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An electrochemical and photoelectron spectroscopy study of a low temperature liquid metal battery based on an ionic liquid electrolyte

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Abstract

We report the design of a low-temperature liquid metal battery (LMB). Li and Ga as the negative and positive electrode, respectively, are used in combination with a room temperature ionic liquid as an electrolyte. 1 mol/L lithium bis(trifluoromethyl)sulfonylimide (Li[TFSI]) in 1-butyl-1-methylpyrrolidinium bis (trifluoromethyl)sulfonylimide ([BMP][TFSI]) is chosen as electrolyte. The battery operates at 220 °C which is a relatively low temperature for a LMB and shows good electrochemical performance at low current density. The cells were cycled for more than 600 h and achieved a round-trip Coulombic efficiency close to 100 % and an average voltage efficiency of 66 % resulting in an overall energy efficiency of 65 %. At higher current densities, however, the system showed up to 75 % irreversible capacity loss after three cycles. To understand the origin of this strong deterioration, we characterized the surface and the bulk properties of the Ga cathode using X-ray Photoelectron Spectroscopy. Especially at higher
current densities a decomposition of the electrolyte was found. The occurring chemical changes and the elemental distribution at the Ga cathode are analyzed based on XPS measurements at different stages of the battery charge/discharge cycling.

1. Introduction

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

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

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

3
2. Experimental

2.1. Electrochemical setup

Cells consisting of a Li negative electrode, a RTIL electrolyte mixture, 1 mol/L lithium bis(trifluoromethylsulfonyl)imide (Li[TFSI]) in 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl)imide ([BMP][TFSI]) and a Ga positive electrode were assembled in the fully charged state inside an insulating aluminum nitride ceramic tube with an active surface area of 0.68 cm² and then placed inside a cylindrical glass container (Fig. 1). Tungsten wires were used as negative and positive current collectors and the inter-electrode distance was 0.5 cm. The assembly process and the electrochemical characterization of the cells were conducted in an inert glove-box with argon atmosphere (OMNI-LAB from Vacuum-Atmospheres – O₂ content < 0.2 ppm, H₂O content < 0.5 ppm). The negative electrode was prepared by immersing the tungsten wire into the molten lithium. Then the gallium metal was added as liquid inside the AlN tube after which the RTIL electrolyte was poured and the negative electrode was placed on top of the electrolyte. The cells were heated up to 220 °C through a coil made of thermoresistive elements which was fixed around the glass tube. The temperature was measured and controlled with a thermocouple. The molten components self-segregate into three layers based on their immiscibility and density differences (0.512 g·cm⁻³ for Li, 1.4 g·cm⁻³ for [BMP][TFSI] and 6.095 g·cm⁻³ for Ga). Thus, based on the chosen geometry and the used materials, the assembled cells have a theoretical capacity of approximately 0.2 A·h.

According to the Ga-Li binary phase diagram, in order to maintain the all liquid metal alloy during operation at the chosen working temperature (220 °C) a fully discharged target composition of 7 mol. % Li in Ga was used [14].
Li and Ga were selected on the basis of their relative low melting points as compared to other existing electrode pairs (180.5 °C for Li and 29.7 °C for Ga). As precursors for battery assembly, Li (purity 99.9 %, supplier Alfa Aesar), Ga (99.99 %, Alfa Aesar), Li[TFSI] (99.9 %, Alfa Aesar) and [BMP][TFSI] (99.95 %, Iolitec) were used as received without further purification. The moisture content in the RTILs was monitored by Karl Fischer titration (model 831 KF from Metrohm) and an average value of 40 ppm water content was recorded.

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

2.2. Sample preparation for XPS analyses

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

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

XPS analysis were carried out with a Specs SAGE spectrometer (base pressure < 1 \times 10^{-8} \text{ mbar}) equipped with a Phoibos 150 electron analyzer using a focused monochromatized AlKα radiation \((h\nu = 1486.7 \text{ eV})\). During the experiments the pressure in the analysis chamber was \(~ 5 \times 10^{-8} \text{ mbar}\). Core level spectra were recorded at a constant analyzer pass energy of 13 eV allowing a total energy resolution of 0.6 eV and no charge neutralization was used. For binding energy calibration, the energy scale was corrected by aligning the N1s signal to the N1s cation state of the neat ionic liquid at 402.7 eV [BMP][TFSI] [16], while the binding energy (BE) scale of the cathode sample was calibrated from the gallium signal using the Ga2p3/2 peak at 1116.7 eV [17]. The core level spectra were analyzed by subtracting a Shirley-type background [18] and peak areas were calculated by a weighed least-square fitting of model curves (70 % Gaussian, 30 % Lorentzian) to the experimental data using the software package CASA XPS (Version 23.16 Dev52, Casa Software Ltd.). For quantification the atomic percentage (at. %) was calculated on the basis of photoionization cross sections by Yeh and Lindau [8].

