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Summary of the Lithium-Air Battery Research Program

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SUMMARY OF THE LITHIUM-AIR BATTERY RESEARCH PROGRAM

The ultimate objective of the joint LLL-LMSC Lithium-Air Battery Research Program is to determine the feasibility of a lithium-air battery (or an analogue) as an automotive power source. Toward this goal, LMSC is developing a prototype electric vehicle battery. This laboratory has (1) obtained extensive data on the lithium electrode kinetics for scientific and battery development purposes; (2) defined the efficiency limits for existing lithium production technology; (3) developed an innovative approach to the production of lithium from aqueous solutions of its compounds at a total process energy efficiency of 81% to 87%; and (4) explored for analogue cells utilizing cheaper materials.

Based on existing $\text{Li}/\text{H}_2\text{O}$ and $\text{Li}/\text{H}_2\text{O}_2$ batteries and on the performance of experimental Li/air batteries, the Li/air battery is expected to have specific energy and power values of 300 to 450 Wh/kg at 90 W/kg, and an energy efficiency (discharge cycle) of 69% to 75%.* When combined with the newly-proposed process for lithium production from the battery reaction products, the turn-around energy conversion efficiency of the battery is expected to lie in the range of 56% to 65%. Transport of battery reaction products ($\text{LiOH}\cdot\text{H}_2\text{O}$) and lithium metal to and from fixed site recycling plants would degrade the energy conversion efficiency of the system by less than 1%. (See Table 1.) A vehicle powered by a Li/air battery should have the range and speed of current compact automobiles. In addition, the electric vehicle would have a capability for indefinite range extension through rapid and convenient mechanical refueling. Finally, the Li/air vehicle and recycling system fulfills ERDA specifications for transportation energy efficiency.

The lithium recycling process proposed by LLL is in an experimental stage of development. The process is similar in concept to one developed by Atomics, International for the production of sodium metal from aqueous sodium hydroxide solutions and which demonstrated a process energy efficiency of 86% to 88%.¹ The lithium production cell employs a lithium-

*See Figure 1

mercury amalgam electrode which circulates continuously between an aqueous and a fused-salt electrolysis cell. (Figure 2) Lithium amalgam (1-2 at.%) is produced in the aqueous cell and is electrochemically refined to a lithium melt in the fused-salt cell operating at a temperature below 250°C. The fused salt is a low-melting eutectic based on the LiI-KI eutectic (m.p., 260°C)² with halide additions. The efficiencies projected for the process (81-87%) are based on published single electrode and conductivity data (Table II). (The current industrial technique for lithium production employs a high temperature (410°C) fused salt (LiCl-KCl) electrolysis cell with purified, anhydrous LiCl feed; the total energy efficiency is approximately 20%.)³

To complete this feasibility study, the following critical tasks remain: (1) The lithium-air battery prototype must be developed and demonstrated; (2) a bread-board demonstration of the reprocessing technique must be completed and evaluated; (3) from battery prototype and reprocessing model, scale-up designs must be made and capital and operating costs must be accurately predicted; and (4) the scientific understanding of the unusual kinetics of the lithium-water class of batteries must be pursued in order to provide a rational basis for the search for analogues and for the developing of practical batteries of this class.

In addition to our work with lithium, a calcium/aqueous-electrolyte combination has been discovered showing electrode behavior similar to that of lithium.

TABLE I: Calculation of Energy Efficiency Degradation Resulting from the Transport of Li and $\text{LiOH}\cdot\text{H}_2\text{O}$ between Electric Vehicle and Fixed-Site Recycling Centers.

<u>Transport Truck Specification</u>	<u>Metric</u>	<u>English</u>	<u>Symbol</u>
1. Gross vehicle weight, kg (lb)	27,300	(60,000)	w_p
2. Payload weight, kg (lb)	18,200	(40,000)	
3. Frontal area, m^2 (ft^2)	8.8	(95)	
4. Aerodynamic drag coefficient	0.8		
5. Rolling resistance coefficient	0.012		e_t
6. Drive train efficiency	0.75		
7. Propulsion energy requirements (roadload) for 89 km/h (55 mph) reference velocity, Wh/km (Wh/mi)	1620	(2610)	E_t/R_t
<u>Refueling Matrix</u>			
8. Average trip length (one-way) km (mi)	40	(25)	R_t
<u>Lithium Energy Density</u>			
9. Discharge energy density (Wh/kg-Lithium (Wh/lb-Lithium))	9600	(4260)	$E_{\text{Li}}/w_{\text{Li}}$
10. Turn-around energy conversion efficiency	0.58		e_b
<u>Results</u>			
11. Energy cost of transporting kg of Li plus 6 kg $\text{LiOH}\cdot\text{H}_2\text{O}$ over matrix: = $(E_t/R_t) R_t (w_p/w_{\text{Li}})/(w_p e_t)$	33 Wh/kg-Li		
12. Energy cost of producing 1 kg of Li from 6 kg $\text{LiOH}\cdot\text{H}_2\text{O}$ = $(E_{\text{Li}}/w_{\text{Li}})/e_b$	16,600 Wh/kg-Li		
13. Ratio of fuels transportation energy consumption to Li production energy consumption.	0.002		

