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Lawrence Livermore Laboratory

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

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August 1, 1976

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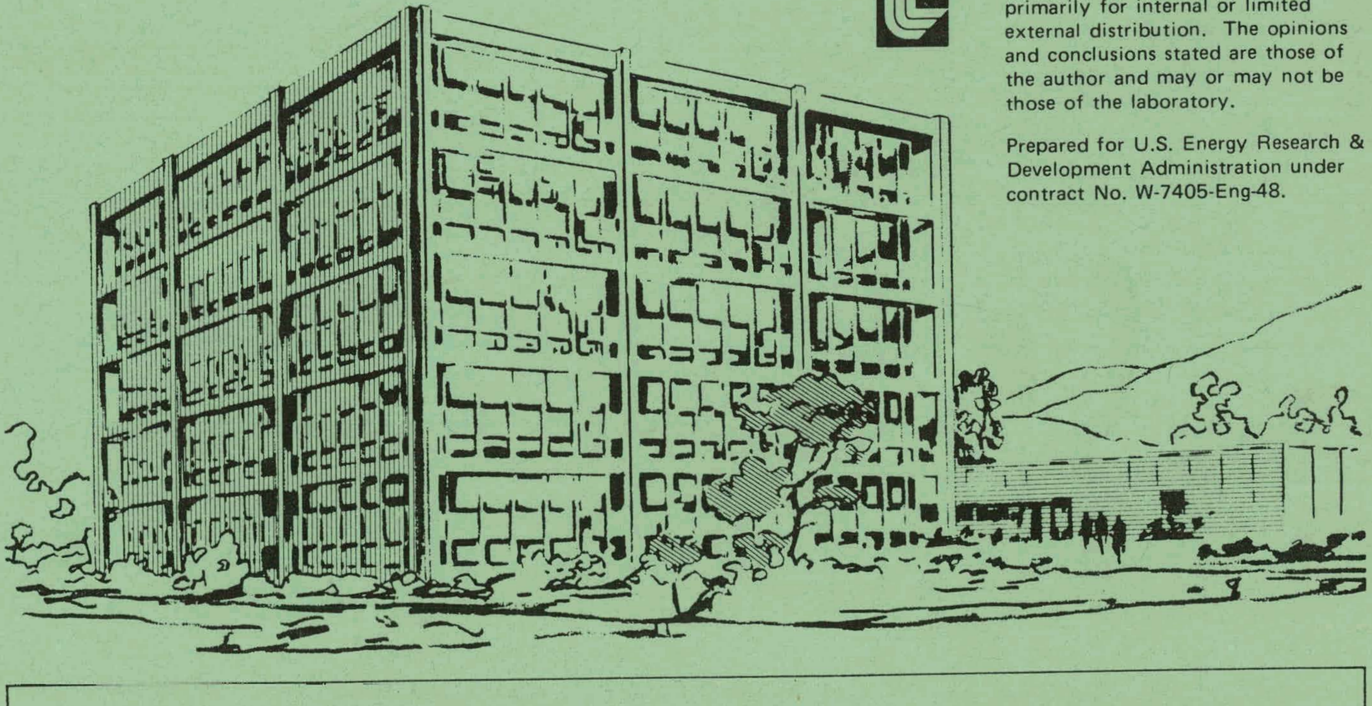

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I. INVESTIGATION OF THE KINETICS OF THE Li/LiOH(aq) ELECTRODE

A. Coulombic Efficiency

As discussed in our previous report,[1] the coulombic efficiency of the lithium dissolution reaction,

$$Li = Li^{+} + 1\ e^{-} \quad , \qquad (1)$$

may be determined by measuring the rate of hydrogen gas evolution from the combined anodic and cathodic reactions in the cell,

$$Li/LiOH(aq)/Pt \qquad (2)$$

The coulombic efficiency, e, may be related to the hydrogen evolution rate, dV/dt, through the equation:

$$e = \frac{IRT}{n\ F \left(P - P_{LiOH}\right) dV/dt} \qquad (3)$$

This month, galvanostatic experiments were performed under constant total pressure using the closed electrolytic cell previously described.[2]

Results

Experimental results are reported in Table I. The determinations were undertaken for two concentrations of lithium hydroxide (4.15 and 4.70M) and at two values of electrolyte circulation rate. The coulombic efficiency was found to increase from nearly zero (at low current densities relative to limiting current densities) to nearly one (as the limiting current density was approached). This suggested representation of the coulombic efficiency as a function of the dimensionless variable, j_g, the reduced galvanostatic current, where

$$j_g = I_g/I_{lim} \qquad (4)$$

The relationship of current efficiency to j_g is shown in Figure 1. Similarly, reduced corrosion current, j_c, and reduced total current, j_t, may be defined:

