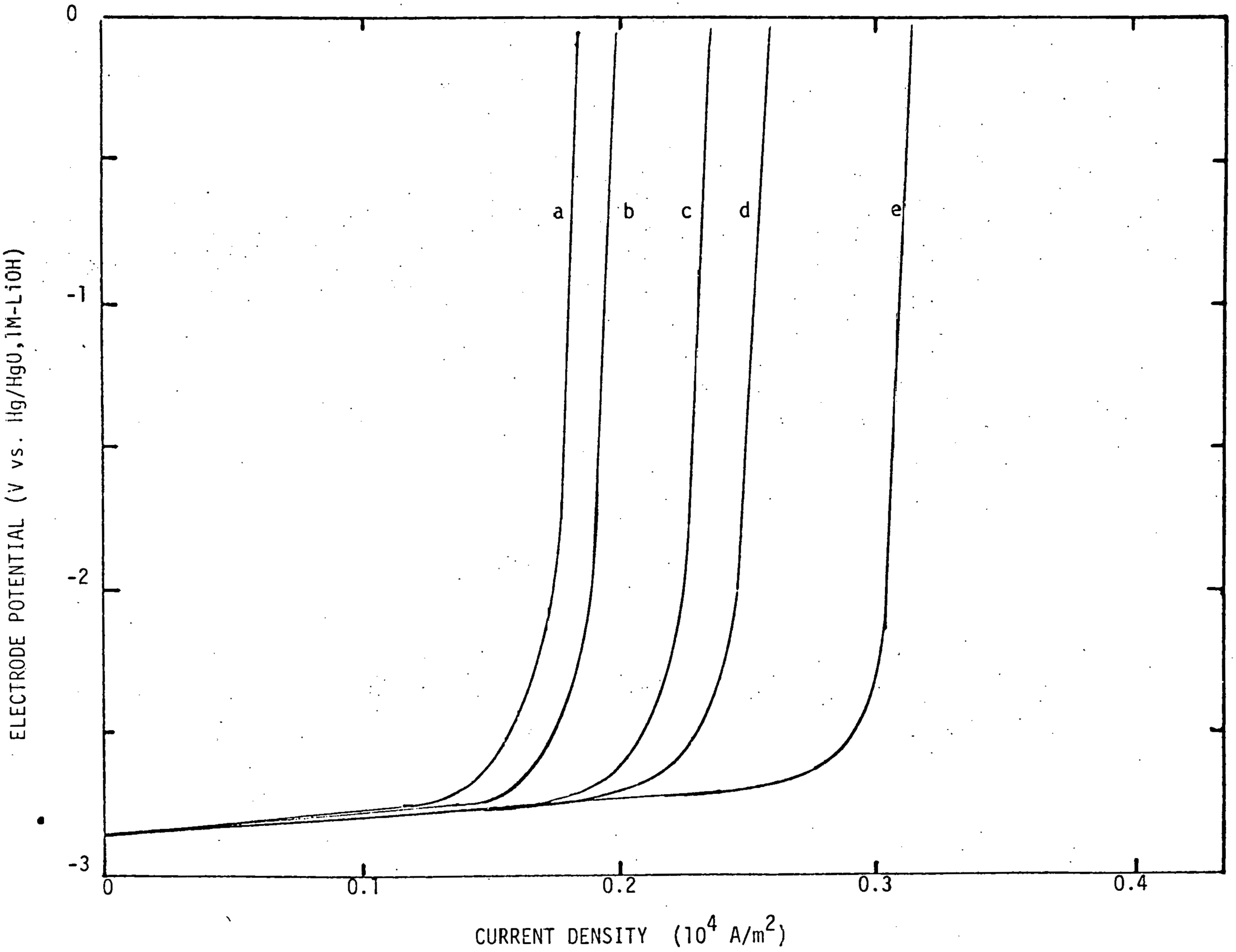

Figure 1. Anodic Limiting Cuurent Density Increases with Flow Rate. Voltammetric traces; di/dt = 0.010 A/s; electrode area = 0.92 cm^2; system: Li/3.9 M LiOH; temperature = 18°C. (a) Re = 230; (b) Re = 310; (c) 530; (d) 910; (e) 2300.

