Lawrence Livermore Laboratory

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

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

A. Electrode Polarization

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Laboratory investigations into the polarization of the lithium electrode at ambient temperatures were concluded this month. Voltammetric techniques employing a current ramp of 0.010 A/s were used to obtain a matrix of data for bulk electrolyte concentrations of 4.25 and 4.70 M LiOH at different electrolyte flow rates. Details of the experimental apparatus and techniques were described in the March 1976 progress letter.

Results and Interpretation:

The anodic limiting current density, i_{lim} , increases with flow rate (Figure 1). Double logarithmic plots of i_{lim} against flow rate for various concentrations of electrolyte are linear with slopes that approach the theoretical value, $1/3$, predicted by the appropriate mass transfer correlation.* The increase of slope, from .23 to .37, with increasing LiOH concentration reflects the increasing similarity between the bulk and the local electrolyte concentrations.

As the LiOH concentration increases, i_{lim} decreases. The limiting current density is an indication that the concentration of the LiOH in the diffusion layer is beginning to exceed the saturation concentration by an amount sufficient to cause precipitation of LiOH on the electrode surface. When the bulk electrolyte concentration increases, less current is required to dissolve enough Li to saturate the local solution. Hence, the limiting current density is lower.

The basic characteristics of the Li/LiOH(aq) electrode polarization are listed in Table 1. All measurements were made at $21 \pm 1^\circ\text{C}$ with scan rates of 0.010 A/s.

B. Apparent Valence

Construction and modification of the stagnation point flow system continued this month. Alterations of the original system, described in the May 1976 progress letter, include an improved flow pattern. In the previous flow mechanism, a stirring bar at the base of the flow channel failed to produce enough force to remove evolving gas from the anode. The accumulated gas kept the solution from the surface of the lithium and

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*See the April 1976 progress letter for a discussion of this topic.

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caused indeterminable decreases in the effective area of the electrode. Substantial difficulty was encountered in improving the flow system, causing a lengthy delay in the acquisition of apparent valence data. Additional modifications include a reference electrode and apparatus for purging the system with hydrogen. The modified version of this system is shown in Figure 2.

C. Electrochemical Properties of Lithium-based Alloys

Results of a spectrochemical study of arc-melted lithium-based alloys were received this month (Table 2). This data indicates that arc melting is a reasonable approach to the production of the desired alloys. Copper appears to be the only introduced contaminant in this process. It occurs in proportions small enough to be acceptable. Additional information on the metallography of alloys produced by arc melting has yet to be received.

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

FIGURE 1 - Limiting current density depends on flow rate and bulk electrolyte concentration system Li/aq-LiOH; temperature = $21 \pm 1^\circ\text{C}$;
 (a) $\square$ (LiOH) = 2.94 M; (b) $\circ$ (LiOH) = 3.91 M; (c) ∇ (LiOH) = 4.25 M
 (d) $\triangle$ (LiOH) = 4.44 M; (e) $\triangle$ (LiOH) = 4.44 M LiOH; $\circ$ (LiOH) = 4.70 M
 $\diamond$ (LiOH) = 4.90 M; $\triangleright$ (LiOH) = 5.10 M. Numbers on lines refer to slope.

Flow		2.94M	3.91M	4.25M	4.44M	4.70M*	4.90M*	5.10M*
90 mm/s	E_{corr}	-2.86	-2.87	-2.85	--	-2.82	--	--
	i_{lim} KA/m ²	2.88	1.29	.71	--	.31	--	--
	h_c $\Omega \cdot mm$	58	89	124	--	130	--	--
120 mm/s	E_{corr}	-2.86	-2.87	--	-2.87	--	--	--
	i_{lim}	3.12	1.47	--	.35	--	--	--
	h_c	64	79	--	98	--	--	--
210 mm/s	E_{corr}	-2.86	-2.87	--	-2.87	--	--	--
	i_{lim}	3.55	1.76	--	.39	--	--	--
	h_c	63	74	--	92	--	--	--
370 mm/s	E_{corr}	-2.86	-2.87	-2.85	2.87	-2.85	-2.86	--
	i_{lim}	4.06	2.08	1.21	.45* .95	.31	.27	--
	h_c	64	64	96	85* 97	100	89	--
550 mm/s	E_{corr}	-2.85	--	-2.86	-2.87	-2.84	-2.86	-2.85
	i_{lim}	4.54	--	1.47	1.16	.31	30	.33
	h_c	59	--	110	117	160	110	68
920 mm/s	E_{corr}	-2.86	-2.87	-2.86	-2.87	-2.85	-2.87	--
	i_{lim}	4.79	2.69	1.61	1.36	.33	.28	--
	h_c	67	55	183	90	170	120	--
1200 mm/s	E_{corr}	--	--	--	-2.87	--	-2.86	--
	i_{lim}	--	--	--	1.49	--	.30	--
	h_c	--	--	--	85	--	160	--

TABLE 1 - Polarization characteristics of the Li/LiOH(aq) electrode.
 $(E_{corr}$ = corrosion potential, volts; i_{lim} = limiting current density, KA/m²; h_c = resistance of linear portion of polarization curve, ohm-mm)

*Total "transient" passivation domination.

FIGURE 2 - Apparatus for Determination of Current Efficiency

A - anode lead; B - lithium anode holder; C - lithium anode;
D - cathode lead; E - platinum screen cathode; F - electrolyte
bridge to reference electrode; G - thermometer; H - H₂ inlet;
I - motor coupling; J - stirring mechanism; K - flow channel tube;
L - outlet to pipette; M - lucite tubing; N - polyethylene tubing;
O - lucite pipette; P - lithium hydroxide solution; Q - lucite
chamber; R - water bath.

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