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# Preparation and Electrochemical Characterization of Aluminium Liquid Battery Cells With Two Different Electrolytes (NaCl-BaCl<sub>2</sub>-AlF<sub>3</sub>-NaF and LiF-AlF<sub>3</sub>-BaF<sub>2</sub>)

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#### Abstract

The possibility of preparation of operating rechargeable liquid battery cells based on aluminium and its alloys is systematically checked. In all cases we started from aluminium as the negative electrode whereas as the positive electrode three different metals were tested: Pb, Bi, and Sn. Two types of electrolytes were selected:  $Na_3AlF_6-AlF_3-BaCl_2-NaCl$  and  $Li_3AlF_3-BaF_2$ . We show that some of these combinations allowed efficient separation of individual liquid layers. The cells exhibited expected voltages, relatively high current densities and could be charged and discharged several times. The capacities were relatively low (120 mAh in the case of Al-Pb system), mostly due to unoptimised cell construction. Improvements in various directions are possible, especially by hermetically sealing the cells thus preventing salt evaporation. Similarly, solubility of aluminium in alloys can be increased by optimising the composition of positive electrode.

Keywords: Liquid batteries, aluminium, alloy, electrochemistry

#### **1. Introduction**

The share of renewable energy sources in production of electrical energy is growing.<sup>1-3</sup> Consequently, the need for storing electricity is also growing, since the supply of renewable energy is not constant (wind, sun, water). Currently, the surplus electricity (especially at night) is stored in pools of pumped hydro plants, by compressing air into underground caves and also in batteries (such us ZEBRA, NaS). The idea of the liquid battery, in which large amounts of electricity could be stored, originates from the aluminium industry, i.e. refining of aluminium from alloy aluminium - copper, process known as the Hoops procedure.<sup>4</sup> Liquid batteries enable large current density (0.5 A/cm<sup>2</sup> and more) and storing large amounts of energy (in the oxidation of 1 kg of aluminium about 3 kAh of electrical charge is released). Sadoway et al. registered the first patent of a liquid battery in 2008 and have since published several different combinations of metals and electrolytes in a form of liquid batteries.<sup>2,3,5,6</sup> Their research focuses primarily on liquid batteries with active metals from 1st and 2nd group of the periodic system.

The battery system is based on three liquid layers, separated from each other vertically and sorted by density. The active metal as a negative electrode with the lowest density is at the top of the battery container, while the metal with the highest density – serving as a positive electrode – is at the bottom of the battery container. Between the two electrodes lies a molten salt as the electrolyte, whose density is higher than the density of the negative electrode and lower than the density of the positive electrode. The main advantages of the liquid batteries are extremely high ionic conductivity of the electrolyte, resistance of individual liquid phases (no structural defects, dendrites, etc.) and good contact between the liquid phases. Disadvantages are primarily related to the high working temperature



**Figure 1.** Scheme of liquid battery cell constructed and used in this study. 1 – stainless steel lid, 2 – graphite rod, 3 – stainless steel container, 4 – positive current collector, 5 – negative current collector, 6 – ceramic sheath, 7 – negative liquid electrode, 8 – electrolyte, 9 – positive liquid electrode.

required for operation of this type of battery associated with high costs for thermal insulation, fast corrosion, usage limited to stationary applications only, and extreme caution during battery handling and operation.

Aluminium electrolysis is performed at temperatures in the range of 930–950 °C, which is too high for energyefficient liquid batteries. High temperatures are needed because  $Al_2O_3$  has to be in the dissolved state in the electrolyte mixture (e.g. NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>). The melting point of pure  $Al_2O_3$  is at even higher temperature – that is 2072 °C. Aluminium metal and aluminium alloys used as positive electrodes have much lower melting temperatures (for example, pure aluminium melts at 660 °C). Likewise, high temperatures are also required in the aluminium refining – Hoops procedure, where temperatures are about 930 °C and the electrolyte used is NaF-AlF<sub>3</sub>-BaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.

