

**An Electrochemical and Photoelectron Spectroscopy Study of a Low Temperature Liquid Metal Battery Based on an Ionic Liquid Electrolyte**

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1 **An electrochemical and photoelectron spectroscopy study of a low**  
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12

13 **Abstract**

14 We report the design of a low-temperature liquid metal battery (LMB). Li and Ga as the negative  
15 and positive electrode, respectively, are used in combination with a room temperature ionic  
16 liquid as an electrolyte. 1 mol/L lithium bis(trifluoromethylsulfonyl)imide (Li[TFSI]) in 1-butyl-  
17 1-methylpyrrolidinium bis (trifluoromethylsulfonyl)imide ([BMP][TFSI]) is chosen as  
18 electrolyte. The battery operates at 220 °C which is a relatively low temperature for a LMB and  
19 shows good electrochemical performance at low current density. The cells were cycled for more  
20 than 600 h and achieved a round-trip Coulombic efficiency close to 100 % and an average  
21 voltage efficiency of 66 % resulting in an overall energy efficiency of 65 %. At higher current  
22 densities, however, the system showed up to 75 % irreversible capacity loss after three cycles. To  
23 understand the origin of this strong deterioration, we characterized the surface and the bulk  
24 properties of the Ga cathode using X-ray Photoelectron Spectroscopy. Especially at higher

25 current densities a decomposition of the electrolyte was found. The occurring chemical changes  
26 and the elemental distribution at the Ga cathode are analyzed based on XPS measurements at  
27 different stages of the battery charge/discharge cycling.

28

## 29 1. Introduction

30 The rapid deployment of renewable energy technologies, such as solar and wind power,  
31 accelerates the need of new generation low-cost and long-life energy storage devices. To this  
32 end, various technologies have been proposed, such as hydroelectric pump storage, compressed  
33 air, fuel cells, flywheels and capacitors. However, they are often unable to provide satisfactory  
34 performance in terms of durability, high power, round trip energy efficiency and costs. Batteries  
35 are attractive as stationary storage devices due to their rapid response times, relatively high  
36 specific energy and energy densities ( $128 \text{ Wh}\cdot\text{kg}^{-1}$  and  $230 \text{ Wh}\cdot\text{L}^{-1}$  for lithium-ion batteries,  $150$   
37  $\text{Wh}\cdot\text{kg}^{-1}$  and  $350 \text{ Wh}\cdot\text{L}^{-1}$  for sodium-sulfur batteries), high storage efficiencies and simple  
38 maintenance. However, their high cost and the safety risk prevent them from being widely  
39 adopted for stationary applications [1-4].

40 Recently the technology of liquid metal batteries (LMBs), first introduced in the early 60's, has  
41 been renewed [5-7]. The LMB tests in the Sadoway group at MIT provide valuable information  
42 about Mg/Sb, Li/Sb-Pb and Li/Bi systems and pointed out the promising features of these  
43 batteries such as their low production costs, their ability to work with high voltage efficiencies at  
44 high current densities when compared with conventional intercalation-type batteries and, last but  
45 not least, their ability to withstand a large number of charge/discharge cycles.

46 Typically, a LMB comprises three liquid layers, a low density alkali or earth alkali metal as  
47 negative electrode on the top, a high density molten metal as positive electrode at the bottom,

48 separated by a molten alkali halide mixture electrolyte with intermediate density [5]. The system  
49 self-stratifies due to density differences and immiscibility. During discharge, the molten metal at  
50 the anode is oxidized and cations are conducted through the electrolyte being reduced at the  
51 cathode and forming a liquid metal alloy. The process is reversed when the cell is charged.  
52 Depending on the selected electrode pairs and the used electrolytes, LMBs typically operate at  
53 high temperatures ranging from 450 to 700 °C. So far molten salt mixtures such as LiCl–LiBr,  
54 LiF–LiCl–LiI, are used as electrolytes in the LMBs [5-7]. In the present study we explore the  
55 suitability of room temperature ionic liquids (RTILs) as electrolytes in LMBs.  
56 In recent years RTILs attracted a great attention due to their non-volatility, non-flammability,  
57 wide temperature range of operation and high conductivity [9,10]. They are already successfully  
58 used as electrolytes in rechargeable lithium batteries [11-13]. Those features of RTILs motivated  
59 us to explore their suitability as alternatives to molten salts for LMBs.  
60 The advantage of operating at this relatively low temperature for such a system is the reduced  
61 reactivity of the molten electrodes with impact on the corrosion of the cell construction  
62 materials.  
63 The electrolyte used in this study was a mixture of lithium bis(trifluoromethylsulfonyl)imide  
64 (Li[TFSI]) dissolved in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide  
65 ([BMP][TFSI]). The RTIL was chosen based on its good thermal and electrochemical stability  
66 and the low reactivity with molten lithium at the operating temperature (220 °C) [9]. In search of  
67 appropriate electrodes, we considered Li and Ga because of their low melting temperatures  
68 coupled with the binary phase diagram and the estimated equilibrium cell voltage [14].  
69 Moreover, liquid Ga was already used as a self-healing negative electrode in lithium ion batteries  
70 and lithium shows good stability towards its halide melts and high discharge capacity [7, 8, 15].

