Liquid metal batteries - materials selection and fluid dynamics

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Abstract. Liquid metal batteries are possible candidates for massive and economically feasible large-scale stationary storage and as such could be key components of future energy systems based mainly or exclusively on intermittent renewable electricity sources. The completely liquid interior of liquid metal batteries and the high current densities give rise to a multitude of fluid flow phenomena that will primarily influence the operation of future large cells, but might be important for today’s smaller cells as well. The paper at hand starts with a discussion of the relative merits of using molten salts or ionic liquids as electrolytes for liquid metal cells and touches the choice of electrode materials. This excursus into electrochemistry is followed by an overview of investigations on magnetohydrodynamic instabilities in liquid metal batteries, namely the Tayler instability and electromagnetically excited gravity waves. A section on electro-vortex flows complements the discussion of flow phenomena. Focus of the flow related investigations lies on the integrity of the electrolyte layer and related critical parameters.

1. Introduction

The increasing penetration of renewables into the energy system poses a number of challenges. One major aspect is that electricity from sun and wind is available only intermittently and with varying timescales. This is in stark contrast to traditional energy systems where electricity generation is driven by demand. Electricity grids with a large share of intermittent input call for storage if electricity demand shall be satisfied independently of daytime and weather conditions [1]. At least equally important, grid stability may suffer from insufficient storage if generation and demand cannot be balanced [2]. Obviously, cost is a determining factor in selecting storage options [3] especially if the massive capacity needed by the economy of a whole country is considered.

Liquid metal batteries (LMBs) might be part of a solution to the gap in massive and economically feasible large-scale stationary storage [4]. LMBs consist of three liquid layers segregated on the basis of their differences in density (\(\rho\)), see Fig. 1. An alkaline or earth alkaline metal floats on top, a heavy metal or half metal fills the bottom space and a molten salt immiscible with both metals is sandwiched in between. Obviously, the operating temperature of an LMB has to exceed the melting temperatures of all cell ingredients and therefore LMBs belong to the high temperature systems. Hence, reactions are comparably fast which implies...
rapid charge transfer but also increased corrosion rates. Likewise, diffusion is much faster than in solids and the absence of solid structures eliminates many mechanisms otherwise causing cell degradation. Fast transport and rapid kinetics can result in extreme current densities of up to 130 kA/m$^2$ [5] allowing for the simple cell construction sketched in Fig. 1a without compromising on power density. This simple cell construction, in turn, facilitates scale-up on the cell level.

Already in the 1960, LMBs were intensively investigated (see, e.g., [6]), mainly as components of energy conversion systems named “thermally regenerative electrochemical systems” (TRES); an overview can be found in [7, 8]. However, using LMBs for off-peak stationary storage was envisioned as well [5]. Active material combinations used at that time were Na||Sn [9, 10] and K||Hg [11] for the reason of good thermal separability. Higher cell voltages could be achieved, e.g., with Na||Bi, Li||Bi, Li||Te, and Li||Se, [6] where in the latter two systems the bonds between Li and the cathode metal are too strong to allow for separation by distillation [12]. According to a recent review by Kim et al. [4] interest in LMBs waned in the 1970s because the low specific energy rendered LMBs unattractive for mobile applications.

Currently, we are observing a renaissance of LMBs sparked and led by the MIT group around Donald Sadoway. Primary targets are now a cost driven development and grid-scale energy storage. Active materials currently under investigation include Mg||Sb [13], Ca||Bi [14], Li||Sb-Pb [15], Li||Bi [16], and Na||Pb-Bi [17].

The completely liquid interior and the high current densities characterizing LMBs can cause a number of fluid flow phenomena that will be primarily important for the operation of future large cells. However, individual aspects, especially mixing in the cathodic compartment, are of immediate relevance for today’s smaller cells as well. Following a section on electrochemistry, we will discuss three electromagnetically driven flow phenomena, namely the Tayler instability, electro-vortex flows, and interface instabilities.