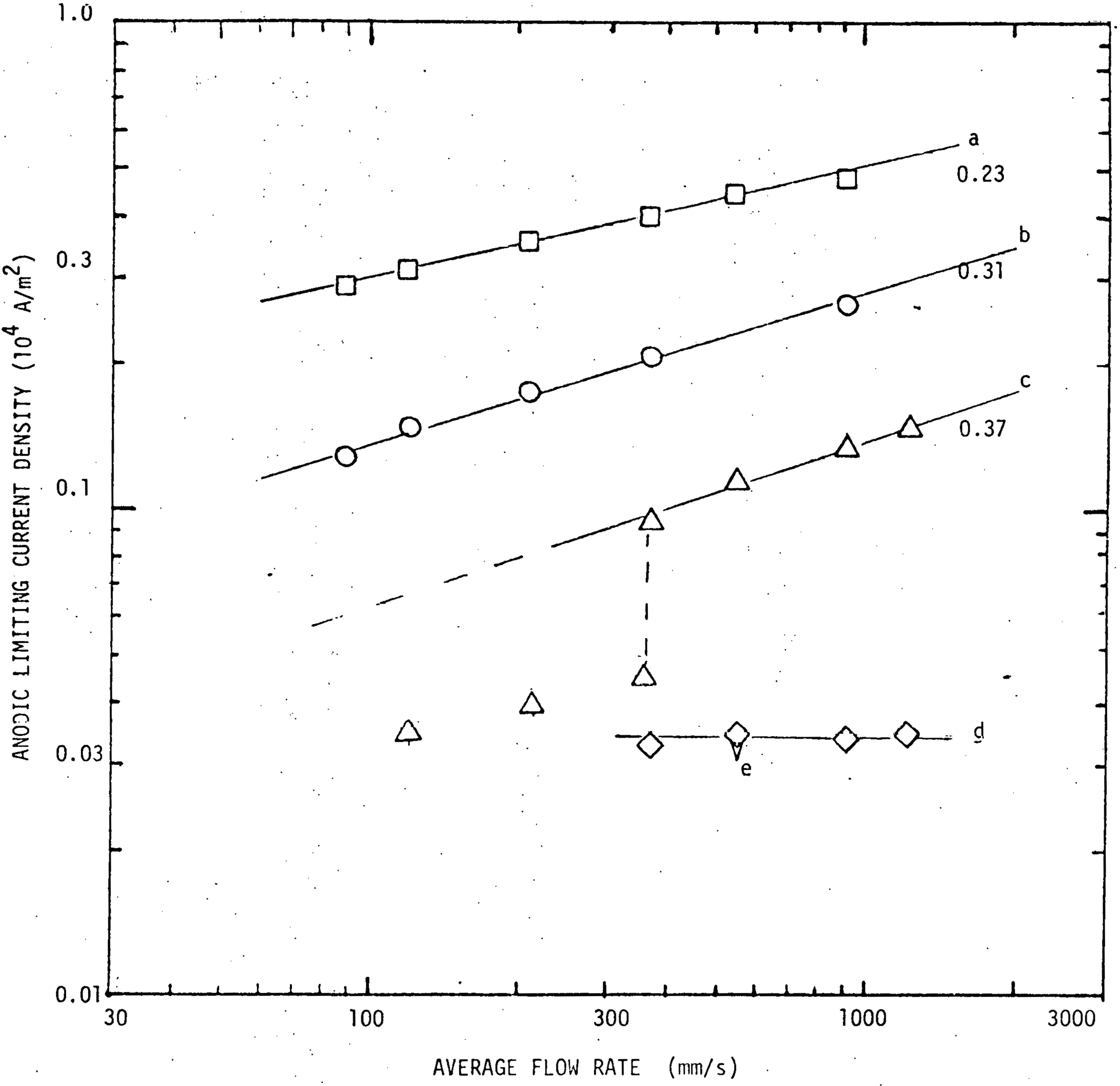

Figure 2. Limiting Current Density Depends on Flow Rate and Bulk Electrolyte Concentration. System: Li/aq.-LiOH; temperature = 19 ± 1°C; (a) (LiOH) = 2.94 M; (b) = 3.91 M; (c) 4.44 M; (d) 4.90 M; (e) 5.1 M (Saturated). Numbers on lines refer to slope.