71

## 72 **2. Experimental**

### 73 2.1. Electrochemical setup

74 Cells consisting of a Li negative electrode, a RTIL electrolyte mixture, 1 mol/L lithium  
75 bis(trifluoromethylsulfonyl)imide (Li[TFSI]) in 1-butyl-1-methylpyrrolidinium bis  
76 (trifluoromethylsulfonyl) imide ([BMP][TFSI]) and a Ga positive electrode were assembled in  
77 the fully charged state inside an insulating aluminum nitride ceramic tube with an active surface  
78 area of  $0.68 \text{ cm}^2$  and then placed inside a cylindrical glass container (Fig. 1). Tungsten wires  
79 were used as negative and positive current collectors and the inter-electrode distance was 0.5 cm.  
80 The assembly process and the electrochemical characterization of the cells were conducted in an  
81 inert glove-box with argon atmosphere (OMNI-LAB from Vacuum-Atmospheres –  $\text{O}_2$  content  
82  $< 0.2 \text{ ppm}$ ,  $\text{H}_2\text{O}$  content  $< 0.5 \text{ ppm}$ ). The negative electrode was prepared by immersing the  
83 tungsten wire into the molten lithium. Then the gallium metal was added as liquid inside the AlN  
84 tube after which the RTIL electrolyte was poured and the negative electrode was placed on top of  
85 the electrolyte. The cells were heated up to  $220 \text{ }^\circ\text{C}$  through a coil made of thermoresistive  
86 elements which was fixed around the glass tube. The temperature was measured and controlled  
87 with a thermocouple. The molten components self-segregate into three layers based on their  
88 immiscibility and density differences ( $0.512 \text{ g}\cdot\text{cm}^{-3}$  for Li,  $1.4 \text{ g}\cdot\text{cm}^{-3}$  for [BMP][TFSI] and  
89  $6.095 \text{ g}\cdot\text{cm}^{-3}$  for Ga). Thus, based on the chosen geometry and the used materials, the assembled  
90 cells have a theoretical capacity of approximately  $0.2 \text{ A}\cdot\text{h}$ .  
91 According to the Ga-Li binary phase diagram, in order to maintain the all liquid metal alloy  
92 during operation at the chosen working temperature ( $220 \text{ }^\circ\text{C}$ ) a fully discharged target  
93 composition of 7 mol. % Li in Ga was used [14].

94 Li and Ga were selected on the basis of their relative low melting points as compared to other  
95 existing electrode pairs (180.5 °C for Li and 29.7 °C for Ga). As precursors for battery assembly,  
96 Li (purity 99.9 %, supplier Alfa Aesar), Ga (99.99 %, Alfa Aesar), Li[TFSI] (99.9 %, Alfa  
97 Aesar) and [BMP][TFSI] (99.95 %, Iolitec) were used as received without further purification.  
98 The moisture content in the RTILs was monitored by Karl Fischer titration (model 831 KF from  
99 Metrohm) and an average value of 40 ppm water content was recorded.

100 Galvanostatic cycling with potential limitation (GCPL), cyclic voltammetry (CV) and  
101 electrochemical impedance spectroscopy (EIS) were employed to characterize the cells, using a  
102 two-electrode setup with Li metal serving as the counter/reference electrode and the Ga as the  
103 working electrode. The voltammetric curves were recorded between +1.1 V and +0.35 V at a  
104 scan rate of 0.5 mV·s<sup>-1</sup> and the impedance spectra were acquired in the frequency range from  
105 100 kHz to 10 mHz with an AC voltage amplitude of ± 10 mV around the open circuit potential.  
106 A Biologic potentiostat model SP300 was used for the electrochemical characterizations.

