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Entry

All-Liquid Metal Battery †

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† The more correct term would be accumulator, but it is less frequently used.

Definition: 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

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1. Introduction

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 caused thermal 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.

2. State of the Art

An early approach avoiding completely the solid electrolyte as a possibly problematic component employs only molten materials. Although possible cell voltages are limited (typically around 1 V) other advantages mentioned above are substantial. Early reviews are available [5,10]. The operating principle is depicted in Figure 1. The driving force is the affinity of metal A to form an alloy with metal B. Metals and alloy constituents for the negative electrode can bound in group 1 and 2 of the periodic table, for the positive electrode elements of group 12 to 16 are of interest (see [5]).

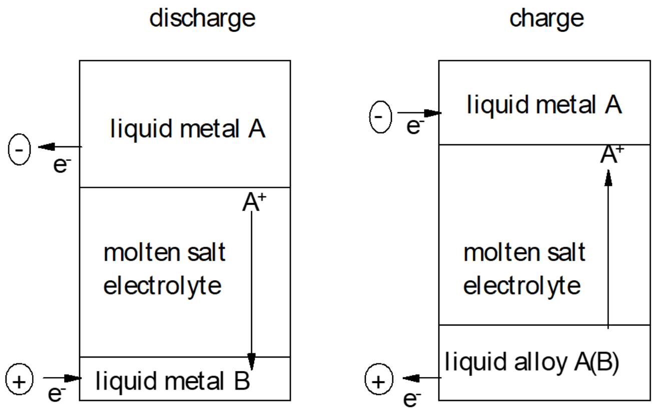

Figure 1. Operating principle of a LMB.

Selected properties of electrode materials and their combinations are listed in Table 1.

Table 1. Selected properties of electrode materials and their combinations (see also [2,8]).

Metal	T_m/°C	E_{SHE}/V	Q/mAh·g^{-1}	z	Studied Combinations #
Li	180	−3.04	3862	1	Li-Te, Li-Bi, Li-Sb, Li-Sb-Pb
Na	92.3	−2.71	1165	1	Na-Sn, Na-Bi (0.65 V), Na-Pb (0.3 V)
K	64	−2.93	685.4	1	K-Hg (0.72 V)
Ca	842	−2.87	1336	2	Ca-Bi (0.8 V), Ca-Sb (0.94)
Mg	650	−2.37	2205	2	Mg-Sb (0.39 V)
		$E_{Li/Li+}$/V			
Te	449.5	≈1.7	420	2	Li-Te
Bi	271.3	≈0.95	384	3	Li-Bi, Na-Bi
Sb	630.7	≈0.92	660	3	Li-Sb, Ca-Sb, Na-Sb (0.8 V)
Sn	231.9	≈0.80	225	1	Li-Sn, Na-Sn (0.35 V)
Pb	327.5	≈0.75	129	1	Li-Pb

Q: Specific capacity according to author's calculations, z: number of electrons transferred in the electrode reaction
#: Typical open circuit voltage in brackets.

With a lithium/molten lithium halide/antimony + lead alloy system a cell voltage around 0.8 V at an operating temperature of 450 °C with 98% Coulombic efficiency and 73% energy efficiency has been described. The molten salt electrolyte is a mixture of LiF, LiCl and LiI, the positive electrode a molten alloy of 30 mol% of Sb with 70 mol% of Pb. Despite the high lead fraction the higher voltage of the lithium/antimony couple determines the cell voltage. The substantially different densities and the immiscibility of the metals and the molten salt enable the simple setup as shown in Figure 2.