2. Electrochemistry

Usually a liquid metal cell is a simple concentration cell and the electromotive force (EMF) or open circuit voltage (OCV) of the cell is solely given by the activity of the alkaline metal in the cathode alloy. This can easily be seen by considering the equations for the transfer reactions at the two interfaces (see Fig. 1b). For the anode/electrolyte interface (1) and the
electrolyte/cathode interface (2) during discharge, we have

\[ M \rightarrow M^{z+} + ze^- \]  
\[ M^{z+} + ze^- \rightarrow M(N) \]

with \( M \) denoting an alkali or earth-alkali metal (e.g., Li, Na, Mg) and \( N \) referring to the heavy or half metal of the cathode (e.g., Bi, Pb, Sb). \( z \) is the valency, i.e., 1 for alkali and 2 for earth alkali metals. The equilibrium potentials \( \varphi_0 \) of both half-cells are then

\[ \varphi_0(1) = \varphi_{00} + \frac{RT}{zF} \ln \frac{a_{M^{z+}}}{a_M} \]  
\[ \varphi_0(2) = \varphi_{00} + \frac{RT}{zF} \ln \frac{a_{M^{z+}}}{a_{M(N)}} \]

with \( \varphi_{00} \) denoting the standard potential, \( R \) the universal gas constant, \( F \) the Faraday constant and \( a \) the activity of the metal in the pure (M), ionic (M\(^{z+}\)) and the alloyed (M(N)) state. From this, the cell’s OCV determined by the difference of the two electrode potentials \( \varphi_0(2) \) and \( \varphi_0(1) \) results as

\[ E_{OC} = -\frac{RT}{zF} \ln a_{M(N)} \]

since the standard potential of both half cells is identical and the activity of the pure anode metal is one by definition. The terminal voltage \( E \) available under current flow is the difference of the OCV and several terms describing voltage losses, i.e., polarizations (cf. [12] and Fig. 1b):

\[ E = E_{OC} - IR_E - \eta_{c,a} - \eta_{c,c} - \eta_{a,a} - \eta_{a,c} \]

with the ohmic losses in the electrolyte of resistance \( R_E \) due to the current \( I \), the concentration polarizations at the anode \( \eta_{c,a} \) and cathode \( \eta_{c,c} \) and the corresponding activation potentials \( \eta_{a,a} \) and \( \eta_{a,c} \).

As mentioned in the introduction, LMBs have to operate at elevated temperatures in order to keep the active materials and the electrolyte in the liquid state. Conductive heat loss through the walls is proportional to the temperature gradient and can be understood as self-discharge. The higher the temperature, the faster the chemical reactions and the more serious material degradation phenomena become. This alone would be motivation enough to aim at lowering the operating temperature of the cells. Concerning flow measurements, temperatures of less than 230°C are required for typical Ultrasound Doppler Velocimetry (UDV) transducers to be directly applicable to the cells. This requirement considerably restricts the available options and is not easily fulfilled. While the typical alkali metals used for the anodes (Na, Li) have low enough melting temperatures (\( T_m \)) by themselves and suitable cathode alloys with \( T_m \) well below 200°C are likewise available (e.g., Pb-Bi), the melting points of traditionally used molten salt systems exceed 350°C and often lie beyond 450°C. Lower melting salt systems typically contain components that are highly hygroscopic (e.g., NaOH) and/or are not stable in direct contact (e.g., NaAlCl\(_4\)) with liquid alkali metals. While interesting developments in terms of low melting salts are underway [17, 18], room temperature ionic liquids (RTILs) pose an alternative option to molten salts. RTILs [19] have found increasing interest during the last decades due to their non-volatility, non-flammability, wide temperature range of operation and high conductivity. In addition, RTILs are already investigated as electrolytes for rechargeable batteries [20, 21]. Therefore, testing the applicability of RTILs as possible low temperature electrolytes in LMBs seemed a logical step to try. The remainder of the section is divided into a first part dealing with traditional molten salt based systems and a second one describing cells using RTILs.
2.1. Molten salt electrolytes

Na is the natural first choice for the anode material because of its abundance [22] and its low price. A combination with Bi gives a comparably high cell voltage (∼0.9 V near full charge, see [6]) that exceeds that of several other pairings, e.g., with Pb, Sn, or Hg [23,24].