107

## 108 2.2. Sample preparation for XPS analyses

109 For analysis of the elemental distribution and the chemical composition of the Ga cathode's  
110 surface and bulk region, two Ga cathode samples (after discharge - lithiation and charge -  
111 delithiation, respectively) were carefully separated from the rest of the battery components prior  
112 to being packed into a hermetically sealed transfer-box for transportation. All the operations  
113 were done in a glove box under argon atmosphere.

114

115

116

117 2.3. XPS measurements and instrumentation

118 To prevent the samples from moisture/air exposure, a nitrogen dry-box (Carl Roth GmbH,  
119 Germany) was mounted to the XPS spectrometer so that the samples could be easily removed  
120 from the transfer-box within the dry-box, and placed into the transfer chamber.

121 XPS analysis were carried out with a Specs SAGE spectrometer (base pressure  $< 1 \times 10^{-8}$  mbar)  
122 equipped with a Phoibos 150 electron analyzer using a focused monochromatized AlK $\alpha$  radiation  
123 ( $h\nu = 1486.7$  eV). During the experiments the pressure in the analysis chamber was  $\sim 5 \times 10^{-8}$   
124 mbar. Core level spectra were recorded at a constant analyzer pass energy of 13 eV allowing a  
125 total energy resolution of 0.6 eV and no charge neutralization was used. For binding energy  
126 calibration, the energy scale was corrected by aligning the N1s signal to the N1s cation state of  
127 the neat ionic liquid at 402.7 eV [BMP][TFSI] [16], while the binding energy (BE) scale of the  
128 cathode sample was calibrated from the gallium signal using the Ga2p $_{3/2}$  peak at 1116.7 eV [17].  
129 The core level spectra were analyzed by subtracting a Shirley-type background [18] and peak  
130 areas were calculated by a weighed least-square fitting of model curves (70 % Gaussian, 30 %  
131 Lorentzian) to the experimental data using the software package CASA XPS (Version 23.16  
132 Dev52, Casa Software Ltd.). For quantification the atomic percentage (at. %) was calculated on  
133 the basis of photoionization cross sections by Yeh and Lindau [8].

134 XPS sputter profiling was performed using a differentially pumped IQE 12/38 ion source  
135 operated with Argon (source pressure  $2.2 \times 10^{-3}$  mbar, Ar $^+$  ion energy keV, emission current  
136 10 mA, ion current 6 mA) and laterally scanning the Ar $^+$  ions across the sample surface (scan  
137 area  $10 \times 10$  mm $^2$ ). Under these conditions, the Ga-cathode can be etched at a rate of  $\sim$   
138 0.2 nm $\cdot$ min $^{-1}$ .

139

### 140 3. Results and discussion

#### 141 3.1 Electrochemical performance

142 In order to investigate the electrochemical behavior of the Li||Ga LMB, several cells were  
143 assembled and tested at 220 °C. At this temperature, before the electrochemical test starts, the  
144 open-circuit potential (OCP) stabilizes at  $\sim 2$  V, which strongly deviates from the reported  
145 thermodynamic data [20]. The deviation is probably caused by the formation of a passivation  
146 layer at the electrode-electrolyte interfaces as a result of interaction with the electrolyte. After  
147 several minutes of galvanostatic cycling, the OCP value stabilized at  $\sim 0.75$  V. This change  
148 could correspond to a disintegration of the passivation layer during cycling.

149 The electrical conductivity of the RTIL electrolyte was estimated from the resistance at high  
150 frequency limit in EIS measurements and it was found to be  $30 \text{ mS}\cdot\text{cm}^{-1}$ , which is considerable  
151 lower than the conductivity of conventional molten halide salts typically used as electrolytes in  
152 LMB's ( $1.7\text{--}3.5 \text{ S}\cdot\text{cm}^{-1}$  for lithium halides).