According to the facts presented above, the greatest challenge in the preparation of liquid aluminium battery is developing a suitable electrolyte that would have a melting point between 700 and 750 °C, the density of which would be higher than that of aluminium and, of course, will have a suitable ionic conductivity. Another important challenge in the operation of liquid aluminium battery is finding a suitable metal or alloy as the positive electrode, which will allow a high-capacity of liquid aluminium battery by reducing the chemical activity of aluminium in alloy (positive electrode). This means that it is necessary to

use a metal or alloy in which the activity of aluminium will not increase significantly with increasing concentration. When the battery is discharging, the active metal is oxidized at the contact between the negative electrode and the electrolyte, and then it is transported through the electrolyte as cation and reduced into the positive electrode at the intersection between the electrolyte and the positive electrode forming the corresponding alloy. The driving force for the described redox reactions is the difference of aluminium activities in different environments (in negative and positive electrode).

Aluminium has one of the most favourable relationships between the mass and the number of external electrons (1 mole of electrons per 9 grams) and is much cheaper compared to majority of metals in the 1st and 2nd group of the periodic system. This makes liquid aluminium batteries very interesting for potential application. In this article we present the results of aluminium liquid batteries experiments in which we used two different molten salts as the electrolyte: NaCl-BaCl<sub>2</sub>-AlF<sub>3</sub>-NaF (electrolyte A) and LiF-AlF<sub>3</sub>-BaF<sub>2</sub> (electrolyte B). Their potential use in liquid batteries was evaluated using cyclic voltammetry, chronopotentiometric (galvanostatic) measurements and impedance measurements.

# 2. Principle of Liquid Battery Operation

In liquid aluminium batteries, aluminium acts as active metal that passes from the negative electrode (aluminium) to the positive electrode (an alloy of aluminium and a suitable denser metal), when battery is discharging. The potential difference is created due to different chemical potential of the active metal (Al) in the negative electrode (pure aluminium; activity a = 1) and in the Al alloy (activity a < 1) and can be presented with the following cell diagram:

$$\begin{array}{l} Al_{(l)}|Al^{3+}_{(electrolyte melt)}|electrolyte_{(l)}| \\ Al^{3+}_{(electrolyte melt)}|Al(in alloy)_{(l)} \end{array}$$
(1)

Individual reactions at the electrodes can be written

Negative electrode:  $AI = AI^{3+} + 3e^{-}$  (2a)

Positive electrode:  $Al^{3+} + 3e^{-} = Al(in alloy)$  (2b)

Thus the total electrochemical reaction can be simply written as:

$$Al = Al(in alloy)$$
(3)

The thermodynamic driving force of the reaction is the change in partial molar Gibbs free energy of the cell:

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as:

$$\Delta \overline{G}_{\text{cell}} = \Delta \overline{G}_{\text{Al(in alloy)}} - \Delta \overline{G}_{\text{Al}}, \tag{4}$$

where the partial molar Gibbs free energy is calculated as:

$$\Delta \overline{G}_{Al(\text{in alloy})} = \Delta G_{Al}^0 + RT \ln \alpha_{Al(\text{in alloy})}$$
(5a)

$$\Delta \bar{G}_{Al} = \Delta G_{Al}^0 + RT \ln \alpha_{Al}$$
 (5b)

and  $a_{Al}$  is the activity of pure metal aluminium,  $a_{Al(in alloy)}$  is the activity of aluminium in the aluminium alloy, *T* is temperature and *R* is the gas constant. Modification of partial molar Gibbs free energy is related to the equilibrium cell voltage,  $E_{cell}$ , by Nernst equation:

$$\Delta G_{\rm cell} = -zFE_{\rm cell} \tag{6}$$

Where z is the number of exchanged electrons (in the case of aluminium z = 3) and F is the Faraday constant.

a)

Combining equations (4) - (6), we get an equation for the calculation of the equilibrium voltage of the cell, which depends on the activity of the metal in the alloy.

$$E_{\text{cell}} = -\frac{RT}{zF} \ln \left( \frac{a_{\text{Al(in alloy)}}}{a_{\text{Al}}} \right)$$
(7)