Several open cells based on crucibles of 30 mm diameter containing Bi and the molten salt mixture were designed with the aim to provide maximum optical access. The negative pole was either formed by a Ta spiral holding a drop of liquid Na or an Inconel® alloy 625 foam wetted with Na, see the insets in Fig. 2a and Fig. 2b. An eutectic mixture of KCl-LiCl-NaCl (36-55-9 mol%, melting point around 346 °C [25]) served as electrolyte. Single cells were operated in an Ar-filled glove-box (cO₂ and cH₂O < 0.1 ppm) at 450 °C. Heating for the cell was provided by a hot plate situated underneath the cell. This kind of cell setup entails an excess of Bi: typically about 100 g of Bi (0.48 M) were combined with ca. 40 mg of Na (1.7 mM) resulting in a relatively large and comparably stable cell voltage. Current densities (calculated with the projected area of the foam anode) shown in Fig. 2a approach 2.5 A cm⁻² during short circuit (Fig. 2b) and are in the range of those measured by [6] for the Na||Bi system. As already observed by those authors, the \( E(j) \)-dependency is almost linear over the whole current density range. This suggests that all polarizations listed in Eq. (6) can be neglected compared to the ohmic losses. This is remarkable because unlike the salt mixture (NaCl-NaF-NaI, 31.6-15.2-53.2 mol%) used by Cairns et al. [6] that contains only Na⁺-ions, here mixed cations with only 9 mol% Na⁺ are present in the electrolyte. Especially under high current conditions, mass transfer limitations in the electrolyte could therefore be expected. Their absence signals good mixing in the electrolyte and indeed intense convection could be observed (with velocities of about 4 mm s⁻¹ to 34 mm s⁻¹ depending on the cleanness of the cathode/electrolyte interface). Flow visualization in a limited sense is enabled by the solubility of Na in its salts resulting in the black clouds that form in the electrolyte near the drop anode (Fig. 2a inset) and disperse rapidly in the electrolyte. The experimental setup enforces convection by heating from below and leaving the large free surface surrounding the Na-drop open to the environment of the glove-box. The electrolyte surface is cooled by convection, radiation, and evaporation of Na since its vapor pressure at the cell temperature is considerable. Na vapor forms the greenish-yellowish clouds seen in the inset of Fig. 2a.
Na solubility in the molten salt electrolyte additionally leads to partly electronic conductivity thereby limiting Coulombic efficiency. Fig. 3a shows the cycling behavior of two open cells with an alkali metal drop anode. Na solubility leads to a steady decline of the open circuit voltage over time and eventually to a situation where the Na available in the anode is not sufficient for a full discharge anymore (~9 h). In contrast, Li||Bi shows a stable $E_{OC}$ for the full time span. While Li itself is almost insoluble in its molten salts, the intermetallic phase Li$_3$Bi has some solubility in molten salts. The tinting of the electrolyte visible in Fig. 3b is possibly caused by dissolved Li$_3$Bi. According to Vogel et al. [26] Li$_3$Bi solutions have a reddish color. During short circuit discharge, current densities beyond 2 A/cm$^2$ were measured. The Ni spiral pinning the Li drop anode can be completely emptied during discharge. Recharging of the fully depleted spiral is possible as well.

While cells containing molten alkaline metals should generally be operated in the absence of oxygen and moisture, Li anodes require N$_2$ removal that is not necessary in case of Na. However, a well controlled Ar atmosphere is sufficient in both cases.

2.2. Ionic liquid electrolytes

The design and operation of a low temperature liquid metal battery based on an ionic liquid as electrolyte was reported for the first time by our group in [27].