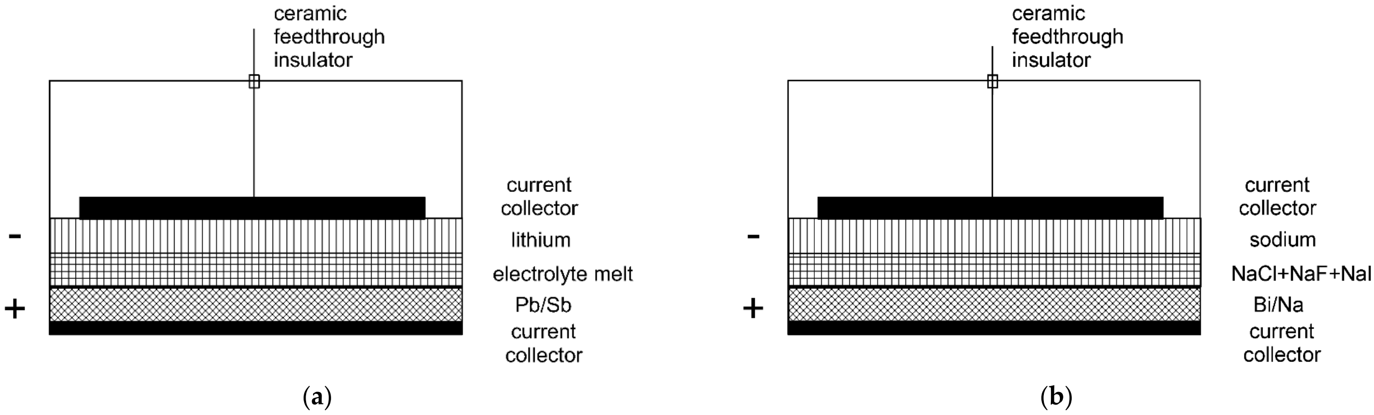

Figure 2. (**a**) Schematic cross section of an all-molten metal accumulator. (**b**) Schematic cross section of an Na | NaCl–NaF–NaI | BiNa cell.

The electrode reaction at the negative electrode (top) is

$$\mathrm{Li} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} \mathrm{Li}^{+} + \mathrm{e}^{-} \tag{1}$$

The reaction at the positive electrode (bottom), which may be considered as an alloying/dealloying reaction also, is

$$\mathrm{Li}^{+} + \mathrm{e}^{-} + (\mathrm{Sb}) \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} \mathrm{Li}(\mathrm{Sb}) \tag{2}$$

and the cell reaction

$$\mathrm{Li} + (\mathrm{Sb}) \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} \mathrm{Li}(\mathrm{Sb}) \tag{3}$$

Although the standard potential of a sodium electrode is less negative than that of a lithium electrode (this is more noble by about 0.3 V), the lower price of sodium and its less violent behavior in case of cell failure mean that its use is recommended instead of lithium. Accordingly a cell with a liquid-sodium negative electrode, a molten mixture of several sodium halides as electrolyte, and a sodium–bismuth alloy as a positive electrode, as sketched in Figure 2, is an option reported earlier [7,11,12].

The sodium activity in both electrodes differs; therefore, the cell may be called a concentration cell [7]. Accordingly the cell voltage depending on activities of the metal moving between the electrodes during discharge from the negative electrode (top) to the positive one (bottom) and during charge in the opposite direction can be calculated using the Nernst equation:

$$U = -\frac{R \cdot T}{z \cdot F} \ln a_{\mathrm{Na(Bi)}} \tag{4}$$

with the number of electrons transferred in the cell reaction $z = 1$ for this cell. Solubility of sodium in its molten halides is slightly larger than that of lithium [5], this negatively affects Coulombic and consequently energy efficiency as previously reported with typically 80% Coulomb efficiency [5]. Again optimization of molten salt electrolytes enabling lower sodium solubility is an approach, reducing the operating temperature of the devices also reduces solubility and thus self-discharge which has accelerated the search for materials enabling lower operating temperatures.

Using a liquid calcium-alloy negative and a solid particle antimony positive electrode with a $CaCl_2$-based molten salt electrolyte Ambri Inc. (Marlborough, MA, USA)has commercialized a cell which is assembled into a multi-cell battery storing 1 MWh electric energy at 250 kW power with >80% DC efficiency at 500 msec response time in a 10-foot container.

