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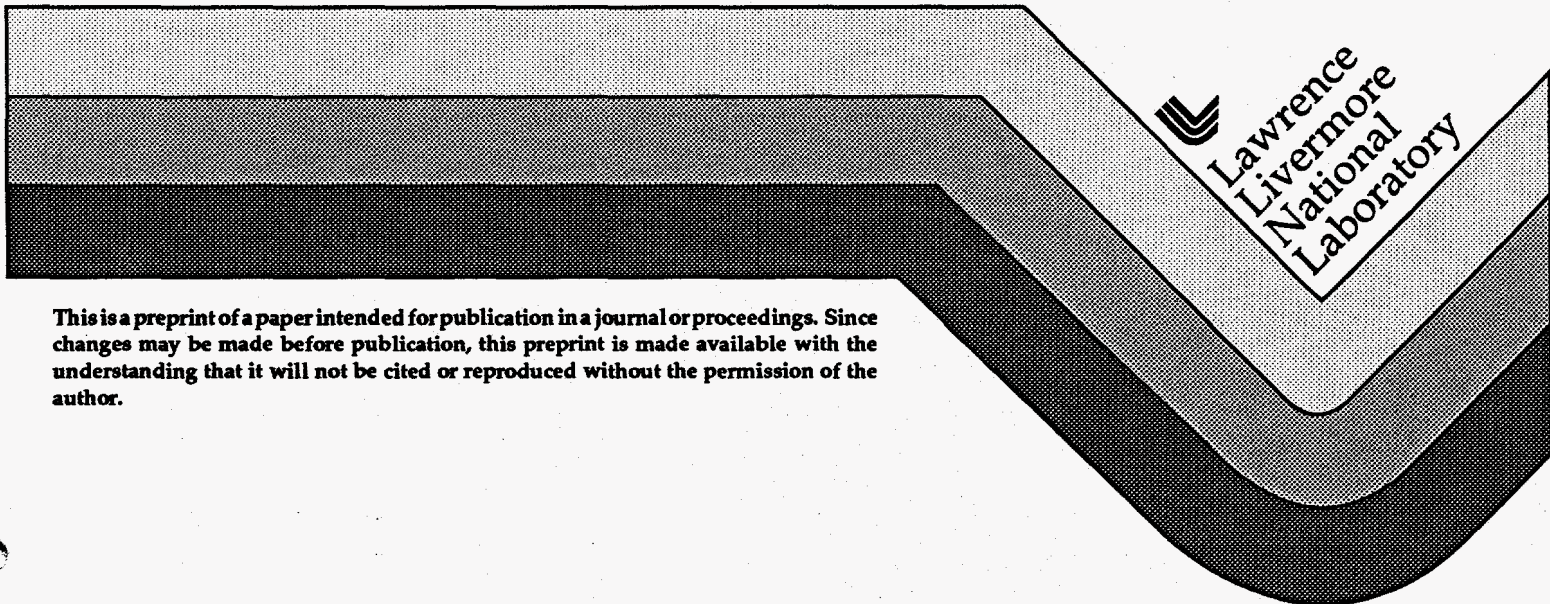
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Development of a Bipolar Cell for Electrochemical Production of Lithium

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Abstract

Lithium metal can be electrolytically refined from aqueous solutions of its compounds by partial reduction to form a lithium amalgam, followed by reduction of the amalgam to liquid lithium in a molten salt cell at 225 C. A bipolar cell (with a continuous, amalgam electrode circulating between the aqueous and salt cells) was designed, constructed and successfully tested on the bench scale, as a proof of principle of an efficient, safe and low-temperature alternative to existing processes.

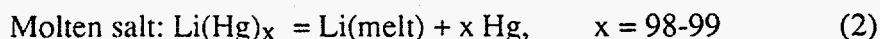
Introduction

For the last century, lithium metal has been produced by various processes involving the electrolysis of anhydrous lithium chloride in a fused salt consisting of LiCl and KCl at ~450 C. Preparation and injection of the anhydrous LiCl is time consuming, energy intensive and expensive. Moreover, the high temperature electrolysis step entails hazards of production of liquid lithium and chlorine gas in close proximity, presents problems of corrosion of cell materials and contamination of the lithium product, and requires the environmentally acceptable disposal of chlorine. These problems motivated us to develop and demonstrate on the bench scale an alternative process of increased safety and efficiency.