The Na||Pb-Bi liquid metal cell operated at 160°C has shown promising results, although system functionality was limited up to now to only four charge/discharge cycles at about 50% depth of discharge [27]. Molten Na metal-electrolyte interaction enhanced by the presence of ppm water traces in the RTIL are probably the reason for the limited performances. Further investigations are under way in order to understand the mechanism behind this interaction. Based on these findings we extended the investigations and focused on a more stable chemistry with improved characteristics. It is comprised of Li and Ga as the negative and positive electrodes, used in combination with an RTIL as an electrolyte, namely the 1 mol/l lithium bis(trifluoromethylsulfonyl)imide (Li[TFSI]) in 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl)imide ([BMP][TFSI]). The battery operates at 220°C which is a relatively low temperature for an LMB and showed good electrochemical performance at low current densities [28]. Several cells of ca. 200 mAh theoretical capacity were assembled inside an argon atmosphere glove-box and galvanostatically cycled at different current densities ranging from 10 mA cm$^{-2}$ (corresponding to a C/40 rate) to 32 mA cm$^{-2}$ (corresponding to a C/12 rate). The batteries cycled at 10 mA cm$^{-2}$ to a 50% depth of discharge were operated continuously for...
about 600 hours, i.e. over 14 charge-discharge cycles with stable cycling performances. The near-
constant voltage plateau observed in the galvanostatic voltage-capacity profile and the absence of
a sharp voltage drop showed that during the operation of the battery no intermetallic compounds
are formed, in agreement with the data from the Li-Ga binary phase diagram. During the tests
the cells exhibited a round-trip Coulombic efficiency of 97% with an average value of voltage
efficiency of 66% resulting in an overall energy efficiency of 65% [28].

In the case of higher charge/discharge current densities (16 mA cm\(^{-2}\) and 32 mA cm\(^{-2}\)), the
battery exhibits higher voltage drop and rapid discharge capacity fade. X-Ray Photoelectron
Spectroscopy (XPS) reveals that during battery operation the RTIL electrolyte decomposes
already after the first discharge cycle and the reduction products accumulate in the Ga-cathode.
Next to the metallic Ga in the bulk of the cathode, two Li-Ga intermetallic species are
also detected: Ga\(_{7}\)Li\(_2\) and Ga\(_{14}\)Li\(_3\). Electrochemical impedance spectroscopy indicated mass
transport limitations of the Li cations in the Ga positive electrode [28]. Further, the cycling
behavior of a Li||Ga cell with ca. 40 mAh theoretical capacity is shown in Fig. 4. The cell was
assembled inside the glove-box under a dry and high purity argon atmosphere, then transferred
outside the glove-box and heated to 220 °C by means of a tube furnace. A continuous and
similar evolution of the potential with time can be perceived. The shape of the charge-discharge
curves shows then a good reversibility of the Li\(^+\) intercalation-deintercalation process. However,
a continuous capacity fade with each cycle is observed which is due to the depletion of Li cations
in the RTIL electrolyte and in the Ga bulk by the formation of intermetallic compounds. Further
investigations are needed in order to stabilize the tested low temperature systems and enhance
the cyclability and mass transport within the cells. The operating temperatures of 160 °C and
220 °C allow the use of commercially available UDVs sensors, which is indispensable for collecting
operating experience with UDVs in the multilayer systems inside model LMB cells.

3. Fluid Dynamics
As already mentioned in the introduction, fluid dynamics of LMBs is quite involved and includes
a multitude of fluid flow phenomena like Rayleigh-Bénard convection driven by the Joule heating
of the electrolyte layer, Marangoni convection due to surface-tension differences resulting from
concentration and temperature gradients, solutal convection in the cathode, etc. The remaining
sections will deal mainly with magnetohydrodynamic (MHD) aspects that will become important

![Figure 4. Electrochemical performances of a Li||Ga cell cycled at ±4 mA cm\(^{-2}\) and operated
at 220 °C: voltage curves as a function of capacity for the ten first cycles (full discharge, a) and
evolution of the capacity with cycling (b).](image-url)
for LMBs with large cell sizes. We start with the Tayler instability, discuss electro-vortex flows, and conclude with a paragraph on interfacial instabilities.