## 3. Experimental

#### **3. 1. Construction of Battery Cell** and Preparation of Cell's Components

The in-house designed apparatus for carrying out the experiments was composed of several parts, as described below. The battery cell consisted of a metal container (stainless steel) and a lid. The container had a drilled hole at



Figure 2. (a) Full battery cell equipped with connectors and Cu wires after electrochemical measurements in inert (Ar) atmosphere at 750  $^{\circ}$ C, (b) detailed image of stainless steel lid with inner coaxial graphite stick; note that both the surface of the stainless steel container and the stainless steel lid are covered with some product(s) of corrosion processes that are taking place at such high temperatures when subjected to vapors of electrolyte components. (c) Technical drawing of the cell.

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the bottom equipped with a wire screw serving as the contact between the positive electrode and the wire (Figures 2a and 2b). The cell's lid had two threaded holes with screws for attachment of graphite or stainless steel rod used as electrical contact between the negative electrode (Al) and the wire. An additional threaded hole at the top of the lid served as attachment of the wire to the lid (Fig. 2b). The chamber of the battery cell consisted of a ceramic sheath  $(Al_2O_3)$  coated several times with BN. The ceramic sheath prevented electrical contact (shortcut) between both electrodes over the walls of the battery container as well as a contact between the battery container and the lid. Additionally, it prevented corrosion of the walls of battery cell. The length of ceramic sheath was bigger than the height of the metal container and therefore protruded from the container. It was covered with a lid made of stainless steel (Figure 2a).

Prior to the electrochemical testing the two electrode materials and electrolyte layer were prepared by pre-melting. We first inserted a ceramic sheath into the stainless steel container and poured a predetermined weighted quantity of the metal powder serving as a positive electrode material. Then we placed stainless steel container in the quartz tube and heated it in an inert atmosphere (argon) from 25 °C to 450 °C in 1 h, maintained at 450 °C for 2 hours and finally, let to cool below 50 °C. Then the tube was opened and the process was repeated for the electrolyte layer: the electrolyte powder mixture in a specific ratio needed for formation of eutectic (see Table 2) was poured into the cell. The cell was re-heated to 750 °C in 1.5 h. maintained at 750 °C for 2 hours and again cooled down to room temperature. In the third step - when preparing a negative electrode - about 6 g of pure aluminium powder was poured into the cell. The same temperature regime as in the second step was repeated. When the aluminium had melted, the graphite (or stainless steel) rod with appropriate length that was beforehand attached to the stainless steel lid was inserted in the liquid aluminium in order to establish a good contact between the negative electrode and the wire. Prior to electrochemical measurements the battery cell was heated to 750 °C and let to stabilize at that temperature for 30 min. When necessary, the temperature of the battery cell was changed to another value.

#### 3. 2. Electrode and Electrolyte Materials

When choosing electrode and electrolyte materials for potential use in liquid batteries, one must pay attention to their density (for correct positioning of the electrodes and the electrolyte layers, see Introduction and Figure 1). Also, one needs to take account of the melting points of selected materials because the layer with the highest melting point determines the lower limit of the operating temperature span of the whole liquid battery cell. To prepare the electrodes and the electrolyte, we used components with a chemical purity of > 98 %. As materials for positive electrodes we selected Pb, Bi and Sn, all of which have a low melting point and a high density, see Table 1.

 Table 1. Melting points and densities of the three metals used as a positive electrode.

Metal	Melting point (°C)	Density (g/cm <sup>3</sup> )*	
Pb	327.5	10.66	
Bi	271.4	6.99	
Sn	231.9	10.05	

\* Density at melting temperature.

Aluminium of a purity > 98% was used as the negative electrode, with a melting point of 660 °C and a liquid state density of about 2.357 g/cm<sup>3</sup> at 750 °C.<sup>7</sup> We used 2 different electrolytes (denoted as A and B) with compositions and properties as given in Table 2.