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

3.1 Electrochemical performance

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

The electrical conductivity of the RTIL electrolyte was estimated from the resistance at high frequency limit in EIS measurements and it was found to be 30 mS·cm⁻¹, which is considerably lower than the conductivity of conventional molten halide salts typically used as electrolytes in LMB’s (1.7–3.5 S·cm⁻¹ for lithium halides).

The cell prototypes of ~ 0.2 A·h theoretical capacity were galvanostatically cycled at 10 mA·cm⁻² (C/40 rate) for a predefined time of 20 h corresponding to a 50 % depth of discharge. The cut-off charging voltage was set to 1.11 V and the cells were operated continuously for about 600 h, i.e. for 14 charge-discharge cycles with stable cycling performance (Fig. 2). The near-constant voltage plateau observed in the galvanostatic voltage-capacity profile and the absence of a sharp voltage drop suggests that during the operation of the battery no intermetallic compounds are formed in agreement with the Li-Ga phase diagram. During the initial cycles the cells exhibited a round-trip Coulombic efficiency of 97 % which slowly increased to 100 % at the end of the test.

This can be caused by an improved wetting of the tungsten negative current collector by molten
lithium during the cycling experiments. The cells achieved an average value of voltage efficiency of 66% during the tests resulting in an overall energy efficiency of 65%.

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

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

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

Further, in order to evaluate the battery capability, the cells were fully discharged (lithiated) at three different current rates: 10 mA·cm\(^{-2}\), 16 mA·cm\(^{-2}\) and 32 mA·cm\(^{-2}\), corresponding to a C/40, C/24 and a C/12 rate, respectively (Fig. 4). The cut-off voltage was set to 0.2 V for lithiation and
1.4 V for delithiation. At 10 mA·cm⁻² the good electrochemical performance of the cells was confirmed by a stable cycling behavior.

In the case of higher current rates (16 mA·cm⁻² and 32 mA·cm⁻²) the batteries exhibit a significant limitation in the delithiation process (see the capacity loss at Fig. 4), which suggest irreversible phenomena occurring in the bulk of the electrolyte, at the SEI, or within the Ga cathode.

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

### 3.2 XPS analyses

As a next step we use XPS to determine the chemical composition on the surface and in the bulk of two cathode samples. One was taken from a cell after the first complete lithiation, while the other after a few electrochemical cycles, the last one being stopped at the end of the delithiation. The BE positions of the surface detected core level states and the atomic concentration of the elements are summarized in Table 1, and show a relatively good agreement between the elemental composition and the peak positions of the neat [BMP][TFSI] ionic liquid [16] and the Ga cathode surface. This refers to an electrolyte film, which does not evaporate after drying...
under vacuum due to the very low vapour pressure of the ionic liquid. The increased amount of [TFSI] anion, suggested by the increased N\textsuperscript{anion}/N\textsuperscript{cation} (i.e., N\textsuperscript{399.5 eV}/N\textsuperscript{402.7 eV}) ratio, originates from the dissolved Li[TFSI] salt. No distinct presence of electrolyte decomposition products is found in this thin layer except a small amount of fluorine compound with BE = 685.3 eV ± 0.1 eV (0.8 at. % and 2.3 at. % after lithiation and delithiation, respectively), which we assign to LiF [22]. Its detection suggests electrochemical reduction of the [TFSI] anion to a reactive radical, •NSO\textsubscript{2}CF\textsubscript{3}−, which further breaks down to CF\textsubscript{2}− or F−-containing species, which easily react with metallic lithium and form RCF\textsubscript{2}Li and LiF, as already proposed by Aurbach et al. [23] and Howlett et al. [24]. The absence of a Li\textsuperscript{+} signal is assigned to the low photoelectron cross section of the Li1s state [19] and the related detection limit of XPS (0.1 at. %).

Further, we analyse the elemental compositions and the distribution in the bulk of the cathode after sputtering the samples with Ar\textsuperscript{+} ions. The BE positions and the quantitative analysis are displayed in Fig. 5 and Table 2. The detection of F, O, C, N and S inside the cathode is a direct indication for the decomposition of the electrolyte in the course of the electrochemical process and supports our assumption based on the EIS data. F, O, S and C – containing reduction products diffused irreversibly into the cathode layer already in the course of the first lithiation cycle and stay accumulated there after the liquid-solid transition during cooling of the battery system. S-containing species intercalate reversibly, while the N–containing reduction products are found only after a few cycles.