3.1. Tayler instability

The Tayler instability (TI) is a current driven kink-type instability akin to the instability of the z-pinch in plasma physics. A cylindrical conductor with a circular cross section bearing an axially directed homogeneous current density $J_0$ produces a magnetic field $B_0$ with a purely azimuthal component $B_\varphi$. The Lorentz force resulting from $J_0$ and $B_0$ is an inwardly directed pinch force that is prone to an axisymmetric "sausage" or a non-axisymmetric "kink" instability mode. For liquid metals that possess a considerable kinematic viscosity $\nu$ when compared to plasmas and have a finite electrical conductivity $\sigma$, the onset of the TI can be described by a critical value of the Hartmann number $Ha = B_0 R \sqrt{\sigma/\rho \nu}$, where $B_0 = B_\varphi(R)$ is the azimuthal magnetic field at the cylinder radius $R$, $\rho$ the liquid's density, $I$ the total current, and $\mu_0$ the vacuum permeability, respectively. TI will set in as a flow with a dominant azimuthal mode $m = 1$ if $Ha$ exceeds a value of about 20 as was predicted by Rüdiger et al. [29] and was experimentally confirmed only recently by Seilmayer et al. [30].

The characteristic velocity of the TIs saturated state scales with $Ha^2$. According to Eq. (7), the critical $Ha$ can directly be transferred to a critical current depending only on the material properties of the liquid metal considered. Doing so (cf., Tab. A.1 in [31]) it becomes apparent that - without considering possibly different aspect ratios - typical anode materials (K, Li, Na, Mg) with critical currents between 1 and 2 kA are more prone to the TI than the denser and less conductive metals used for the cathodes. That means that TI is less likely to contribute to cathode mixing but should be considered as a possible culprit endangering the integrity of the electrolyte layer. Note that it is indeed the total current and not the current density that determines criticality in case of the TI.

As can be seen from the stability criterion derived by Vandakurov [32] and Tayler [33]

$$\frac{\partial (r B_\varphi^2(r))}{\partial r} > 0,$$

the kink-type instability depends on the radial ($r$) dependence of $B_\varphi$. In turn, Eq. (8) opens the possibility to stabilize against the TI by changing $B_\varphi(r)$ as suggested by Stefani et al. [34]. This type of stabilization can be achieved by applying a bore around the cylinder axis changing the cross section from a cylindrical one to an annular gap. This simple measure has proven to be effective in numerical [31] as well as experimental [30] investigations. Increases in critical current are however moderate and the cell shape changes in a way that decreases the overall energy density. Using a small isolated inner bore to hold a massive wire feeding back the cell current along the axis can be shown to stabilize the cell against TI for any current [34] in the inviscid and non-resistive case. Numerical investigations [31] indicate that about one third of the cell current might suffice for stabilization if the beneficial effect of viscous and resistive damping is taken into account.

In plasma physics it has long been recognized that current-driven instabilities can be stabilized by applying an axial magnetic field. The Kruskal-Shafranov condition describes basically a ratio of the axial to azimuthal field above which kink-type instabilities cease to occur. Consequently, adding an axial field to a cylindrical LMB by means of a Helmholtz-like coil can stabilize against the TI as well. Even a horizontal magnetic field has a similar but weaker effect [31]. Stabilization by different magnetic field arrangements was compared by Stefani et al. [35]. Seemingly an axial...
It is however inspirational to compare these technical stabilization measures with saturation mechanisms [37] found at different magnetic Prandtl numbers (Pm=νμ0σ) as is done in Fig. 5.

