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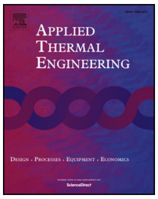

Research Paper

Electromagnetically driven convection suitable for mass transfer enhancement in liquid metal batteries

Norbert Weber[a,*], Michael Nimtz[a], Paolo Personnettaz[a,c], Alejandro Salas[a,b], Tom Weier[a]

[a] Helmholtz-Zentrum Dresden – Rossendorf, Bautzner Landstr. 400, Dresden, Germany
[b] Instituto Tecnológico y de Estudios Superiores de Monterrey, Monterrey, Mexico
[c] Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

HIGHLIGHTS

- Electro-vortex flow is able to enhance mass transfer in liquid metal batteries.
- Electro-vortex flow will induce flow velocities in the order of a few mm/s.
- The stable thermal stratification will dampen only vertical flows.
- A lateral current supply is better suited than a centrical supply.
- Vertical magnetic fields will not always lead to swirling flow.

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ABSTRACT

Liquid metal batteries (LMBs) were recently proposed as cheap large scale energy storage. Such devices are urgently required for balancing highly fluctuating renewable energy sources. During discharge, intermetallic phases tend to form in the cathode of LMBs. These do not only limit the up-scalability, but also the efficiency of the cells. Generating a mild fluid flow in the fully liquid cell will smoothen concentration gradients and minimise the formation of intermetallics. With this application in mind, electro-vortex flow is studied numerically. A recent LMB related experiment is simulated, and it is further discussed how the feeding lines to the cell can be optimised to enhance mass transfer. The Lorentz forces have to overcome the stable thermal stratification in the cathode of the cell; it is shown that thermal effects may reduce electro-vortex flow velocities considerably. Finally, the influence of the Earth magnetic field on the flow is studied.

1. Introduction

Integrating highly fluctuating renewable energy sources (such as photovoltaics and wind power) into the electric grid calls for large scale energy storage. Such storage must be, first of all, cheap and have a long life time [1]. Typical desired values are 7 000–10 000 cycles [1,2] and a price of the active materials of 100 $/kWh [1–3]. The liquid metal battery (LMB) promises both. After being intensively investigated in the 1960s, and abandoned later, LMB research experienced a renaissance some ten years ago. For an overview of the pioneering work, see [4–6] (recommended [7]) and for the recent work [1,3].

Fig. 1a shows a sketch of a typical LMB. A dense metal on the bottom (cathode, positive electrode) is separated by a liquid salt from a lighter metal at the top (anode, negative electrode). All three phases float above each other; the salt acts as the electrolyte. The word “liquid metal battery” names only a family of electrochemical cells (which may consists of many different active metals combinations). Typical anode materials are Ca, Li, K, Na and Mg while Bi, Hg, Pb, Sb, Sn, Te and Zn are often used as cathode metal [4,8–18].

During discharge, the upper metal is oxidised, crosses the electrolyte layer and alloys in the bottom layer with the dense metal (“concentration cell”). It is well known that dthe ohmic resistance of the electrolyte layer represents by far the most important overvoltage [3,19–23]. However, at higher discharge currents concentration polarisation may become important, too [1,12,24–27]. Example: when *discharging* a Li||Bi cell, Li-rich alloy will concentrate at the cathode-electrolyte interface. When a certain local concentration is exceeded, a solid intermetallic phase (Li_3Bi) will form (Fig. 1a) [4,28]. Such intermetallics often float on the cathode metal [29]. Sometimes they expand during solidification. As the walls impede a lateral expansion, the

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* Corresponding author.
E-mail address: norbert.weber@hzdr.de (N. Weber).

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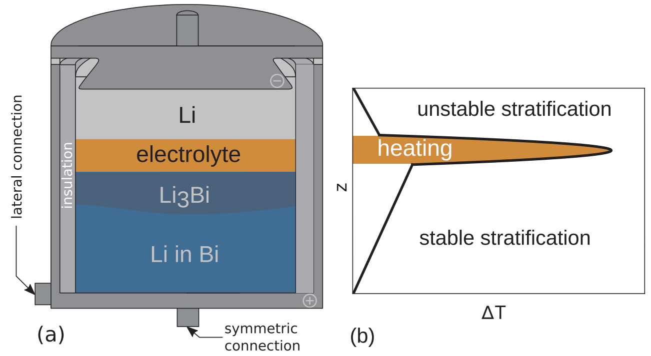

Fig. 1. Sketch of a typical Li||Bi liquid metal battery with an intermetallic phase forming in the bottom electrode (a) and vertical temperature distribution in the three layers (assuming pure diffusion and no intermetallic phase) (b).

intermetallic will form a dome until finally short-circuiting the electrolyte. Especially in Ca based cells, locally growing dendrites may additionally short-circuit the cell [30]. Besides of all the mentioned drawbacks, the formation of intermetallics has one advantage: it removes anode metal from the melt and keeps thereby the voltage constant. It should be also mentioned that some intermetallics have high electrical resistances while others are good conductors.

When *charging* the cell in Fig. 1a, the cathode-electrolyte interface will deplete of Li and a similar concentration gradient may develop [28]. This effect is undesirable, too. Finally, all the same effects may theoretically happen in the anode compartment, too, if an alloyed top electrode is used (e.g. Ca-Mg [16,31]). However, such effects were not reported, yet.