153 The cell prototypes of  $\sim 0.2 \text{ A}\cdot\text{h}$  theoretical capacity were galvanostatically cycled at  $10 \text{ mA}\cdot\text{cm}^{-2}$   
154 ( $\text{C}/40$  rate) for a predefined time of 20 h corresponding to a 50 % depth of discharge. The cut-  
155 off charging voltage was set to 1.11 V and the cells were operated continuously for about 600 h,  
156 i.e. for 14 charge-discharge cycles with stable cycling performance (Fig. 2). The near-constant  
157 voltage plateau observed in the galvanostatic voltage-capacity profile and the absence of a sharp  
158 voltage drop suggests that during the operation of the battery no intermetallic compounds are  
159 formed in agreement with the Li-Ga phase diagram. During the initial cycles the cells exhibited a  
160 round-trip Coulombic efficiency of 97 % which slowly increased to 100 % at the end of the test.  
161 This can be caused by an improved wetting of the tungsten negative current collector by molten



162 lithium during the cycling experiments. The cells achieved an average value of voltage efficiency  
163 of 66 % during the tests resulting in an overall energy efficiency of 65 %.

164 To gain further insight in kinetics of the LMB, we applied cyclic voltammetry (Fig. 3a) and  
165 electrochemical impedance spectroscopy (Fig. 3b). The charge-transfer overpotential, indicated  
166 by the deviation of the  $I=f(V)$  linear dependence in the CV experiment (Fig. 3a), is also  
167 confirmed by the presence of the depressed semicircle in the EIS scan (Fig. 3b). In the former the  
168 presence of more pronounced hysteresis in the anodic scan profile suggests irreversible  
169 phenomena during the charging (delithiation) process, which are further proved by XPS  
170 measurements (see Section 3.2).

171 The presence of the semicircle in the high frequency region can be attributed to the formation of  
172 a layer at the cathode-electrolyte interface, resulting from electrolyte decomposition products and  
173 can be defined as a solid-electrolyte interface (SEI). Based on these findings one could estimate  
174 that the potential drop coupled with the charge-transfer overpotential plays an important role in  
175 the overall loss mechanism in the investigated system [21].

176 Our experimental results suggest that at low current densities and moderate time cycling a porous  
177 SEI layer is formed, facilitating the  $\text{Li}^+$  diffusion into the cathode. This is confirmed by the slight  
178 decrease in the cell internal resistance observed in the figure 3b (EIS spectrum). At higher rates  
179 however, dense and impenetrable SEI structures might form, which hinder  $\text{Li}^+$  diffusion out and  
180 into the cathode and lead to an increased capacity fade.

181 Further, in order to evaluate the battery capability, the cells were fully discharged (lithiated) at  
182 three different current rates:  $10 \text{ mA}\cdot\text{cm}^{-2}$ ,  $16 \text{ mA}\cdot\text{cm}^{-2}$  and  $32 \text{ mA}\cdot\text{cm}^{-2}$ , corresponding to a C/40,  
183 C/24 and a C/12 rate, respectively (Fig. 4). The cut-off voltage was set to 0.2 V for lithiation and

184 1.4 V for delithiation. At  $10 \text{ mA}\cdot\text{cm}^{-2}$  the good electrochemical performance of the cells was  
185 confirmed by a stable cycling behavior.

186 In the case of higher current rates ( $16 \text{ mA}\cdot\text{cm}^{-2}$  and  $32 \text{ mA}\cdot\text{cm}^{-2}$ ) the batteries exhibit a  
187 significant limitation in the delithiation process (see the capacity loss at Fig. 4), which suggest  
188 irreversible phenomena occurring in the bulk of the electrolyte, at the SEI, or within the Ga  
189 cathode.

190 In order to clarify the failure mechanisms within the battery, cells at different charge states were  
191 slowly cooled down to room temperature and post mortem analyses were performed. When  
192 opening the cell, it was visible that the RTIL electrolyte showed signs of degradation proved by a  
193 change in color which turned to light-brown and also by the presence of fine particles  
194 accumulated at the cathode-electrolyte interface. This might be caused by a SEI instability  
195 coupled with RTIL decomposition products. Within the fracture cross-section of the cathode, a  
196 distinct gray layer corresponding to the Li-Ga alloy, is present at the top, while liquid Ga is  
197 observed beneath.