Aqueous electrochemical cells using amalgams to refine lithium are common, and have been used in isotope separation [2].

Technical Approach

We have developed and tested on the bench scale a process which uses electrolysis to reduce various lithium compounds to metal through the intermediate formation of a 1-2-at.% Li amalgam (Figure 1) [1]. The amalgam is produced in an aqueous cell at 30-40 C, and then refined across a fused LiI/CsI eutectic at 225 C. The amalgam circulates continuously between the two cells with a counter current exchange of heat between the streams exiting and entering the higher temperature cell. The reactions are:



Since the amalgam serves as a single electrode sustaining a reduction reaction at one electrolyte interface and an oxidation reaction at the same current density at the other interface, it is called a "bipolar electrode." The mercury remains encapsulated by an impervious molten salt or aqueous solution, and the presence of lithium prevents

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formation of volatile or soluble mercury compounds. Our safety analysis found that continuous mercury emissions are well below air emissions control standards, while losses of mercury from the system during catastrophic failure need not expose workers to a health hazard.

Experimental System

The experimental system consists of an aqueous cell containing a ring-shaped amalgam electrode (100 cm^2), a molten salt cell ($10\text{-}100 \text{ cm}^2$, variable), and interconnecting plumbing for circulation of the amalgam. The molten salt cell consists of a stainless steel tray (anode) and lid (cathode) separated by a boron nitride insulator. Efficient, coaxial tube heat exchangers minimize heat losses by transfer of the heat of the amalgam stream exiting the molten salt cell to the incoming stream. An intermediate vessel maintains the amalgam with a free surface at 120 C , to prevent the inadvertent entrainment of water from the aqueous cell into the molten salt. The bench unit has separate flow circuits (1) for maintaining temperature of the aqueous cell and providing for a high relative velocity of aqueous solution and amalgam to overcome mass transport resistance; (2) for transferring molten salt from a holding vessel to the high temperature cell; (3) for circulation of argon above the molten salt, and (4) for entrapment of any mercury vapor that might escape from the amalgam due to system upsets.

The unit is scaled for operation at $20\text{-}40 \text{ A}$ ($125\text{-}250 \text{ g-Li/day}$), which requires an exchange rate of 0.3 ml/s of amalgam at a near saturation concentration (30 C) of 1.5 at-\% . The amalgam serves as a barrier between the aqueous and molten salt cells. To prevent entrainment of water, we promote complete wetting of the nickel tubing by the amalgam by cathodic polarization of the nickel before and during first contact with the mercury. This polarization reduces nickel oxides to pure nickel, followed by immediate formation of a permanent Ni/Hg bond.

Our initial plans called for the use of a LiCl-LiI-KI eutectic, which we found to melt at approximately 225 C [1] contrary to subsequently published work [3]. A possibly improved electrolyte was found with CsI \cdot 2LiI [3], which in theory should have a lower melting point [4].

Experimental Results

Efficiency of the aqueous deposition of $1\text{-}2\%$ lithium amalgams was found to approach 100% at current densities of 3 kA/m^2 and temperatures of $30\text{-}35 \text{ C}$. A competing reaction, the reduction of water to hydrogen gas, must be carefully controlled to prevent the accumulation of explosive hydrogen within the vessel.

The polarization curves of the aqueous and molten salt cells during steady state operation of the integrated system (Figure 2) shows linear dependencies on current density over the range of operation. The intercept voltage (1 V in molten salt cell) is consistent with the published values of lithium activity in the amalgam [6], and the low, linear electrode polarizations indicate that both Li/Li(Hg) cell reactions are fast.

Lithium amalgam will react with trace water in the molten salt to form hydrogen and Li_2O (or LiOH), which may be soluble in the melt. Provided that these species do not precipitate within the melt, the lithium reduction of trace water may be used to achieve the strict anhydrous conditions required by the molten salt process.

It has been reported that a CsI/LiI eutectic should have a low melting point (217 ± 50 C) at 66% mol fraction LiI , as extrapolated theoretically from the melting points of the pure constituents based on solution theory with the assumption of zero excess entropy [4]. Moreover, a compound $\text{Li}_3\text{Cs}_2\text{I}_5$ has been identified [5]. Using commercially supplied anhydrous CsI and LiI to prepare mixtures of the molar ratio of $\text{LiI/CsI} \sim 2$, we found a melting point of 218 C for a LiI/CsI composition found to contain 64.2 mol-% LiI by independent chemical analysis. Subsequent melting point determinations using differential thermal analysis confirmed a melting point of 218 ± 2 C, but contamination with water lowered the apparent melting point as low as 175 C.