For astrophysical bodies like the sun, magnetic Prandtl numbers are typically high and in the order of 10^{-2}. To access the modification of the electromagnetic fields by the flow we can resort to mean-field MHD [38] and the α effect introduced by Krause and Rädler for helical turbulence.

The α effect drives an electromotive force parallel to the prevailing large scale magnetic field $\bar{B}$. In a similar way turbulence leads to an increase in resistivity by the β effect. The mean electromotive force can then be written as $\varepsilon = \alpha \bar{B} - \beta \nabla \times \bar{B}$. α essentially produces a mean axial magnetic field $\langle b_z \rangle$ while β induces a mean axial current $\langle j_z \rangle$ opposing the applied one $J_0$. For high Pm $\langle b_z \rangle$ and $\langle j_z \rangle$ are large enough to interfere with $B_0$ and $J_0$ (Fig. 5, a, c) in such a way that TI goes into saturation. A similar mechanism lies behind the TI suppression with superposed azimuthal or axial magnetic fields. However, for low Pm the situation changes completely. Both, $\langle b_z \rangle$ as well as $\langle j_z \rangle$, are much too small to interact with the main fields. Instead, the saturation mechanism is a purely hydrodynamic one (Fig. 5, b, d): the quadratic
3.2. Electro-vortex flows

The Tayler instability (TI) discussed in the previous section can be understood as a generic case of a current driven instability under the ideal condition of a perfectly uniform current. In this sense it constitutes sort of an upper bound for a current-carrying fluid to remain at rest. Non-uniform current distributions are more typical for real settings. They give rise to rotational Lorentz force distributions and will thereby also generate electro-vortex flows (EVFs). Inhomogeneities in the current density distribution will, e.g., occur if the positive and/or negative current collector at the cell has a finite thickness, as is always the case. An extreme case discussed by Shercliff [39] and sketched in the inset of Fig. 6a is that of a point current source embedded in an insulating flat plate. When the current enters the conducting half space above the plate, it spreads radially outwards. The resulting Lorentz force distribution has - in contrast to the canonical base state of the TI - a non-vanishing rotational part. This rotational part is present for currents of any strength and drives a flow that cannot be balanced by pressure but only by friction. For the inviscid case, a singularity results as was shown by Shercliff [39,41]. EVFs are relevant for a number of industrial processes, e.g., electroslag remelting [42], weld pools [43], and aluminium refining [44]. For a comprehensive overview of EVFs refer to Bojarevičs et al. [41].

Here we look at a much milder case than that considered by Shercliff [39] with comparably gentle gradients of the electric field, see the left contour plot in Fig. 6b. The setup used for the computations is sketched in the inset of Fig. 6b. A cylinder of diameter $D$ and height $H$ filled with a liquid metal of conductivity $\sigma$ is bounded by current collectors of the same diameter, height $h$, and conductivity $\sigma_{cc}$. Over the circular area with diameter $d$ a constant potential is applied at the outer surfaces of the current collectors. The numerical solution shows in good approximation a linear dependence of the mean velocity $\langle u \rangle$ on the total applied current $I$ (Fig. 6a). This finding is somewhat in line with the observations of Vlasyuk [45] who found that for the EVF in a cylinder the relationship between total current and axial flow velocity is quadratic for $S < 10^3$ and linear for $S > 10^5$, where $S = \mu_0 I^2 A^{-1} \pi^{-2} \rho^{-1} \nu^{-2}$ is a dimensionless parameter [46] characterizing the ratio of the electromagnetic force to the fluids resistance due

![Figure 6](image-url)

**Figure 6.** Sketch of the driving mechanisms of electro-vortex flows after [39] (inset in a), distribution of current density and residual force density in a cell (inset in b), mean velocity vs. total current (a), and mean velocity vs. current collector height/diameter (b). $D = 1$ m, $d/D = 0.5$, $H/D = 2.4$, material properties of Na at 580 °C (see [40]).

combination of the $m = 1$ velocity perturbations produces $m = 0$ and $m = 2$ velocity components which suppress the further growth of the TI.
to viscosity and density [43]. The lowest current shown in Fig. 6a corresponds to $S \sim 10^8$. The mean velocities are in the order of magnitude that is expected for confined EVFs [47].