198

### 199 3.2 XPS analyses

200 As a next step we use XPS to determine the chemical composition on the surface and in the bulk  
201 of two cathode samples. One was taken from a cell after the first complete lithiation, while the  
202 other after a few electrochemical cycles, the last one being stopped at the end of the delithiation.  
203 The BE positions of the surface detected core level states and the atomic concentration of the  
204 elements are summarized in Table 1, and show a relatively good agreement between the  
205 elemental composition and the peak positions of the neat [BMP][TFSI] ionic liquid [16] and the  
206 Ga cathode surface. This refers to an electrolyte film, which does not evaporate after drying

207 under vacuum due to the very low vapour pressure of the ionic liquid. The increased amount of  
208 [TFSI] anion, suggested by the increased  $N^{\text{anion}}/N^{\text{cation}}$  (i.e.,  $N^{399.5 \text{ eV}}/N^{402.7 \text{ eV}}$ ) ratio, originates  
209 from the dissolved Li[TFSI] salt. No distinct presence of electrolyte decomposition products is  
210 found in this thin layer except a small amount of fluorine compound with  
211 BE = 685.3 eV  $\pm$  0.1 eV (0.8 at. % and 2.3 at. % after lithiation and delithiation, respectively),  
212 which we assign to LiF [22]. Its detection suggests electrochemical reduction of the [TFSI] anion  
213 to a reactive radical,  $\bullet\text{NSO}_2\text{CF}_3^-$ , which further breaks down to  $\text{CF}_2^-$  or  $\text{F}^-$ -containing species,  
214 which easily react with metallic lithium and form  $\text{RCF}_2\text{Li}$  and LiF, as already proposed by  
215 Aurbach et al. [23] and Howlett et al. [24]. The absence of a  $\text{Li}^+$  signal is assigned to the low  
216 photoelectron cross section of the  $\text{Li}1s$  state [19] and the related detection limit of XPS  
217 (0.1 at. %).

218 Further, we analyse the elemental compositions and the distribution in the bulk of the cathode  
219 after sputtering the samples with  $\text{Ar}^+$  ions.

220 The BE positions and the quantitative analysis are displayed in Fig. 5 and Table 2. The detection  
221 of F, O, C, N and S inside the cathode is a direct indication for the decomposition of the  
222 electrolyte in the course of the electrochemical process and supports our assumption based on the  
223 EIS data. F, O, S and C – containing reduction products diffused irreversibly into the cathode  
224 layer already in the course of the first lithiation cycle and stay accumulated there after the liquid-  
225 solid transition during cooling of the battery system. S-containing species intercalate reversibly,  
226 while the N-containing reduction products are found only after a few cycles.

227 The deconvolution of the F1s spectrum reveals the presence of several species, which we assign  
228 to LiF ( $\text{BE}^{\text{F}1s} \sim 685.5 \text{ eV}$ ,  $\text{BE}^{\text{Li}1s} \sim 56 \text{ eV}$ ) [22] and three organic fluorine compounds detected at  
229 BE  $\sim 687$ , 689 and 691 eV. The peak at ( $\sim 689 \text{ eV}$ ) has a position, which correlates with the

230 trifluoromethyl ( $-\text{CF}_3$ ) group from the  $[\text{TFSI}]^-$  anion. The corresponding C1s peak however  
231 appears at BE  $\sim 289$  eV, which is relatively low with respect to the  $[\text{TFSI}]^-$  C1s peak of the neat  
232 ionic liquid (i.e. 293 eV) [16]. We assign this to an anion decomposition via cleavage of the F–C  
233 bond and formation of a  $\text{CF}^-$  containing  $[\text{TFSI}]^-$  fragment (denoted as  $\text{R}_1\text{CF}^-$  in Fig. 5). Its further  
234 reduction leads to the formation of smaller species resulting in F1s state at  $\sim 687$  eV. Finally, the  
235 fluorine component at  $\sim 691$  eV points out to a subsequent rearrangement of the decomposition  
236 products and formation of species with O– $\text{F}_x$  fragment with a O1s peak at  $\sim 534.7$  eV. Two  
237 additional oxygen states at  $\sim 533.2$  and  $531.2$  eV indicate further incorporation of  $\text{O}-\text{C}-\text{O}$  or  $\text{C}=\text{O}$   
238 containing  $[\text{TFSI}]^-$  reduction products (with corresponding C1s features at  $\sim 286$ – $287$  eV) and  
239 oxidation of Ga atoms, respectively. The  $\text{Ga}2p_{3/2}$  state at  $\sim 1119$  eV is characteristic for Ga–O  
240 bonds and the quantitative analysis of the corresponding components indicates formation of  
241 gallium oxyhydroxide ( $\text{GaOOH}$ ) during lithiation and further transformation to gallium oxide  
242 ( $\text{Ga}_2\text{O}_3$ ) during delithiation.

