A Zwitterionic Liquid Electrolyte for Magnesium Batteries

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Rechargeable magnesium batteries are promising energy storage devices due to their high theoretical capacity. However, currently a crucial hindrance for their realization is the limited number of suitable electrolytes, all of which show severe disadvantages. We circumvent volatility, flammability, and instability issues of other systems by presenting an electrolyte based on magnesium borohydride and the zwitterionic liquid (ZIL) 1-butyl-3-methylimidazol-2-ylidene borane. We investigate the structure and properties of the electrolyte and compare it to a similar conventional system. Pronounced intermolecular interactions in the new electrolyte are investigated by ^{1}H and ^{11}B NMR spectroscopy. We also characterize galvanostatic cycling and deposition of magnesium on different electrodes and analyze the deposited material. Because of high reversibility and stability of the ZIL based electrolyte system, it shows promising potential for future magnesium based batteries.

1. Introduction

Small, mobile electronic devices like smartphones, laptops, and even electrical cars, powered by lithium-ion batteries (LIBs), define and enable our high standard of life.[1] For increasing energy storage in such devices, however, current LIBs may not be suitable, as the possible charge is limited. While in theory, 3862 mAh g^{-1} or 2061 mAh cm^{-3} may be accessible when using lithium metal electrodes, the high reactivity of lithium metal and its tendency to form dendrites in dissolution and re-deposition cycles hamper its applicability.[2,3] Consequently, intercalation electrodes are used, which significantly lower the achievable capacity of the battery (LiC$_6$-intercalation electrode: 372 mAh g^{-1} or 837 mAh cm^{-3}).[4] Concerns regarding safety as well as limited supply and/or questionable mining conditions of lithium and other necessary LIB elements such as cobalt, manganese, and nickel, additionally contribute to the need for alternative technologies.[2,3,5,6,7,8]

The use of magnesium as active ionic species in rechargeable batteries presents a possible solution to these issues. It possesses a high capacity (Mg metal: 2205 mAh g^{-1} or 3832 mAh cm^{-3}) and a low redox potential which enables the fabrication of high voltage batteries (Mg^{2+}/Mg: −2.3 V vs. standard hydrogen electrode (SHE); Li$^+$/Li: −3 V vs. SHE).[4] Most importantly, the formation of dendrites has not been observed as a problem despite a multitude of publications on magnesium electrochemical cycling, which facilitates the use of magnesium metal anodes.[4,9] On the cathode side, vanadium, sulfur, or molybdenum based electrodes as previously investigated for lithium based batteries may be used, all of which are cobalt-free and consequently avoid socio-economic problems related to the use of cobalt.[10,7] Furthermore, magnesium is much more abundant than lithium (Mg: 2.1% of the earth's crust by weight; Li: 0.006%).[11]

Also, while magnesium is highly reactive, it passivates rapidly, which makes it much safer than lithium metal, as battery failures or accidents will less likely expose reactive metal to the environment.[11,12,13] All of the above make magnesium based batteries the possible next stage of battery technology, surpassing lithium-ion batteries in terms of capacity, safety, and socio-ecologic impact.

The mentioned tendency of magnesium to form passivating layers in the presence of reducible species is one of the key factors that complicate magnesium battery research, as high reductive stability of electrolytes is necessary. Impurities as well as exposure to the ambient environment (e.g., in case of battery failure or an accident) will passivate the magnesium surface even when stable electrolytes are used.[4,14,10] In order to avoid stability problems of common electrolyte salts and solvents (used in LIBs) in the presence of magnesium metal,[14] state of the art research focusses on the use of toxic and/or volatile ethers as solvents in conjunction with various magnesium salts.[12,15,16,17] Out of the latter, magnesium borohydride or the use of borohydrides in general is especially appealing because of high reductive stability and prevention of the formation of a passivating layer on magnesium metal anodes.[16,14,18]

For increased safety, not only the magnesium salt but also the other components of an electrolyte system require attention. A better electrolyte system should be sustainable, non-volatile, and non-hazardous, possess low-flammability, and show excellent electrochemical performance. Ionic liquids (ILs) may comply with all of those prerequisites, which is why some designer ionic liquids are receiving increasing attention in magnesium battery research.[19,20,21,22,23] In contrast, simple imidazolium based ILs (ImILs), which are accessible in a fast and efficient way from renewable resources,[24,25,26,27] have been abandoned by the scientific community due to instability issues of the imidazolium ring.[22,28] Furthermore, some common