Since upper and lower current collector are symmetric in the setup of Fig. 6b, so are the electric field and the residual Lorentz force $F_{\text{mod}}$ distributions, where $F_{\text{mod}}$ is the difference between the Lorentz force distribution resulting from a perfectly uniform current and the actual one. Consequently, a symmetric flow comprising two toroidal vortices develops shortly after switching on the current. However, this flow situation is not stable under the given parameters and is eventually replaced by an irregular flow akin to thermally driven convection. The smaller the current collectors height, the more pronounced are the electric field gradients and the stronger the rotational part of the Lorentz force. The mean velocity increases steeply with decreasing $h/D$, see Fig. 6b. If the current is above the critical one for TI, a current collector’s height to diameter ratio $h/D \gtrsim 3$ is necessary to ensure that the EVF is weak enough to allow the TI to develop for the current densities used here. Already at $h/D = 2$ the base state is so different from that of a fluid at rest that TI does not occur. Instead the initial EVF prevails and saturates into a completely different flow pattern [40].

Strong enough EVFs are indeed able to disrupt the electrolyte layer of LMBs [35]. If the characteristic flow velocity is known, a proper criterion to assess the danger for the electrolyte layer’s integrity is the Richardson number

$$\text{Ri} = \frac{g \Delta \rho h_0}{\rho_m u^2}$$

where $\Delta \rho$ is the density difference between metal and electrolyte, $h_0$ the initial electrolyte thickness, $\rho_m$ the metal density, and $u$ a characteristic velocity of the metal. Ri describes the ratio of the potential energy of stratification $E_{\text{pot}}$ to the kinetic energy of the flow $E_{\text{kin}}$. Its critical value is in a good approximation 0.5 corresponding to an equality of potential and kinetic energy [35]. Similar reasoning can be applied to the action of the TI as was done by Herreman et al. [48]. Kelley and Sadoway [49] studied experimentally the interplay of heat driven convection and EVFs in a molten Bi-Pb alloy simulating the cathode of an LMB.

### 3.3. Interfacial instabilities

By far the largest electrical resistance of the cell is due to the electrolyte layer. Their electrical conductivity is in most cases four orders of magnitudes less than that of the electrode metals. So any small displacement of the electrolyte layer influences the current distribution in the whole cell. The situation is related to that found in aluminium reduction cells (ARCs) and indeed the mechanisms of wave excitation are similar. In Fig. 7a a cylindrical LMB subject to a vertical component $B_z$ is sketched. Such a field component is typically generated by the feed lines connecting single cells to the current supply or load and is well known from large installations of ARCs. This $B_z$ gives rise to an instability mechanism explained for ARCs by Sele [50]. If one or both of the electrolyte/electrode interfaces are inclined from the horizontal position, the formerly homogeneous current density will redistribute to minimize the total resistance. Due to its low conductivity, current passes nearly vertically through the electrolyte. Horizontally directed currents $I_h$ will appear mainly in the metal layers. These horizontal currents together with the vertical magnetic field $B_z$ generate Lorentz forces pointing in azimuthal direction. The forces give rise to motions that culminate in rotating waves with the help of constant redirections by the cell walls. In ARCs the rotating wave is generated in the bottom layer consisting of pure aluminum. In LMBs Lorentz forces with opposing directions are produced in the anode (top) and in the cathode (bottom) layers. However, for typical material combinations mainly the anode/electrolyte interface will develop waves because of the much lower density difference and therefore weaker restoring gravity force compared to the electrolyte/cathode interface. A typical wave shape is shown in Fig. 7b. The wave’s surface is colored with the vertical current density
Figure 7. Electromagnetic excitation of gravity waves in LMBs. Mechanism (a, see text for explanation); shape of a rotating wave (b) colored by vertical current density (red: high, blue: low) with contour lines of the electrolyte height; and dimensionless minimal electrolyte height vs. Sele’s parameter $\beta$ (c).

