

ELECTROCHEMICAL PROPERTIES OF THE LAN TYPE LITHIUM ELECTRODES IN MELTED HIGH IONIC SALTS OF ALKALI METALS

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Introduction

Development of novel thermally activated Li/FeS₂ batteries have been attracting the attention of researchers in the field of power sources. In this paper we study lithium half-cell with a layer of alkali metal salts adhering to lithium electrode. The salts of different chemical composition [1] after melting constitute a high-conductive electrolyte, however most of the published works report on the use of (LiCl, KCl)_{eut.} Since lithium melting temperature amounts to 454 K and working temperature of thermal batteries is higher than 670 K the lithium electrode is most often made of lithium alloys LiSi or LiAl, that feature much higher melting temperatures. Another way to tackle the problem is the design of the LAN type. Here, the layer of lithium mixed with a powder of other metal, e.g.: Fe, is placed in a flat, thin-walled vessel where it adheres to a layer of salt-electrolyte with a filler, e.g.: MgO [2]. This ensures that molten lithium as well as salt-electrolyte are immobilized at high temperatures and the lithium half-cell of this type constitutes a compact and stable element of thickness less than 1.5 mm.

The anodic lithium reaction is: $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$, and the transitions for alloys are:



Experimental

The LAN lithium half-cells, whose electrochemical properties were studied were prepared by two ways. The half-cells of type (I) had the layer of Li(Fe) created by adding to lithium molten in the vessel a fine-dispersive Fe powder in the amount sufficient to immobilize the layer at temperatures up to 900K (ca. 90 wt. %). The type (II) half-cells were porous compacts with voids amounting to about 50% made of Fe powder of grain size up to 180µm. The compacts were heated in hydrogen atmosphere to ensure their good mechanical strength [3] and then in the atmosphere of dry argon saturated with molten lithium.

By comparison we have also evaluated alloy electrodes moulded of LiSi (40 wt.% Li) and LiAl (20 wt.% Li) powders with addition of 15 wt.% electrolyte salt (LiCl, KCl)_{eut.}, like in work [4]. Lithium electrodes together with the adhering layer of electrolyte, which contained of (LiCl, KCl)_{eut.}+ MgO filler (35 wt.%) were placed in a flat vessel extruded of Fe ARMCO foil. Then these half-cells along with the counter molibden electrode and the reference Ag/AgCl electrode were put in a quartz vessel for electrochemical measurements and immersed shallowly in the basic molten electrolyte. The studied Li electrodes had surface of 3cm². Electrochemical parameters of the half-cells were measured using a computer controlled stand, that made it possible to use continuous and pulse current loads (up to a few A/cm² of electrode) in accordance with the programmed algorithms.

Results

In figure 1 we show some selected characteristics of work potentials of the type II Li(Fe) LAN half-cells taken at continuous load of 1.5 and 2 A and cyclic pulse load of 0 to 3.5 A. In figure 2 are displayed typical characteristic of the anodic potential as a function of lithium utilization (Q/Q_{theor}) for different types of lithium electrodes in half-cells.

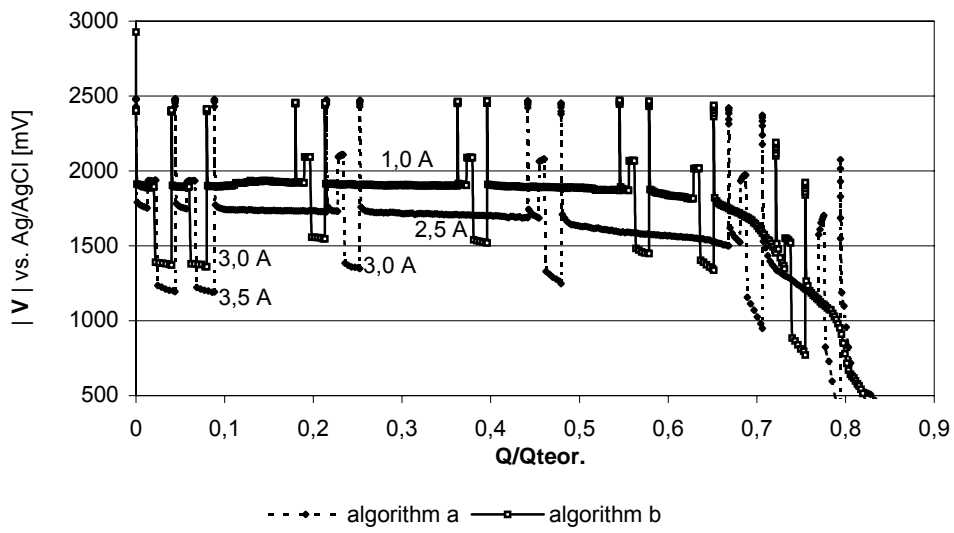


Fig. 1. Anodic potential characteristics $V/(Q/Q_{theor.})$ for lithium half-cells: $Li(Fe)LAN$ type II/ $(LiCl, KCl)_{eut.} + MgO$ (35 wt.%) under different current loads, according to algorithms:
 a.) continuous load 2000mA, puls loads 0.1000, 3000, 3500 mA.
 b.) continuous load 1500mA, puls loads 0.1000, 2500, 3000 mA.