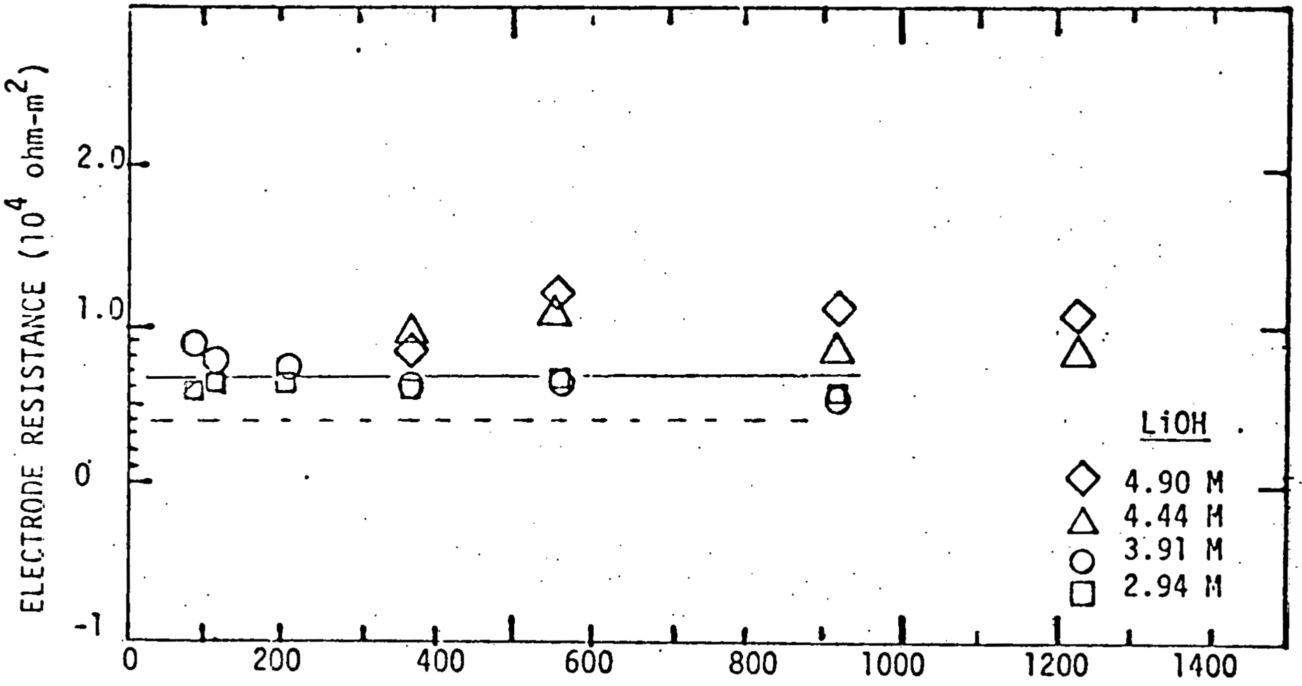

Figure 4. Electrode Resistance is Weakly Dependent on Flow Rate. System: Li/aq.-LiOH; temperature = 19 ± 1°C; voltammetric scan rate, 0.01 A/s; anode area, 92 mm^2.

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