

All-Liquid Metal Battery

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A secondary battery (accumulator) employing molten metals or molten metal alloys as active masses at both electrodes and a molten salt as electrolyte in between is called an all-liquid-metal accumulator battery (LMB). Separation of the electrodes and the liquid electrolyte based on segregation caused by different densities and immiscibility of the materials is a characteristic feature. High coulometric storage capabilities of the molten-metal electrodes combined with the relatively low cell voltage and the high stability of the system and the operational principle yield a secondary battery suitable for grid applications and, in particular, for power-quality management and large-scale stationary storage.

Keywords: alloys ; molten metals ; all-liquid metal ; high-temperature battery ; stationary energy storage

High storage capabilities of electrodes in secondary batteries and consequently high energy densities can be achieved with conversion-type electrodes utilizing in particular light elements with electrode potentials as much different as possible and a solid ion-conducting electrolyte as the only practically feasible separation option between them. The sodium/sulfur battery using a molten sodium metal negative and a sodium polysulfide (instead of the plain sulfur electrode even more promising in terms of charge storage capability) is just one example ^{[1][2]}. Substantial drawbacks in terms of costs of the solid electrolyte and the cell container, low material conductances and long-term stability of such secondary systems discussed elsewhere in this collection are related to the relatively high operating temperatures necessary to keep the active electrode materials in a liquid state required for their proper operation and the solid ion-conducting electrolyte in a sufficiently good ionically conducting state. Possibly the elevated temperature of operation is a reason these batteries are also called molten salt batteries, but apparently this term is preferably applied to thermally activated primary batteries or to thermally rechargeable batteries. Systems called molten salt batteries show slight differences in terms of materials: This term includes the batteries addressed above as well as the liquid metal batteries presented in this entry. As already suggested by the designation molten salts employed in whatever function are the name givers. They have some common advantages:

- Cheap and abundant electrode materials;
- They have high rate capabilities because of fast electrode reactions and highly conducting materials;
- There are no problems related to shape change, etc., of the electrodes or the electrode/electrolyte interface and there is no dendrite formation during deposition, no phase change, and no grain size or grain boundary effects due to the continuous annihilation/recreation of the electrode;
- Assembly/production is simple because of “self-assembly” of the components;
- It is easy to scale up.

Starting from a much earlier idea, and inspired by cells for aluminum refining, the development expanded of secondary batteries utilizing molten metals or metal alloys as liquid-metal electrodes (LMEs) with a liquid electrolyte composed of a molten salt or an organic liquid. Major challenges, in particular the high self-discharge when using molten salts as electrolytes, and the desirable reduction of the operating temperature have been addressed. Possible developments and trends for liquid-metal batteries (LMBs) are indicated below.

The basic concept of this system and the closely related sodium-nickel chloride system ^[3] can be traced back to the Hoopes cell developed at ALCOA in the 1920s for winning of high-purity aluminium (refining) in a three-liquid-layer cell with a bottom raw aluminium layer, a molten salt mixture composed of AlF_3 , NaF and BaF_2 and on top the purified aluminium layer ^[4]. Separation of the layers was afforded by segregation of the three components based on immiscibility and density differences of the three melts (density stratification). Liquid metal electrodes are frequently encountered in electrolytic processes (production of sodium, aluminium etc.). Actually this concept can be related also to the gravity cells of the 19th century with e.g., the diaphragm-less Daniell-cell invented around 1860 by Callaud (crowfoot cell). In this

design the zinc sulfate solution layer of the negative half-cell with a slightly lower density resides on top of the copper sulfate layer of the positive half-cell with a slightly higher density. The limitations of this concept are obvious: Diffusion will cause the two solutions to mix and only a constant current drawn from the cell may slow down this unwanted effect. This limits usability of this type of cell. In addition movement of the cell or a very large current may result in unwanted mixing. Nevertheless, the cells were in use in the United States well into the 1950s with telegraph networks. Another problem—evaporation of water from the top electrolyte solution—was minimised by placing a layer of oil on top. A fundamental difference is the fact, that this cell is not a concentration cell (see below) like a LMB.

Basically the Hoopes cell may be considered as a battery, but the estimated cell voltage around 30 mV [5] does not make it an attractive one whereas this low voltage is of course highly advantageous for metal refining purposes wherein a low cell voltage directly affects energetical operating expenses. In the search for energy conversion systems possibly useful in space exploration Yeager reported a concept of a thermally rechargeable cell using an all liquid galvanic cell and a thermal regenerator wherein the cathode alloy formed during discharge of the galvanic cell was split into the constituents by heat supplied externally from solar collectors etc. [6]. Substantial research into thermoregenerative cells followed [7], for overviews see e.g., [5][8][9]. Success was moderate only; with the advent of lithium-ion batteries research almost completely stopped. With rapid growth of renewable energy use interest in heap and large-scale electrical energy storage caused by the highly volatile supply of energy from these sources has grown dramatically again with a focus slightly different from the one that propelled metal-ion batteries forward. Now large-scale, long-term stable and moderately expensive, even cheap, stationary storage suitable for grid-connected operation is of specific interest.

As reviewed elsewhere in detail numerous criteria including economic and ecological ones should be taken into account when selecting metals and their alloys for closer examination as material for a liquid metal electrode [8]. The relatively low gravimetric energy density is of minor importance when stationary applications are considered. From a technological point of view some major challenges can be identified

- High self-discharge because of significant solubility of many metals suggested as electrode material in the chemically aggressive molten-salt liquid electrolyte results in significant electronic conductivity of the melt;
- Operating temperatures are too high for the use of many popular construction materials.

Accordingly research has been focused into either new directions (e.g., using organic electrolytes as addressed below, thus avoiding the need for molten halide-liquid electrolytes or the use of solid ion-conducting electrolytes) or into using very-low-melting-point alloys.

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