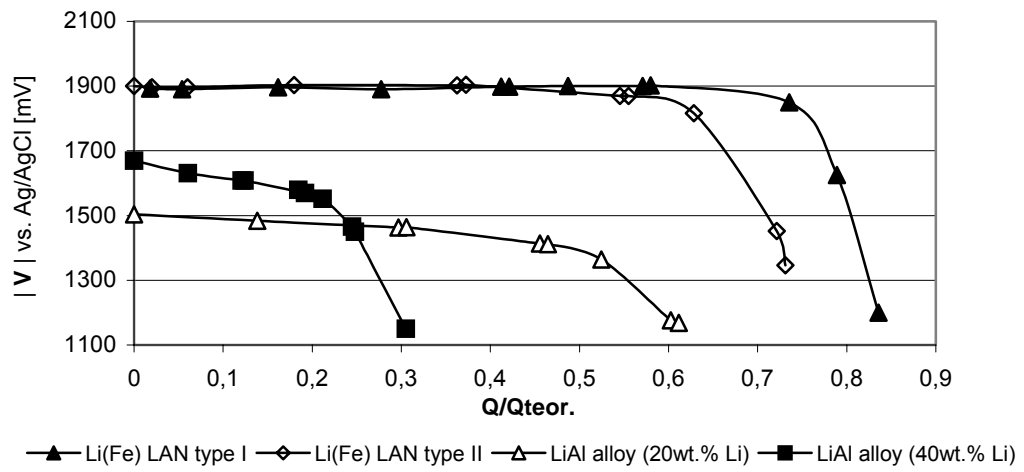


Fig. 2. Typical anodic potential characteristics $V/(Q/Q_{theor.})$ for different types of lithium electrodes in half-cells $Li/(LiCl, KCl)_{eut.} + MgO$ (35 wt.%).

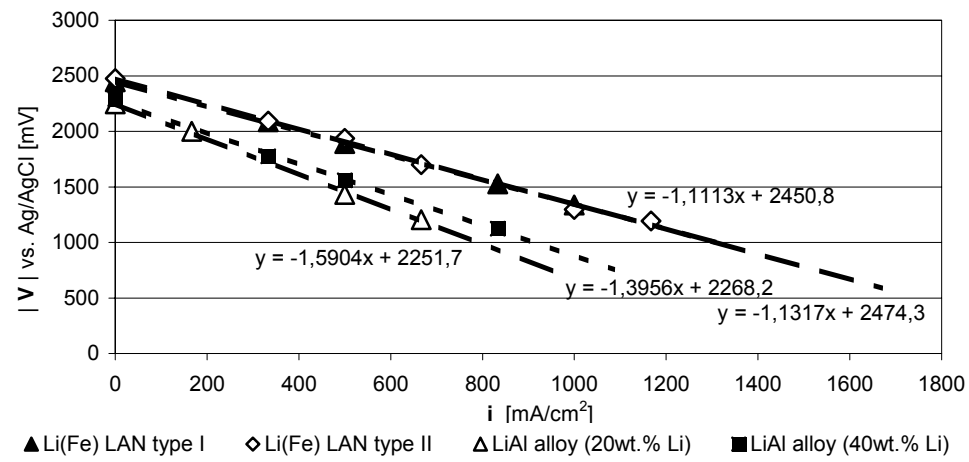


Fig. 3. The potential - current characteristics for different types of lithium electrodes in half-cells $Li/(LiCl, KCl)_{eut.} + MgO$ (35 wt.%).

In figure 3 we present dependences of work potentials of different lithium half-cells as a function of current load – $V(I)$. Slopes of the obtained lines characterize the cells internal resistance – R_w . In Table 1 we listed basic parameters essential for quality evaluation of various types of lithium electrodes.

Table I. Characteristics of halfcells: $Li/(LiCl, KCl)_{eut.} + MgO(35 \text{ wt. } \%)$ with various types of lithium electrodes.

Parameter	Unit.	Type of lithium electrode			
		Li(Fe)LAN type I	Li(Fe)LAN type II	LiAl alloy (20 wt.% Li)	LiSi alloy (40 wt.% Li)
Internal resistance of Li halfcell R_w	$\Omega \cdot \text{cm}^2$	1,11	1,13	1,60	1,40
Electrochemical Li efficiency [Q/Qteor.]·100%	%	81,5	78,9	67,6	30,2
Energy density of Li electrode	$\frac{W \cdot s}{g}$	2141	1034	2225	2358
Anodic potential (vs Ag/AgCl) half-cell 500mA/cm ²	mV	1820	1890	1460	1620

The parameters are useful for design of thermal batteries and cells. Measurements, that yielded these parameters were carried out at the same experimental conditions at 720K. We have been also studying other electrolyte salts [1]. The obtained results show that the Li(Fe) LAN half-cells feature much lower internal resistance and much higher electrochemical efficiency than half-cells having electrodes of lithium alloys. Their current efficiencies are also higher and they feature lower negative anodic potential. As a consequence the thermal Li/FeS₂ cells feature higher work voltage than the cells with electrodes of lithium alloys [2]. Limitations of the Li(Fe) LAN half-cells are associated with their low specific energy (energy yielded by unit mass) caused by high specific mass of iron. This refers especially for the type II compacts. Yet this type of half-cells feature some advantages, e.g.: fewer operation in the dry argon atmosphere, easy to automatize manufacture, high repeatability of properties.

Conclusion

The choice of lithium half-cell for use in the thermal Li/FeS₂ batteries (lithium alloys or the Li(Fe) LAN) depends on production technology, production scale, appropriation, and requirements the battery is expected to meet.

Acknowledgements

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