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$$j_c = (I_g/e - I_g)/I_{lim} \qquad (5)$$

$$j_t = I_g/(e\ I_{lim}) \qquad (6)$$

In Figures 2 and 3, j_g, j_c, and j_t are plotted against j_g. the graphs show at once the distribution of the lithium dissolution process between parasitic corrosion and net current producing reactions. At the lower concentration, the total flux of lithium ions from the anode surface remained relatively constant or decreased somewhat as the net current density was allowed to approach the anodic limiting current density. In the more concentrated solution, the total current approached the net (galvanic) current as the state of transient passivation was approached.

In the last column of Table I, the electrode potential and efficiency data is reduced to a dimensionless "figure of merit":

$$eE(Li)/E° \qquad (7)$$

This term compares the performance of the lithium electrode to the performance of a lithium electrode in a hypothetical, reversible galvanic cell (of unit efficiency):

Li/LiOH(aq)/HgO/Hg

It can be seen that coulombic efficiency, not electrode polarization, is the limiting factor in the total energy efficiency of the lithium/lithium hydroxide(aq) electrode.

Conclusions

Several conclusions may be advanced as a consequence of this work. (1) A coulombic efficiency of 1.0 may be approached over a range of lithium hydroxide concentrations. (2) Unit coulombic efficiencies are approached linearly with external cell current as the conditions of "mechanical" or "transient" passivation are approached.

(3) Electrode polarization data indicate that energy losses due to the polarization of the lithium electrode are small even at current densities where the coulombic efficiency exceeds 0.9. (4) Hydrogen gas evolution at currents below $j_g = 1.0$ results in enhanced convection of electrolyte near the lithium anode.

Further investigation of coulombic efficiency as a function of current density, electrode polarization, temperature, and concentration is underway.

II. LITHIUM PRODUCTION TECHNIQUES

A survey of current processes for lithium production has been completed. The results are presented in a report which will be published within August.

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1. John F. Cooper, Pamela K. Hosmer, Robert V. Homsy, "Memorandum", June 3, 1976.
2. John F. Cooper, Pamela K. Hosmer, Robert V. Homsy, "Memorandum", July 1, 1976.
3. Robert V. Homsy, "Industrial Production of Lithium Metal: Review of the Literature", UCID ; July 13, 1976.

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

Symbols

e	coulombic efficiency of the reaction, $Li = Li^+ + I\ e^-$
F	Faraday's constant
i	galvanic current density
I, I_g	galvanic current (external circuit current)
i_{lim}	limiting current density
I_{lim}	limiting current
I_c	parasitic (corrosion) current
I_t	lithium dissolution current
j_c	reduced corrosion current (I_c/I_{lim})
j_g	reduced galvanic current (I_g/I_{lim})
j_t	reduced lithium dissolution current $(I_t/_{lim})$
E(Li)	electrode potential of lithium relative to Hg/HgO, 1M-LiOH
E°	reversible electrode potential of lithium, $(Li = Li^+ + 1\ e^-)$, -3.15 V
n	number of electrons transferred per unit reaction
P	atmospheric pressure
P_{LiOH}	partial pressure of H_2O above lithium hydroxide solution
R	universal gas constant
V	volume of hydrogen gas
t	time
T	temperature

TABLE I. DEPENDENCE OF COULOMBIC EFFICIENCY ON SYSTEM PARAMETERS

Experimental conditions: Electrolyte temperature = 21-22°C
Partial pressure hydrogen = 97-98 kPa
Anode area (geometrical = 535-552 mm^2
Hydrodynamics: stagnation point flow

[LiOH] (molar)	i_{lim} (kA/m^2)	i_g (kA/m^2)	E(Li) (V)*	j_g	j_c	j_t	e	eE(Li)/E° **
4.15	1.09	0.19	-2.88	0.17	1.31	2.48	0.07	0.06
		0.37	-2.86	0.34	1.14	1.48	0.23	0.21
		0.56	-2.82	0.51	0.69	1.20	0.43	0.38
		0.75	-2.87	0.69	0.44	1.13	0.61	0.56
		0.93	-2.85	0.85	0.24	1.09	0.78	0.71
		1.12	-2.60	1.03	-0.02	1.01	1.02	0.84
4.15	1.86	0.18	-2.9	0.10	1.08	1.18	0.08	0.07
		0.37	-2.9	0.20	0.82	1.02	0.20	0.18
		0.54	-2.9	0.29	0.62	0.91	0.32	0.29
		0.72	-2.9	0.39	0.52	0.91	0.42	0.39
		0.91	-2.9	0.49	0.37	0.86	0.52	0.48
		1.09	-2.9	0.59	0.27	0.86	0.67	0.62
		1.27	-2.9	0.68	0.18	0.86	0.78	0.72
		1.45	-2.9	0.78	0.13	0.91	0.87	0.80
		1.63	-2.9	0.88	-0.02	0.86	1.01	0.93
		1.81	-2.7	0.97	-0.06	0.91	1.09	1.00