The deconvolution of the F1s spectrum reveals the presence of several species, which we assign to LiF (BE\textsubscript{F1s} ∼ 685.5 eV, BE\textsubscript{Li1s} ∼ 56 eV) [22] and three organic fluorine compounds detected at BE ∼ 687, 689 and 691 eV. The peak at (∼ 689 eV) has a position, which correlates with the
trifluoromethyl (-CF$_3$) group from the [TFSI]$^-$ anion. The corresponding C1s peak however
appears at BE $\sim$ 289 eV, which is relatively low with respect to the [TFSI] C1s peak of the neat
ionic liquid (i.e. 293 eV) [16]. We assign this to an anion decomposition via cleavage of the F–C
bond and formation of a CF$^-$ containing [TFSI]$^-$ fragment (denoted as R$_1$CF$^-$ in Fig. 5). Its further
reduction leads to the formation of smaller species resulting in F1s state at $\sim$ 687 eV. Finally, the
fluorine component at $\sim$ 691 eV points out to a subsequent rearrangement of the decomposition
products and formation of species with O–F$^x$ fragment with a O1s peak at $\sim$ 534.7 eV. Two
additional oxygen states at $\sim$ 533.2 and 531.2 eV indicate further incorporation of O–C–O or C=O
containing [TFSI]$^-$ reduction products (with corresponding C1s features at $\sim$ 286-287 eV) and
oxidation of Ga atoms, respectively. The Ga$_{2p3/2}$ state at $\sim$ 1119 eV is characteristic for Ga–O
bonds and the quantitative analysis of the corresponding components indicates formation of
gallium oxyhydroxide (GaOOH) during lithiation and further transformation to gallium oxide
(Ga$_2$O$_3$) during delithiation.

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

Next, we try to distinguish possible metallic and intermetallic states of Li and Ga. While the
metallic Ga peak at 1116.7 eV is the most intensive one in the Ga$_{2p3/2}$ spectrum, there is no
metallic Li detected in the bulk of the cathode (Fig. 5). The deconvolution of the Li$_{1s}$ spectrum
identifies three components at $\sim$ 56, 58 and 60 eV. As mentioned already, the first one originates
from LiF, while the other two components at higher BE can only be explained by the presence of
lithium–species, in which the Li$^{5+}$ positive charge is higher than that of LiF. This correlates well
with two Ga-Li intermetallic states existing at room temperature: Ga$_7$Li$_2$ (BE = 58.0 eV) and
Ga₁₄Li₃ (BE 60 eV) [14]. The corresponding Ga₂p₃/₂ states are expected around 1120 eV, but are not undoubtedly identified in the measurement. We anticipate that this is primarily connected to an unexpectedly low amount of Ga detected after Ar⁺ sputtering (Table 2), which might be due to the sample roughness and the inhomogeneous distribution of the elements. Moreover, due to the difference in kinetic energy the depth of information of the Ga₂p photoelectrons is much smaller than that of the Li₁s photoelectrons.

4. Conclusion

A low temperature liquid metal battery with Li and Ga molten electrodes and an ionic liquid based electrolyte (1M Li[TFSI] in [BMB][TFSI]) operated at 220 °C has been proposed and its performances was evaluated. Low temperature LMBs are interesting candidates for fluid flow measurements in multilayer systems. Cell prototypes of ca. 0.2 A·h theoretical capacity were constructed and galvanostatically cycled at different current densities ranging from 10 mA·cm⁻² (C/40 rate) to 32 mA·cm⁻² (C/12 rate). The cells show promising performances at relatively low current densities. The cells tested at 10 mA·cm⁻² showed stable alloying and de-alloying with discharge capacity values of about 100 mA·h at 50 % depth of discharge. Furthermore, the round-trip Coulombic efficiency is close to 100 % with an overall energy efficiency of 65 %. Further we checked the electrochemical behavior at higher current rates. At 16 mA·cm⁻² and 32 mA·cm⁻² the cells have almost identical performances, showing irreversible delithiation. Increasing the current density rate induces a higher IR voltage drop coupled with charge transfer losses contributing to a faster capacity fade. There are also indications of mass-transport limitations of the Li ions at either of the electrode-electrolyte interfaces or within the electrolyte or the Ga cathode. Our attempts to improve the battery performances by modifying the system.
design did not succeed so far. However, in order to control the system, we tried to understand the processes which lead to the irreversible delithiation phenomena. X-ray Photoelectron Spectroscopy reveals that during the battery operation at 16 mA cm\(^{-2}\), the ionic liquid based 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 states are also detected: Ga\(_7\)Li\(_2\) and Ga\(_{14}\)Li\(_3\).

Acknowledgement

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References


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

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

<table>
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Figure captions

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

Fig. 2 Electrochemical performance of a Li||Ga cell cycled at 10 mA·cm⁻² for 50 % depth of discharge operated at 230 °C.

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

Fig. 4 Voltage profiles during charge-discharge cycles at different current densities of LMBs with theoretical capacity of 0.21 A·h.

Fig. 5 Ga2p₃/₂, Li1s, C1s, F1s and O1s core level peaks XPS spectra of the bulk of the Ga cathode after lithiation (1) and after delithiation (2). The spectra are recorded after 30 min sputtering with Ar⁺. The dashed spectra are the experimental ones, while the envelope peak is colored in blue and all fitted components are colored in black. The XPS spectra are presented in the order they are mentioned in the text.