As expected, the vertical current density is largest where the distance $h_{\text{min}}$ between the electrodes is smallest. Overall, the vertical current density distribution is similar to the level curves shown by solid contours.

The wave’s onset as well as the electrolyte layer rupture can be described in good approximation using Sele’s criterion expressed by the parameter $\beta$

$$\beta = \frac{I \cdot B_z}{h_0 h_A (\rho_E - \rho_A) g}$$ (10)

with $h_0$ denoting the initial height of the electrolyte, $h_A$ the height of the anode metal layer, and $\rho_E$ and $\rho_A$ the densities of electrolyte and anode metal, respectively. If $\beta$, the ratio of Lorentz force to buoyancy, exceeds a certain critical value, sloshing will set in. Please note that cells with circular or quadratic cross sections are always unstable against sloshing, if a vertical magnetic field is present and the damping influence of several dissipation mechanisms is neglected, see Bojarevics and Romero [51]. A proper measure against sloshing in ARCs is to use rectangular cross sections with short and long sides.

The numerics used to study sloshing in LMBs [52,53] included ohmic and viscous dissipation, therefore there is a critical value of $\beta$ beyond which sloshing sets in for the circular cell considered here. As can be seen from Fig. 7c this value is around $\beta_{\text{cr}} \approx 0.35$ for the considered setup. Zikanov [54] used a mechanical analog related to that proposed by Davidson and Lindsay [55] and arrived at a somewhat different formulation.

The ordinate in Fig. 7c displays the minimum electrolyte height $h_{\text{min}}$ normalized by its initial value $h_0$. Different curves belong to variations of different single parameters noted in the legend. For $\beta$ above but near $\beta_{\text{cr}}$ a wave develops but approaches a saturated state were $h_{\text{min}}/h_0$ reaches a stationary finite value. Electrolyte rupture happens only later for $\beta_{\text{cr}} \approx 2$.

It is obvious from Fig. 7c that $\beta$ is still a reasonable parameter choice but far from perfect to
describe electrolyte layer rupture. This discrepancy might have various reasons, one of them is that for thin electrolyte layers waves of the upper and lower interface start to interact as was shown by Weber et al. [53]. In addition, the transition from an intact electrolyte layer to a ruptured one is rather abrupt changing from \( h_{\text{min}}/h_0 \approx 0.4 \) to \( h_{\text{min}}/h_0 = 0 \) in one \( \beta \)-increment. A better description of the electrolyte layer rupture needs further investigation of the processes involved and is underway.

4. Conclusions
Liquid metal batteries are promising candidates for future economical large-scale electricity storage as required for energy systems dominated by volatile sources. While present-day cells are still relatively small, scalability on the cell level is one of the appealing aspects of the concept. Larger cells will show a multitude of flow phenomena that should be properly understood in order to profit from beneficial aspects like mixing and to prevent potentially dangerous features like electrolyte layer ruptures. Molten salt based cells are generally high temperature devices complicating measurements. Using room temperature ionic liquids is a promising way towards low temperature cells, even more so if electrical conductivities of the electrolytes could be increased and degradation phenomena prevented.

Two magnetohydrodynamic instability mechanisms were discussed, the Tayler instability and electromagnetically excited surface waves. The latter are more dangerous for the integrity of the electrolyte layer than the former if a sufficiently strong vertical magnetic field exists. Electro-vortex flows will most likely be present in real life liquid metal batteries since perfectly uniform current distributions are seldomly met in large installations. They should be taken into account as possibly endangering the electrolyte layer’s integrity but are good candidates to promote gentle mixing in the cathode as well.

Due to space limitations we had to omit own ongoing work on thermally driven convection but the interested reader may refer to Zikanov and Shen [56, 57] and Köllner et al. [58] for information on this aspect of LMB fluid dynamics.

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