After assembling a cell we attached Cu wires and placed the cell in a specially designed quartz tube housing to ensure inert (Ar) environment during the cell operation at elevated temperatures. The quartz tube with a battery cell was inserted in the furnace that was in upright position. The furnace opening was covered with insulating bricks for better thermal insulation. Temperature regime was controlled by a suitable controller. The lid of the quartz tube had two openings for purging with an inert gas (Ar) and three connectors, one to connect the temperature sensor and the other two for connecting the battery cells to the measurement device. The latter two had a form of cylinder with a drilled hole for attachment of cell (4 mm connectors). On the outer side of the quartz tube lid there were 2 mm connectors leading to a measuring device. Connectors were sealed using Teflon gaskets. The supply of argon in quartz tube was regulated. Drainage was fed through rubber tubes submerged in water of measuring cylinder. A ventilator cooled the outside of the quartz tube. Cooling was especially important because of Teflon seals on the lid of the quartz tube that can only withstand temperatures up to about 230 °C.

Table 2. Composition and selected properties of electrolyte A and B.

Electrolyte	Electrolyte composition	Components ratio (wt %)	Melting point (°C)	$\begin{array}{c} Conductivity \\ (\Omega^{-1}cm^{-1}) \end{array}$	Density (g/cm <sup>3</sup> )
A	Na <sub>3</sub> AlF <sub>6</sub> -AlF <sub>3</sub> -BaCl <sub>2</sub> -NaCl	41.7 : 3.3 : 45 : 10	670.5	1.4078*	2.7688*
<u>B</u>	Li <sub>3</sub> AlF <sub>3</sub> -BaF <sub>2</sub>	55:45	655	_ **	_ **

\* 7 \*\* no data

#### 3. 3. Electrochemical Characterization of the Cells and Inspection of the Separation of the Phases

As described in section 3. 1. the individual components of the battery cell (electrolyte and electrodes) for every experiment were prepared by pre-melting each component. During the electrochemical measurements the battery cells were placed inside a quartz tube (filled with an argon atmosphere) that was inserted in an upright positioned tube furnace. The electrochemical properties (cyclic voltammetry and galvanostatic measurements) of the tested battery cells were measured using "VPM3" (Biologic) potentiostat/galvanostat and for impedance measurements a "MPG2" (Biologic) with EIS module was used; both instruments running with EC – Lab® software.

Required vertical separation of individual liquid layers in the melted state due to differences in their densities was checked by preparing those layers in the alumina crucible (using the same temperature protocol as for cell preparation). After cooling down alumina crucible was carefully removed by gradually breaking off the shards to reveal the interior. Similarly the cells after the electrochemical testing were inspected by preparing a longitudinal cross-section of the cells by first cutting to a half the outer stainless steel container and followed by a gradually breaking off of the shards of ceramic sheath.

#### 4. Results and Discussion

We investigated the electrochemical properties of the cells with starting composition Al|electrolyte $|M_{host}$ , where  $M_{host}$  denotes pure host metal. During initial cathodic (reduction) process part of aluminium from negative electrode is being transferred over the electrolyte phase into the host metal of the positive electrode and forming Al- $M_{host}$  alloy. The obtained results for different tested systems will be here denoted using only the latter rational expression for the chemical composition of the formed positive electrode alloy.

#### 4.1. Electrochemical Characterization

First we studied the electrochemical behaviour of three different alloy systems in electrolyte A. In cyclic



**Figure 3.** Cyclic voltammograms of different liquid battery cells in electrolyte A: (a) Al-Sn at the rates of  $1 \text{ mVs}^{-1}$  (first 3 cycles) and  $10 \text{ mVs}^{-1}$ , (b) Al-Bi at the rate of  $1 \text{ mVs}^{-1}$ , (c) Al-Pb at the rate of  $0.5 \text{ mVs}^{-1}$  (2 cycles). (d) Cyclic voltammograms of a liquid Al-Pb cell with electrolyte B.