It was early proposed that a mild fluid flow may counterbalance concentration gradients and increase thereby the efficiency of LMBs [4,27,28]. While “mechanical stirring” [4,27] seems difficult to realise, electro-vortex flow (EVF) may be a very good option [32–34]. Simply saying, EVF always develops when electric current lines are not in parallel. The magnitude of EVF can therefore easily be adjusted by choosing the diameter/geometry of the current collectors and feeding lines appropriately. EVF drives a jet away from the wall, forming a poloidal flow [35]. For a classical example of the origin of EVF, see Lundquist [35] and Shercliff [36], for a good introduction Davidson [37] and for a detailed overview including many experiments Bojarevics et al. [38]. The special relevance of EVF for LMBs is outlined by Ashour et al. [34]. It should also be mentioned that other flow phenomena like the Tayler instability [39–47], Rayleigh-Bénard convection [48,49] or interface instabilities [50–56] may enhance mass transfer in LMBs, as well. Finally, a localised heating or cooling inducing thermal convection may be a very good option for mixing, too [57,58] (for 3D studies of heat transfer in Li-LMBs, see [49,59]).

This article is dedicated (mainly) to electro-vortex flow. It’s aim is twofold: first, we will show how the connection of the supply lines to the cell influences the flow. Second, we study how electro-vortex flow and stable thermal stratification interact. For this purpose we combine numerical simulation with a simple 1D heat conduction model. These two models – and the experiment which inspired our studies – are described in the following section.

2. Physical, mathematical and numerical model

In this section we will first discuss heat generation and thermal boundary conditions for a liquid metal battery (LMB), and present then the experiment [60] which inspired this article. Thereafter, we explain the way in which we estimate the temperature gradient appearing in the bottom electrode of an LMB. Finally, we give an introduction to the 3D numerical model used.

2.1. Heat management system, heat sources and thermal boundary conditions

We will explain in the following our choice of thermal boundary conditions and why we include Ohmic heating as the only heat source.

As an LMB has a comparably low cell voltage, several cells will be connected to a cell stack. Although up to now little information about LMB cell stacks was published, much can be learned from Li-ion cell stacks. Operating at high temperature, the whole stack must be insulated. Nevertheless, the stack might possibly need even cooling during operation [61–64]. The thermal management system is of crucial importance for an optimal operation [65,66] and needs to be optimised [67,68] to ensure only small deviations from the working temperature [69–71]. The system will surely be very complex, possibly including heat pipes [72,73] or phase change materials for thermal energy storage [74–82] in order to avoid freezing of the cells. Research on thermal engineering of LMBs is highly needed.

A single LMB, as illustrated in Fig. 1a, needs to be electrically insulated at the side walls. The current collectors will typically be made of steel. It is therefore reasonable that heat exchange between thermal management system and a single cell happens only through the current collectors, and not the side walls. A perfect thermal management system would hold the current collectors always at the operation temperature. We will assume therefore a constant temperature boundary condition at top and bottom, and an adiabatic one at the sidewalls.

During charge and discharge, heat will be generated by a number of different overvoltages. As charge transfer happens very fast at the liquid-liquid interfaces, the corresponding overvoltage is negligible [10,20,22]. Ohmic losses are well known to be the most important heat source of an LMB [3,19–23,83]. The electrolyte layer has typically a resistance 10^3–10^4 times higher than the liquid electrodes – most heat will always be generated in the liquid salt layer. A current study [84] shows that the heat of reaction (or entropic heat) may reach up to 30% of the total heat generated in a Li||Bi cell. However, this value depends very much on the state of charge and chemistry used. We will include therefore only Ohmic heat generation in our study.

2.2. Liquid metal electrode experiment & material properties

Fig. 2 illustrates the mentioned experiment, conducted by Kelley & Sadoway [60]. A cylindrical steel vessel contained a melt of eutectic lead-bismuth. An electric current (up to 0.375 A/cm^2) was applied between a bottom and top electrode. The bottom current was supplied centrically or laterally. The upper electrode consisted of a nickel-iron foam; such foam is often used in LMBs to contain the anode metal [3]. As the setup was heated from below, Rayleigh-Bénard cells appeared. If an internal current was applied, the flow became much more regular at 0.05 A/cm^2. It was deduced by the authors that convection cells align with the magnetic field. We will demonstrate how electro-vortex flow may give an alternative explanation for the increase in order.

We use the following material properties of lead bismuth eutectic at 160 °C [34]: a kinematic viscosity of $\nu = 2.7 \cdot 10^{-7}$ m^2/s, a thermal expansion coefficient of $\beta = 1.3 \cdot 10^{-4}$ K^{-1}, an electrical conductivity of $\sigma = 9 \cdot 10^5$ S/m, a density of $\rho = 10\,505$ kg/m^3, a specific heat capacity of $c_p = 148$ J/kg/K, a thermal conductivity of $\lambda = 10$ W/m/K, a thermal diffusivity of $\alpha = 6 \cdot 10^{-6}$ m^2/s, a Prandtl number of $Pr = 0.04$ and a sound velocity of $u_s = 1765$ m/s [85–87]. The electrical conductivity of the vessel is assumed to be $\sigma = 1.37 \cdot 10^6$ S/m and of the wires and copper plate $\sigma = 58.1 \cdot 10^6$ S/m. The electrical conductivity of the Fe-Ni foam is not easy to determine [88,89]. Especially, because we do not know the porosity and saturation of the foam, we assume an electric conductivity of $\sigma = 1.37 \cdot 10^6$ S/m without further justification.

Geometrically, the described experiment perfectly represents a liquid cathode of an LMB. However, the temperature gradient in a working LMB depends on the boundary conditions. For a single cell