TABLE II: Estimates of Cell Operating Voltages in Proposed Recycling Process

Cell Description:

O₂ (1 atm) (Ni)/sat. LiOH, LiCl (Aq)/Li (1 at.%) (Kg)...Li(1 at.%) (Hg)/
LiI, KI/Li

	Estimates	
	Low	High
<u>Aqueous Cell, T = 50°C</u>		
1. Oxygen electrode on Ni ($i=0.02 \text{ A/cm}^2$) Tafel equation: $E_h=0.78 + 0.04 \log(i \text{ (A/cm}^2))$ Based on Fig. 4 and 7 of Ref. (4)	0.71 V	0.71 V
2. Interelectrode IR drop. $IR = id/k$; $i = 0.1 \text{ A/cm}^2$ Low estimate: $d=0.7 \text{ cm}$; $k=1.67 \text{ ohm}^{-1} \text{ cm}^{-1}$ based on data for 5M LiCl and formula, $k_T=k_O \exp(0.023(T-T_O))$; Ref. (5)	0.04	
High estimate: $d=1 \text{ cm}$; $k=0.69 \text{ ohm}^{-1} \text{ cm}^{-1}$ based on data for 5.3 M LiOH; Ref. (6) and formula $k_T=k_O \exp(0.023(T-T_O))$		0.14
3. Mercury-Lithium Amalgam: $X=1.0 \text{ at.}\% \text{ Li}$; negligible polarization; data for $T=25^\circ\text{C}$; Ref (7) $E_h(\text{Li (Hg)}) = -3.045 + (0.8433 - 0.0591 \log_{10}(10^{14.6X}))$	-2.09	-2.09
<u>Fused Salt Cell (T = 205-235°C)</u>		
4. Equilibrium cell voltage: $E_{\text{Li}} - E_{\text{Li(Hg)}} = 0.95 \text{ V}$	0.95	0.96
5. Interelectrode IR drop; $IR = id/k$; $i = 0.1 \text{ A/cm}^2$ Low estimate: $d=1.7 \text{ cm}$; $k=1 \text{ ohm}^{-1} \text{ cm}^{-1}$ High estimate: $d=3 \text{ cm}$; $k=0.8 \text{ ohm}^{-1} \text{ cm}^{-1}$	0.17	0.38
<u>Total Cell Voltage</u>	3.96 V	4.28 V
<u>Theoretical Cell Voltage (at 25°C)</u>	3.45	3.45
<u>Voltage Efficiency</u>	87%	81%

References

1. L. A. Heredy, H. L. Recht, and D. E. McKenzie, "The Atomics International Sodium-Air Cell," Proc. Symposium on Power Systems for Electric Vehicles, Columbia University, NY (April, 1967) p. 245. (See also U.S. Patents #3,472,745, and 3,472,746, October 14, 1969.)
2. Leiser and Whittemore, Jour. Am. Cer. Soc., 50, 60 (1967).
3. Robert V. Homsy, "Industrial Production of Lithium Metal: Review of the Literature," Lawrence Livermore Laboratory, UCRL-52124, September 2, 1976.
4. B. E. Conway, M. A. Sattar, and D. Gilroy, "Electrochemistry of Nickel-oxide Electrode-V," Electrochimica Acta, 14, 677 (1969).
5. Robert C. Weast, Handbook of Chemistry and Physics (Chemical Rubber Company Press, Cleveland, 1976-1977, p. D-234.)
6. E. W. Washburn, Ed., International Critical Tables of Numerical Data, Physics, Chemistry, and Technology, (McGraw-Hill, NY 1926; v. 6 pp 246, 254.).
7. D. Cogley and J. Butler, Jour. Phys. Chem. 72, 1017 (1968).

Figure 1. Lithium-Air and Lithium-Water Cell Discharge Curves. Data from Lockheed Missiles and Space Company (Progress Report, January, 1977).

LITHIUM PRODUCTION CONCEPT

Figure 2: Advanced process for the production of lithium from aqueous solutions of lithium compounds. Aqueous cell to operate at $T = 50^{\circ}\text{C}$; fused salt to operate at $T \geq 205^{\circ}\text{C}$. Amalgam transport between cells is accompanied by countercurrent heat transfer between mercury leaving and entering a cell. Candidate fused salt is KI , LiI , LiCl , KCl .

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