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voltammograms of the Al-Sn system (Fig. 3a) we can observe two local peak cathodic currents (reduction peaks) in the potential region between about 1.0 and 0.5 V. In the initial cycle with scan rate 10 mVs<sup>-1</sup> (red curve) the second cathodic peak at about 0.6 V reached magnitude close to 200 mA. However, when the rate is decreased from 10 mVs<sup>-1</sup> to 1 mVs<sup>-1</sup> (blue curve in Fig. 3a), the two peaks decrease consistently. Surprisingly we observed that both the peaks increase from the first to the second cycle at 1 mVs<sup>-1</sup> (blue and black curve in Fig 3a, respectively) but afterwards considerably decrease in the third cycle (green curve). In the case of the Al-Sn system the value(s) of potential for the anodic peak(s) are higher that the upper cut-of voltage (1.5 V). In the testing of the Al-Bi cell (Fig. 3b) we selected voltage window that was shifted slightly to lower potentials. In the corresponding cyclic voltammograms two vaguely discernible cathodic peaks in the potential region between about 0.7 and 0.3 V can be observed. In the anodic scan a hump at around 0.9 V is potentially indicating an anodic peak. However, we can see that consecutive cycles are well reproducible. The slight difference in shape of the 1st cycle may be due to (still) incomplete dissolution of electrolyte (prior to testing the cell was for 30 min held at 740 °C). Overall, the Al-Bi system is considerably more electrochemically stable than Al-Sn. In the case of Al-Pb (Fig. 3c) a clear and broad single cathodic current peak at about 0.9 V is observed. Its magnitude in the second cycle with corresponding current density of more than 100 mAcm<sup>-2</sup> (electrode's square section is  $2 \text{ cm}^2$ ) is significantly higher than in the previous two systems. Note that the scan rate used in the case of Al-Pb was lower (0.5 mVs<sup>-1</sup>) than for the two previous systems. Due to this fact we selected the Al-Pb system to serve as a positive electrode in further experiments in which electrolyte A was used.

In electrolyte B the typical cathodic currents were significantly smaller than in electrolyte A, as seen on the example of Al-Pb alloy shown in Fig. 3d. Still, a clear peak was observed in the cathodic direction at potentials around 1.5 V, what is considerably higher compared to the values obtained for the system comprising electrolyte A (see Figs. 3c. and 3d.). The origin of this difference is not yet understood. Again, also in the case of the Al-Pb system with electrolyte B the value of potential for the anodic peak is higher that the upper cut-of voltage (1.74 V).

In partial summary, maximum currents measured in present cyclic voltammetry experiments were observed for the Al-Pb cell in electrolyte A. If the maximum value of 250 mA is recalculated per unit cross section area of the cell, one gets a value of about 100 mA/cm<sup>2</sup>. In the case of Al-Sn and Al-Bi cells slightly lower current densities were achieved, but still higher than for cells containing electrolyte B. For comparison, for a liquid Ca-Bi battery cell a current density up to 200 mA/cm<sup>2</sup> was reported during charge-discharge cycles, in a LiCl-NaCl-CaCl<sub>2</sub> elec-

trolyte at 600 °C.<sup>5</sup> The reason for that may be significantly more soluble electrolyte, although in some papers it has been shown that both electrolytes, that we used in this study, melt at a lower temperatures than those that were used for carrying out the electrochemical testing.<sup>7,8</sup> The melt of electrolyte A is a colourless liquid at temperatures around 700 °C, whereas electrolyte B still shows a white (milky) appearance at 800 °C.

Our results demonstrate that in principle a combination of Al and Al alloys show a reasonable potential as a liquid battery systems. We here note that in these type of cells the current density depends on various factors, first of all on the ionic conductivity of electrolyte (ionic conductivity of LiCl-NaCl-CaCl<sub>2</sub> is 2.94  $\Omega^{-1}$ cm<sup>-1</sup>,<sup>5</sup> and ionic conductivity of electrolyte A is 1.41  $\Omega^{-1}$ cm<sup>-1</sup>) and on transport properties (migration, diffusion, convection) of active metal into and in the liquid-metal positive electrode.<sup>7</sup> And as demonstrated in the work of Sadoway et al. a formation of a possible new solid phases inside a positive electrode has to be taken into account.<sup>5</sup>



**Figure 4.** Galvanostatic measurement of (a) Al-Bi in electrolyte A; the constant current value was 10 mA whereas the voltage window was from 0.1 to 1.0 V. (b) Al-Pb in electrolyte B; the constant current value was 20 mA whereas the voltage window was from 0.6 to 1.3 V or 1.2 V for the first and next cycles, respectively.