*Lithium electrode potential measured against Hg/HgO, 1M LiOH reference electrode: Potential corrected for iR drop in electrolyte.

**E° is taken as -3.15 V vs Hg/HgO, 1M LiOH.

TABLE I. DEPENDENCE OF COULOMBIC EFFICIENCY ON SYSTEM PARAMETERS

[LiOH] (molar)	i_{lim} (kA/m^2)	i_g (kA/m^2)	E(Li) (V)*	j_g	j_c	j_t	e	eE(Li)/E° **
4.70	1.80	0.05	-2.87	0.03	1.25	1.28	0.02	0.02
		0.09	-2.87	0.05	0.95	1.00	0.05	0.05
		0.14	-2.86	0.08	1.03	1.11	0.07	0.09
		0.18	-2.86	0.10	0.90	1.00	0.10	0.09
		0.27	-2.86	0.15	0.68	0.83	0.18	0.16
		0.32	-2.86	0.18	0.82	1.00	0.18	0.16
	1.75	0.41	-2.40	0.23	0.01	0.24	0.96	0.73
		0.43	-2.00	0.25	-0.01	0.24	1.02	0.65
		0.45	0.09	0.26	-0.03	0.23	1.10	0.03
		0.23	-2.86	0.13	0.78	0.91	0.14	0.13
4.70	2.36	0.41	-2.67	0.17	0.05	0.22	0.79	0.67
		0.45	-2.59	0.19	0.03	0.22	0.85	0.70
		0.50	-2.37	0.21	0.02	0.23	0.93	0.70
		0.54	-1.23	0.23	0	0.23	0.99	0.39

*Lithium electrode potential measured against Hg/HgO, 1M LiOH reference electrode: Potential corrected for iR drop in electrolyte.

**E° is taken as -3.15 V vs Hg/HgO, 1M LiOH.

Figure 1. Dependence of coulombic efficiency on reduced galvanic current density. (LiOH) = 4.15, 4.7 M; Temperature = 21 = 22°C; stagnation point flow.