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anions are not compatible with magnesium electrochemistry. For example, the bis(trifluoromethane)sulfonimide (TFSI) anion, one of the most used anions for IL-based systems in electrochemical applications, can only be considered electrochemically stable enough for magnesium based batteries under special conditions, i.e., in absolutely water free electrolytes where TFSI was barred from taking part in the direct coordination with magnesium, e.g., by addition of long chain ethers which replace TFSI in the coordination sphere of magnesium.[29,4,22,10]

In this work, we combine the good properties of magnesium borohydride as salt species of the electrolyte with a simple yet well performing ionic liquid as solvent species of the electrolyte. We investigate a way to circumvent stability problems of imidazolium ionic liquids by using an electrolyte system based on the zwitterionic liquid (ZIL) 1-butyl-3-methylimidazol-2-ylidene borane and magnesium borohydride. As we discussed recently, this zwitterionic liquid is remarkably stable and has a high liquidity range with low viscosity.[30] We characterize the electrolyte system and investigate reversible magnesium deposition. This could reopen the door for the use of ImILs in magnesium battery research and allow the combination of truly sustainable ionic liquids with state-of-the-art energy storage technology.
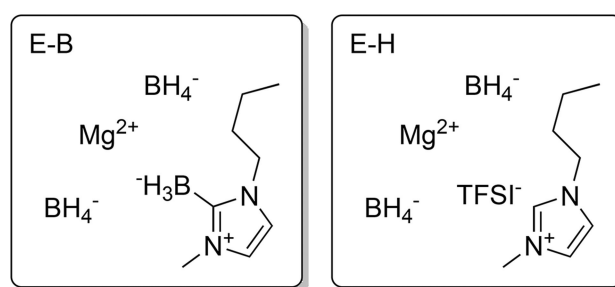
Experimental Section

The synthesis of the zwitterionic liquid 1-butyl-3-methylimidazol-2-ylidene borane (BBH_3MIm) and a similar conventional ionic liquid, 1-butyl-3-methyl imidazolium bis(trifluoromethane)sulfonimide (BMImTFSI), were carried out as reported previously.[30] The electrolyte systems (0.5 M solution) were prepared by dissolving magnesium borohydride in the ILs. NMR measurements were performed on a Bruker ascend400 Avance III or a Varian 400MR or a Varian 600MR spectrometer. SEM was measured on a LEO 1550 Gemini microscope and on a JEOL JSM-7001F FE-SEM. Electrochemical behavior was investigated in 2-electrode Swagelok-type cells using an MPG-2 potentiostat (Bio-Logic). Details about the sample preparation and measurements are summarized in the Supporting Information.

2. Results and Discussion

The electrolyte systems **E–B** and **E–H** were prepared by dissolving magnesium borohydride in BBH_3MIm and BMImTFSI, respectively (cf. Scheme 1). BMImTFSI was chosen for comparison to the ZIL as it is a) isostructural to BBH_3MIm (disregarding the C2 position) and b) the bis(trifluoromethane)sulfonimide anion is known to convey favorable electrochemical properties to the resulting ionic liquid.[15] Magnesium borohydride was chosen due to the aforementioned benefits and because it reacts with residual traces of water in the ionic liquid during electrolyte formulation, leading to a truly water-free electrolyte (see Equation 1 of the experimental part in the Supporting Information for details).[15,16,14]

To investigate the nature of the obtained electrolyte systems **E-B** and **E-H**, ^{11}B and ^1H NMR-spectroscopy were conducted. The electrolyte systems are sensitive to moisture,

Scheme 1. Structures of the electrolyte systems compared in this work.