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Despite relatively good current densities, the cycling experiments revealed various problems, many of them also linked to unoptimised cell construction. Nevertheless, some cells displayed quite promising and reproducible cycling such as the examples shown in Fig. 4, where capacity of Al-Pb liquid battery was approximately 120 mAh. Note, however, that the capacities delivered were rather small. One of the reasons could be a very rapid increase in activity of aluminium in the alloy (positive electrode), thereby rapidly reducing the potential of the cell during discharge and reaching prematurely the cut-off voltage. This problem could in future be addressed by measures in which the kinetic contribution(s) to overpotential would be reduced (e.g. by reducing sources of internal resistance). We here need to stress that the main focus of this preliminary investigation was primarily to find stable electrolytes of Al-based alloys at temperatures below 800 °C. While the principle was successfully demonstrated, there is still a long path to find an appropriate alloy showing small overpotential and a wide compositional range of operation.

In order to inspect possible reasons for battery failure, we employed impedance spectroscopy. This technique was used prior, between and after cycling – as a sort of an additional means for monitoring the state of cell. Examples of complex plane impedance spectra measured before first cycling and after a collapse of a cell are shown in Figs. 5a and b. In this particular case, the reason for col-



Figure 5. Complex plane impedance spectra for (a) two measurements of Al-Pb cell, (b) for Al-Pb in electrolyte B at three different temperatures, (c) for a "collapsed" Al-Pb cell.

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lapse could be a change in composition of electrolyte due to evaporation of some of its components (chlorides). Strong increase of the real part of the impedance at high frequencies, pronounced scattering and complete absence of defined impedance spectra reveals that the cell basically lost connectivity between the two electrodes due to electrolyte degradation. Further investigations are needed in order to elucidate the cause for the observed loss of connectivity. This may simply be a result of a gradual decrease of amount of the electrolyte phase present in the cell and associated with voids formation (evaporation of the electrolyte) and finally yielding in a strongly reduced effective cross section of connected electrolyte phase. Indeed in some cases we got an indication that this may be the case (see below, the results of inspection of separation of layers). Additionally chemical and electrochemical degradation processes of electrolyte components may take place in the cell during the operation at elevated temperatures.

From the measured impedance values and the currents used in galvanostatic experiments one can roughly estimate the potential polarization of given cell during cycling. For Al-Pb cell (Fig. 5a) the estimated polarization at a current of 20 mA (Fig. 4) would be about 100 mV, an acceptable range for operating battery cell.

# 4. 2. Inspection of the Separation of the Phases

Vertical separation of individual liquid layers in the melted state (Al|electrolyte $|M_{host}$ ) was checked in the parallel experiment by preparing those layers in the alumina crucible. Generally for all the tested systems the separation of individual layers is quite efficient as shown for



**Figure 6.** Vertical separation of phases after cooling to RT with the designations: N-negative electrode material, E-electrolyte phase, P-positive electrode material. (a) A typical parallel experiment where the melts were prepared in the alumina crucible (N = aluminium, E = NaF-AlF<sub>3</sub>-BaCl<sub>2</sub>-NaCl, P = bismuth). (b) Longitudinal section of Al-Pb cell after electrochemical testing (N = aluminium, E = LiF-AlF<sub>3</sub>-BaF<sub>2</sub>, P = lead).

the case of Al|electrolyte|Bi system (Fig. 6a). Similarly in the longitudinal cross-section of the cells after the electrochemical testing we can observe electrolyte layer separating the two metal electrodes that appear as a two plug-shaped chunks on the top and bottom of the cell (Fig. 6b). In the case of battery cells prepared with electrolyte B, dissolution of the insulating sheath made of alumina and coated with BN could be detected. We presume that with increasing concentration of  $Al_2O_3$  in the electrolyte, the melting temperature of the electrolyte also increases and, consequently, the ionic conductivity decreases.