Safety

The presence of mercury at elevated temperatures behooved us to conduct a thorough safety analysis of the process prior to construction and testing. Both continuous and catastrophic losses of mercury as mercury vapor were predicted. The continuous losses from the aqueous cell amounted to 0.003 g/day (c. EPA allowable of 1.38 g/day), scaleable with output. Catastrophic losses (due to rupture of the molten salt cell) are minimized by a rapid thermal quenching of the mercury, and predicted evaporative losses are <1% of inventory.

Discussion

In large systems, amalgam-side mass transport of lithium at the amalgam/aqueous electrolyte interface will be controlling, as the diffusion coefficient of lithium in mercury is low ($1.5 \cdot 10^{-6} \text{ cm}^2/\text{s}$) and stirring is difficult. The overriding mechanical challenge of scale-up is to maintain isolation of the molten lithium from the lithium amalgam. Fabric separators of boron nitride or zirconia allow closer separation of the electrodes and lower resistive losses. Efficiency of the system is limited by the irreversibility of the oxygen evolution electrode, for which transition-metal-oxide catalysts are available. Mercury transport through the molten salt as a reduced monatomic species is theoretically possible but unlikely at these temperatures.

Conclusions

While this work demonstrates bipolar cell production of lithium, there is a need for continuous testing to establish materials stability, failure modes, and steady state product purity. The efficiency of the process is expected to be 75%, for an optimized cell voltage of 4.6 V operating at $\sim 2 \text{ kA/m}^2$, requiring a molten salt cell separator and closely spaced electrodes. Stainless steels and the eutectic are thermodynamically stable with respect to lithium and lithium amalgam at operating temperatures.

Figure 1. The bipolar cell supports electrolytic production of lithium metal from aqueous solutions of its compounds. In the aqueous cell, a 1-2 at% amalgam is formed, which is subsequently refined across a low melting eutectic of LiI-CsI. Counter-current heat exchangers prevent heat loss from the amalgam circulation system, and an intermediate vessel held at 120 C prevents accidental entrainment of water.

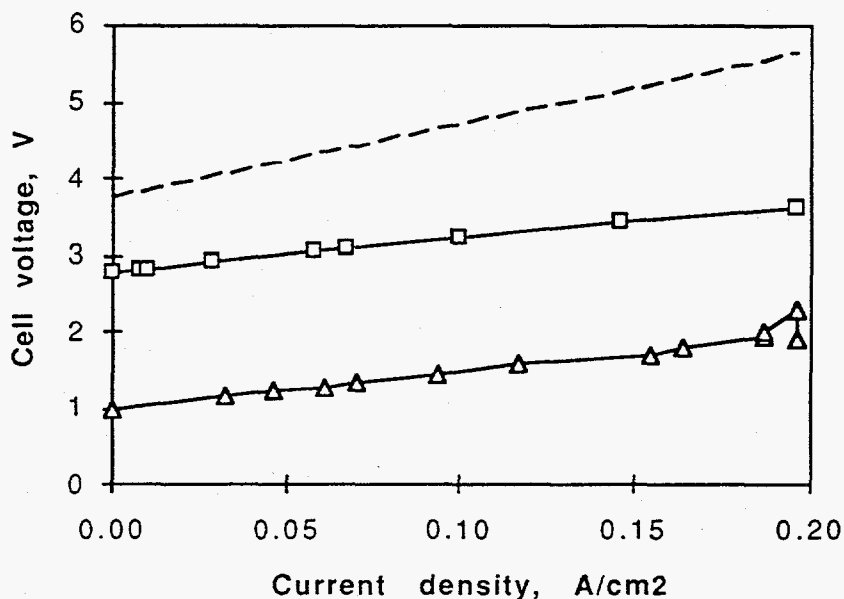


Figure 2. Cell potentials of molten salt cell (triangles), aqueous cell (squares) and total bipolar system showed a linear dependence on current density, indicating a dominance of the interelectrode gap resistance. The maximum efficiency of the cell is 93% (based on theoretical cell voltage of 3.45 V); practical efficiencies of 75% (at 4.6 V) are achievable at 1 kA/m², and at higher rates if electrode separations are reduced.