243 The C1s peak at  $\sim 285$  eV has a characteristic BE for C–C/H bonds and most probably originates  
244 from the  $[\text{BMP}]^+$  cation  $\text{C}_4\text{H}_9$ -alkyl chain. The detection of sulphur refers to  $[\text{TFSI}]^-$   
245 fragmentation, while the nitrogen signal might originate from both, the anion or the cation.

246 Next, we try to distinguish possible metallic and intermetallic states of Li and Ga. While the  
247 metallic Ga peak at 1116.7 eV is the most intensive one in the  $\text{Ga}2p_{3/2}$  spectrum, there is no  
248 metallic Li detected in the bulk of the cathode (Fig. 5). The deconvolution of the Li1s spectrum  
249 identifies three components at  $\sim 56$ , 58 and 60 eV. As mentioned already, the first one originates  
250 from LiF, while the other two components at higher BE can only be explained by the presence of  
251 lithium-species, in which the  $\text{Li}^{\delta+}$  positive charge is higher than that of LiF. This correlates well  
252 with two Ga–Li intermetallic states existing at room temperature:  $\text{Ga}_7\text{Li}_2$  (BE = 58.0 eV) and

253 Ga<sub>14</sub>Li<sub>3</sub> (BE 60 eV) [14]. The corresponding Ga2p<sub>3/2</sub> states are expected around 1120 eV, but are  
254 not undoubtedly identified in the measurement. We anticipate that this is primarily connected to  
255 an unexpectedly low amount of Ga detected after Ar<sup>+</sup> sputtering (Table 2), which might be due  
256 to the sample roughness and the inhomogeneous distribution of the elements. Moreover, due to  
257 the difference in kinetic energy the depth of information of the Ga2p photoelectrons is much  
258 smaller than that of the Li1s photoelectrons.

259

#### 260 4. Conclusion

261 A low temperature liquid metal battery with Li and Ga molten electrodes and an ionic liquid  
262 based electrolyte (1M Li[TFSI] in [BMB][TFSI]) operated at 220 °C has been proposed and its  
263 performances was evaluated. Low temperature LMBs are interesting candidates for fluid flow  
264 measurements in multilayer systems. Cell prototypes of ca. 0.2 A·h theoretical capacity were  
265 constructed and galvanostatically cycled at different current densities ranging from 10 mA·cm<sup>-2</sup>  
266 (C/40 rate) to 32 mA·cm<sup>-2</sup> (C/12 rate). The cells show promising performances at relatively low  
267 current densities. The cells tested at 10 mA·cm<sup>-2</sup> showed stable alloying and de-alloying with  
268 discharge capacity values of about 100 mA·h at 50 % depth of discharge. Furthermore, the  
269 round-trip Coulombic efficiency is close to 100 % with an overall energy efficiency of 65 %.  
270 Further we checked the electrochemical behavior at higher current rates. At 16 mA·cm<sup>-2</sup> and  
271 32 mA·cm<sup>-2</sup> the cells have almost identical performances, showing irreversible delithiation.  
272 Increasing the current density rate induces a higher IR voltage drop coupled with charge transfer  
273 losses contributing to a faster capacity fade. There are also indications of mass-transport  
274 limitations of the Li ions at either of the electrode-electrolyte interfaces or within the electrolyte  
275 or the Ga cathode. Our attempts to improve the battery performances by modifying the system

276 design did not succeed so far. However, in order to control the system, we tried to understand the  
277 processes which lead to the irreversible delithiation phenomena. X-ray Photoelectron  
278 Spectroscopy reveals that during the battery operation at  $16 \text{ mA cm}^{-2}$ , the ionic liquid based  
279 electrolyte decomposes already after the first discharge cycle and the reduction products  
280 accumulate in the Ga-cathode. Next to the metallic Ga in the bulk of the cathode, two Li-Ga  
281 intermetallic states are also detected:  $\text{Ga}_7\text{Li}_2$  and  $\text{Ga}_{14}\text{Li}_3$ .