As seen in Fig. 6 in electrolyte phase some cracks and voids can be observed. It has to be taken into account that the observation of the separation of the layers and appearance of the cracks and voids in the testing alumina crucible (and real cell) does not necessary reflect the separation and arrangement of the components when being in melted state. Some cracking and void formation definitely takes place during cooling down of the system as the solidification takes place and additionally the thermal expansion coefficients of the two metal and ionic components are different. Some additional cracking is introduced during gradual removal of ceramic sheath. Therefore from the observation of the obtained cross sectional views of the cells after electrochemical testing we cannot directly speculate about presence of cracks and about void formation in the cell during electrochemical operation. For this means some other experimental techniques will have to be developed that would allow to follow the state of such electrochemical system during operation with electrodes and electrolyte in melted state.

## 5. Conclusion

We have successfully demonstrated that it is possible to prepare various types of operating liquid battery cells on the basis of metallic aluminium and corresponding alloys. The separation of individual liquid layers is quite efficient and is clearly observed even in cells that underwent prolonged electrochemical testing. Although the concept has been successfully confirmed, it needs to be pointed out that the cells had rather small capacities and relatively short operating times. In the case of electrolyte A, the reason for the limited operation may be in the raising melting point of the electrolyte during the cell operation. This may be due to evaporation of certain components of the electrolyte (chlorides). In the case of battery cells prepared with electrolyte B, dissolution of the insulating sheath made of alumina and coated with BN could be detected. With increasing concentration of  $Al_2O_3$  in the electrolyte, the melting temperature of the electrolyte increases and, consequently, the ionic conductivity decreases. For prolonged operation of the present types of cells it would be necessary to hermetically seal battery cell, thus preventing salt evaporation. Implementation of this kind of battery cells would probably require advanced technical solutions connected with considerable resources. To increase the robustness of such cells, a safety valve should be implemented because high pressures would be expected in a sealed battery version. It would also be reasonable to use a different material for the sheath – it has been observed that the use of a ceramic sheath of alumina coated with BN is not entirely resistant to corrosion against electrolyte B. Additionally some new experimental techniques would have to be developed that would allow to follow the state of such electrochemical systems during operation at elevated temperatures.

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# Povzetek

V pričujoči eksperimentalni študiji smo sistematično raziskali možnosti priprave delujoče (ponovno-napolnjive) baterije s tekočimi elektrodami na osnovi talin kovinskega aluminija in zlitin le-tega. Pri vseh eksperimentih smo v začetnem stanju sistema kot negativno elektrodo uporabili aluminij, za pozitivno elektrodo pa smo uporabili tri različne kovine: Pb, Bi in Sn. Izbrali smo dva različna elektrolita:  $Na_3AlF_6-AlF_3-BaCl_2-NaCl$  in  $Li_3AlF_3-BaF_2$ . V prispevku pokažemo, da je možno z nekaterimi od omenjenih kombinacij elektrod in elektrolita pripraviti baterijske celice, ki imajo učinkovito ločene posamezne tekoče faze. Testirane celice so imele pričakovano napetost in jih je bilo možno nekajkrat izprazniti/napolniti z relativno visoko gostoto toka. Dosežene kapacitete so bile razmeroma nizke (najvišja 120 mAh v primeru Al-Pb sistema), kar pripisujemo ne-optimizirani konstrukciji celic. Delovanje prikazanih aluminijevih baterijskih celic bi bilo možno izboljšati z različnimi pristopi – zlasti s hermetično zatesnitvijo, s čimer bi preprečili izhlapevanje elektrolita. Z optimizacijo sestave pozitivne elektrode bi bilo možno tudi povečati topnost aluminija v zlitinah.