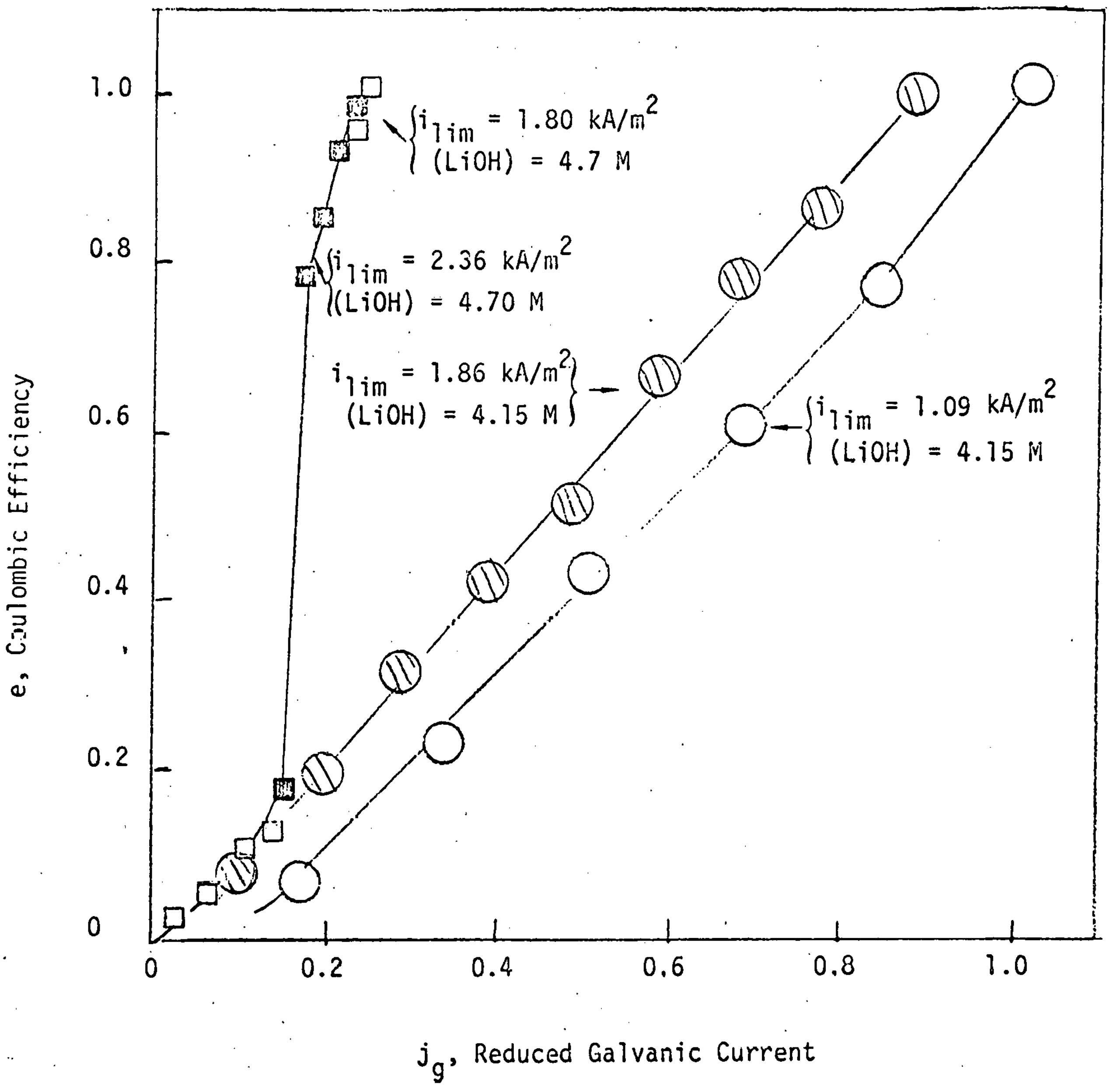


Figure 3. Dependence of reduced total and galvanic current on galvanic current. (LiOH) = 4.70 M; T = 21°C; stagnation point flow.