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342 **Table 1.** Binding energy (BE in eV) and atomic percentage (at. %) of the elements F, O, N, C  
 343 and S from XPS spectra of the neat IL alone and the cathode surface after lithiation (measured at  
 344 the end of the first discharge cycle) and delithiation (measured after three cycles), corresponding  
 345 to Figure 5.

[BMP][TFSI]			Cathode surface after lithiation		Cathode surface after delithiation	
State	BE	at. %	BE	at. %	BE	at. %
F1s	689.0	25.7	688.9	28.3	688.9	22.8
			685.4	0.8	685.2	2.3
O1s	532.8	12.8	532.8	16.6	532.8	13.8
					531.2	1.4
N1s	402.7	2.6	402.7	2.8	402.7	2.3
	399.6	2.6	399.5	3.6	399.5	3.6
C1s	293.0	8.1	293.0	7.7	293.1	5.1
	286.8	21.6	286.8	13.6	286.7	11.6
	285.5	18.2	285.4	19.0	285.3	31.2
S2s	233.3	7.7	233.2	6.7	233.2	5.0
			230.2	0.9	229.5	0.8

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371 **Table 2.** Binding energy (BE in eV) and atomic percentage (at. %) of the elements F, O, N, C, S,  
 372 Li and Ga from XPS spectra of the Ga cathode after sputtering with 3 keV Ar<sup>+</sup> for 30 min  
 373 (corresponding to Fig. 2)

State	LITHIATION (30 min sputtering)		DELITHIATION (30 min sputtering)	
	BE	at. %	BE	at. %
F1s	690.8	2.7	690.9	4.3
	688.9	3.5	689.2	3.1
	687.3	16.1	687.2	9.1
	685.6	6.3	685.7	2.7
O1s	534.5	4.0	534.9	2.7
	533.2	2.9	533.4	6.7
	531.2	1.5	531	1.8
N1s	—	—	391.9	5.4
	—	—	388.6	1.8
C1s	288.8	1.9	289	2.5
	287.4	7.0	287.3	11.1
	286.1	9.1	285.9	6.5
	285.1	10.6	285	11.3
S2s	234.4	1.5	—	—
	228.7	2.4	—	—
Li1s	59.9	—	60.6	—
	58.0	28.0	58.0	29.5
	56.3	—	56.6	—
Ga 2p	1120.4	0.5	1120	0.4
	1118.2	0.6	1118.3	0.6
	1116.7	1.3	1116.7	0.7
	1115.7	0.2	1115.9	0.1

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399 **Figure captions**

400 Fig. 1 Schematic layout of the Li||Ga liquid metal battery.

401 Fig. 2 Electrochemical performance of a Li||Ga cell cycled at  $10 \text{ mA} \cdot \text{cm}^{-2}$  for 50 % depth of  
402 discharge operated at  $230 \text{ }^\circ\text{C}$ .

403 Fig. 3 Comparative cyclic voltammetric curves for a Li||Ga cell: initial (first – black and second  
404 – red voltammetric scans) and after 14 charge-discharge cycles at  $10 \text{ mA} \cdot \text{cm}^{-2}$  (first – blue and  
405 second – magenta voltammetric scans). Scan rate:  $0.5 \text{ mV} \cdot \text{s}^{-1}$  (a) and the Nyquist plots of a  
406 Li||Ga cell. Frequency range from 100 kHz to 10 mHz (b).

407 Fig. 4 Voltage profiles during charge-discharge cycles at different current densities of LMBs  
408 with theoretical capacity of  $0.21 \text{ A} \cdot \text{h}$ .

409 Fig. 5  $\text{Ga}2\text{p}_{3/2}$ ,  $\text{Li}1\text{s}$ ,  $\text{C}1\text{s}$ ,  $\text{F}1\text{s}$  and  $\text{O}1\text{s}$  core level peaks XPS spectra of the bulk of the Ga  
410 cathode after lithiation (1) and after delithiation (2). The spectra are recorded after 30 min  
411 sputtering with  $\text{Ar}^+$ . The dashed spectra are the experimental ones, while the envelope peak is  
412 colored in blue and all fitted components are colored in black. The XPS spectra are presented in  
413 the order they are mentioned in the text.

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