The system keeps its operating temperature without external heating; it can undergo multiple thermal cycles without deterioration. Compared with other systems superior safety is claimed. As reported before alloying calcium with magnesium significantly reduces self-discharge and the melting point of the negative electrode without magnesium participating in the electrode reaction [13]. Modification of the melt composition of the liquid electrolyte resulted in decreased calcium solubility and thus decreased self-discharge. The solubility of metals in halide metals differs substantially from metal to metal, thus selection of a combination of halide or halide mix with a metal should also be examined with respect to this property when looking for options to limit self-discharge [14,15]. Unfortunately metals like magnesium showing a low solubility in its molten halides [5] have higher melting points. Alloying may provide a pathway to lower melting points.

The advantages of the various proposed systems are the use of common and easily available active materials, the almost complete absence of electrode and cell degradation because of the continuous renewal of the electrodes by charge/discharge, the good scalability, and the extremely high current capabilities (up to 130 $kA \cdot m^2$). The latter advantage may turn into a problem because material fluxes induced by the high currents in the liquid metals (magnetohydrodynamic instabilities) may disturb the layered arrangement of materials enabled by immiscibility, and segregation may be disturbed to the point of short-circuit caused by contact between the molten electrodes penetrating the electrolyte melt [16].

Energy densities at the cell level are rarely reported (for a notable exception with 200.4 $Wh \cdot kg^{-1}$ see [17]), a range of values 50 to 200 $Wh \cdot kg^{-1}$ has been stated elsewhere [8].

3. Trends and Developments

Progress in the development of solid ion-conducting electrolytes (with CaF_2 as an early example [18] and $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ LLZTO as a more recent one [19]) has rekindled interest in using a solid electrolyte in a liquid metal battery instead of a molten salt electrolyte with its associated drawbacks, in particular fast self-discharge in case of metal electrodes showing solubility in the molten salt electrolyte. Studies of specific material properties like wetting of the solid with the LME have been reported, for a review see [20]. In such cell design detrimental effects of magnetohydrodynamic instabilities will be no problem anymore. Other options to suppress them are under investigation [16]. Increasing the thickness of the electrolyte layer as done in aluminium refining is a limited option because it raises the internal cell resistance and thus decreases energy efficiency of the cell. A reduction of operating temperature is possible when alloys and electrolytes with lower melting points suitable for operation at decreased temperatures become available. This approach has stimulated research in "fusible alloys" with this term designating alloys with lower melting points [19]. Decreased wetting of materials (as a current collector and in case of a solid electrolyte of this mostly ceramic material) at lower temperatures may pose challenges possibly growing with decreasing temperatures [10]. Alloys with melting points in the range of ambient temperature may permit the use of organic electrolyte solutions which generally show much lower solubility's for metals; in a typical example a liquid Na-K-alloy negative electrode was combined with a gallium-based binary or ternary alloy as positive electrode and an organic electrolyte solution of 1 M $NaClO_4$ in a mixture of DME/FEC [20]. Environmental concerns sometimes vented when the in some cases highly reactive constituents of LMBs are considered have been addressed when suggesting a Li/Sb-Sn cell [17].

Because both the molten electrodes and the molten salt electrolytes are sensitive towards moisture and possibly also to other constituents of the ambient atmosphere effective sealing of cells is important, because the chemical reactivity of the used cell ingredients selection and application of sealing materials are challenges asking for further improvements. Similar considerations apply to cell construction materials [5]. Up to 200 °C elastomeric compression seals are feasible, they meet the requirement of being electrically insulating. For higher temperatures adhesive sealing systems are explored [5].

4. Conclusions and Prospects

The conversion reaction of the electrode materials in LMBs during their electrode reactions equivalent to their renovation causes cyclic regeneration of the active materials, essentially inhibiting problems commonly associated with electrode degeneration during battery cycling with solid electrodes. Liquid-metal batteries are particularly suitable for large-scale electric energy storage in stationary applications both for power-quality management and for remote-area power supply on time-scales ranging from very short (as a primary reserve) up to long-term storage, provided that the issue of self-discharge can be resolved. From economical, ecological, and technological points of view LMBs appear to be an interesting and valuable option for electric-grid use. Further research into materials that enable lower operating temperatures and slow self-discharge will improve these perspectives.

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