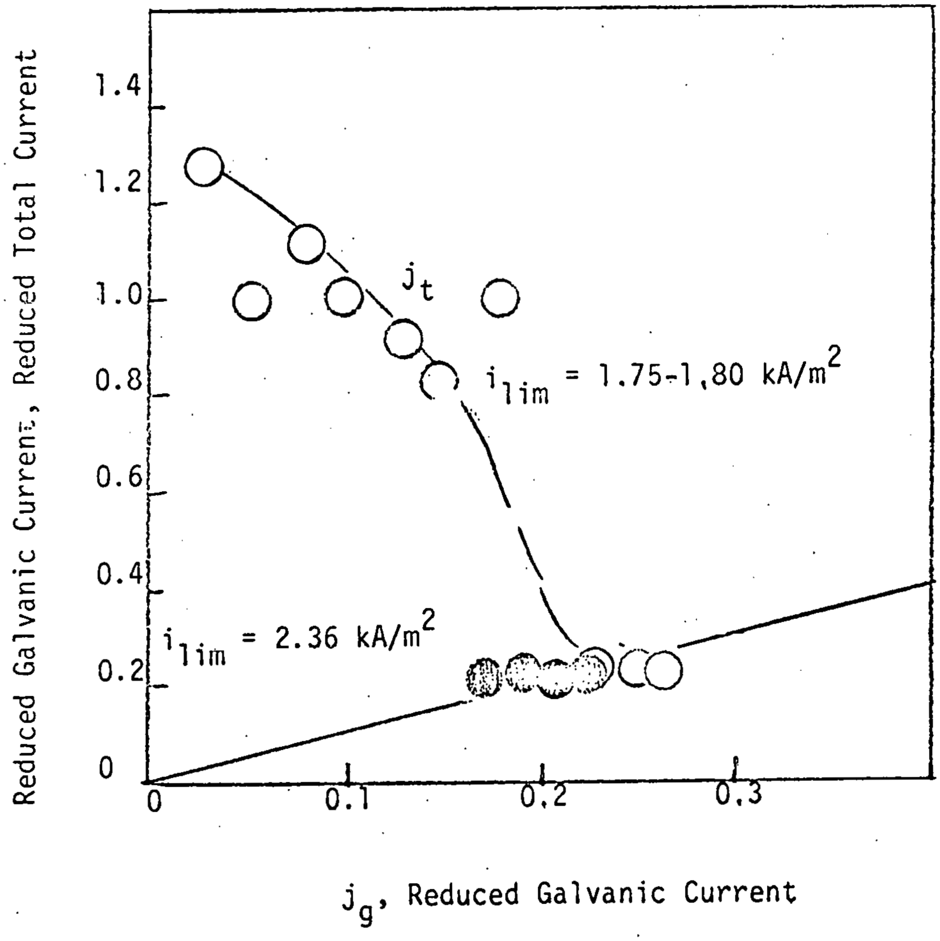
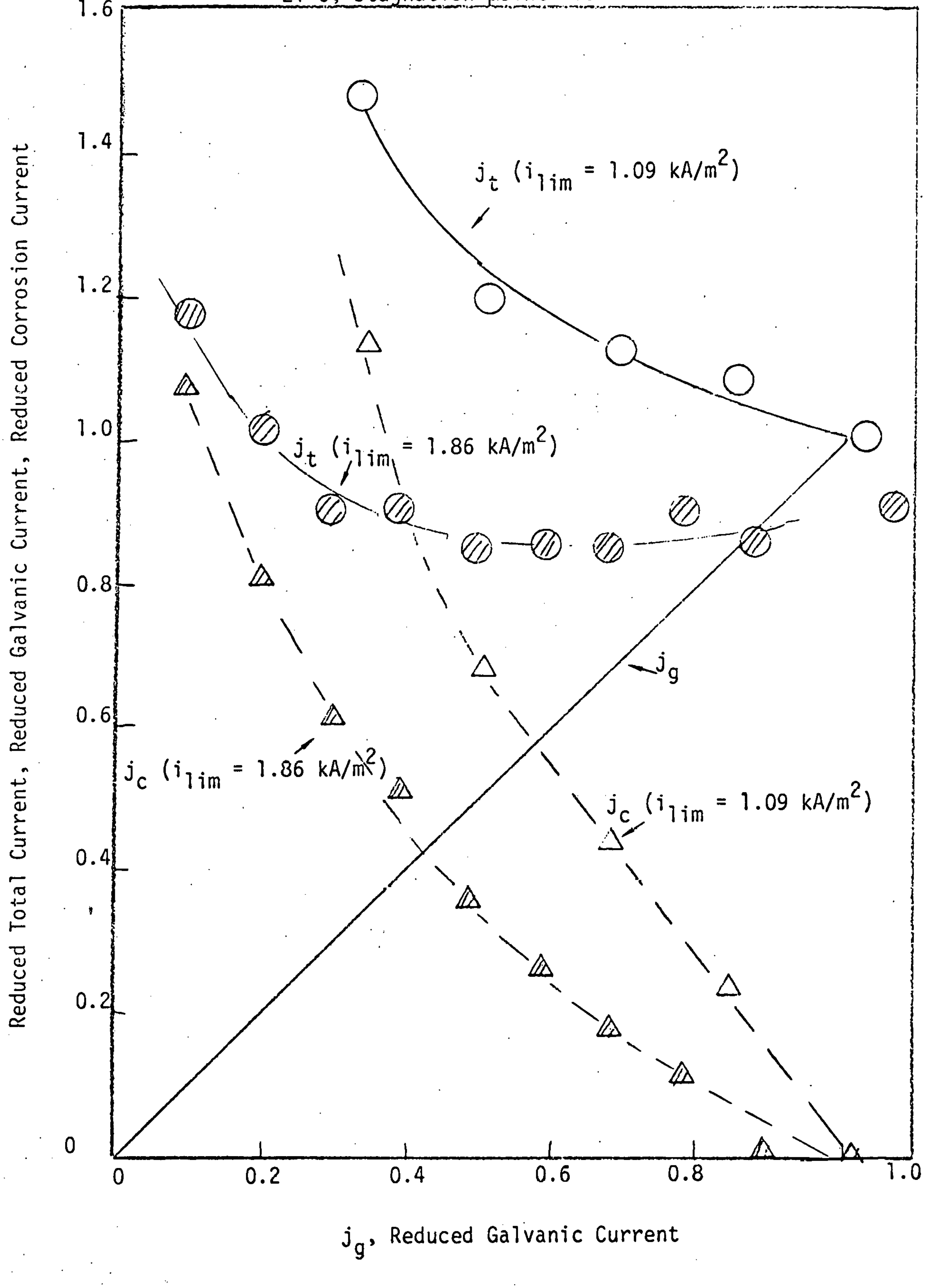


Figure 2. Dependence of total and corrosion currents (reduced) on reduced galvanic current. (LiOH) = 4.15 M; Temperature = 21°C; stagnation point flow.



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