and hence NMR sample preparation was carried out inside a glovebox (preparation and ^1H-NMR spectra see Supporting Information). Spectra were measured in bulk if not denoted otherwise. This allows the observation of the sample under conditions of the actual electrolyte system. Figure 1 shows the relevant region of ^{11}B NMR spectra obtained from the electrolyte systems and, as a reference, from BBH_3MIm and magnesium borohydride. The spectrum of magnesium borohydride in deuterated THF shows a clear quintet as expected from coupling with four hydrogen nuclei.[31] The same quintet is observed in **E–H** (BMImTFSI+$Mg(BH_4)_2$), as expected. After background subtraction of the broad peak within the spectrum of **E-B** (BBH_3MIm+$Mg(BH_4)_2$), the quintet is also clearly observable. When comparing the chemical shift of this quintet
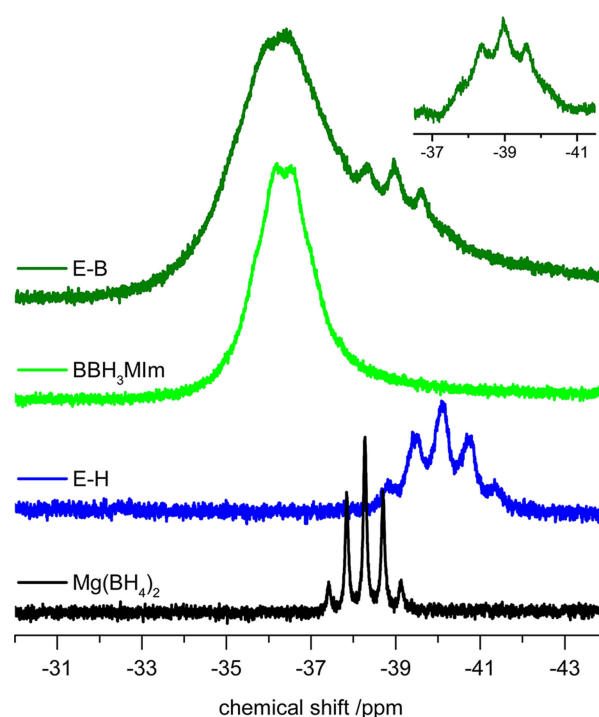

Figure 1. ^{11}B NMR spectra of $Mg(BH_4)_2$, the neat zwitterionic liquid BBH_3MIm, and the electrolyte systems **E-H** (BMImTFSI+$Mg(BH_4)_2$) and **E-B** (BBH_3MIm+$Mg(BH_4)_2$). With the exception of $Mg(BH_4)_2$ (measured in THF-d_8), all spectra were obtained without dilution of the samples with additional solvents (cf. Supporting Information). The inset shows the spectrum of **E-B** after subtracting the broad peak around −36 ppm.

in **E-H** and **E-B**, a significant downfield shift in **E-B** is observed, which is likely caused by the different solvent (BBH$_3$MIm in the case of **E-B** and BMImTFSI in the case of **E-H**). This downfield shift may indicate that in **E-B** the negative charge of the borohydride group is distributed over a more expanded network between the BH$_3$ groups of BBH$_3$MIm and Mg(BH$_4$)$_2$, leading to decreased negative charge density near the nucleus. This is further supported by the presence of broader peaks in **E-B** compared to **E-H** (or even compared to Mg(BH$_4$)$_2$ in deuterated THF) and from the position and broadening of the four BH$_4$ peaks in the ^{1}H-NMR spectra of **E-H** and **E-B** in the Supporting Information (coupling of ^{1}H with the spin 3/2 nucleus ^{11}B).

Even more intense peak broadening is observed in ^{11}B-NMR spectra for the quartet denoting to the BH$_3$ group in BBH$_3$MIm around −36.5 ppm, both in the neat ZIL and in **E-B** (BBH$_3$MIm + Mg(BH$_4$)$_2$). Clearly separated peaks of this quartet may only be observed upon measurement in CDCl$_3$ or at elevated temperature as demonstrated in the Supporting Information. For both the neat zwitterionic liquid and **E-B**, this indicates limited mobility of the observed nuclei in the bulk samples, similar to solvents with strong intermolecular interactions like water, or polymers where constraints impede the averaging of the bulk magnetization. Consequently, both the zwitterionic liquid and the electrolyte system composed of the zwitterionic liquid and magnesium borohydride exhibit strong intermolecular interactions.

Intermolecular interactions are preferably centered on the hydrogen and boron atoms of the BH$_3$ and BH$_4$ groups, as broadening of NMR signals mainly affects the corresponding signals (cf. Supporting Information for further spectral data). We note that ^{13}C is of negligible abundancy and does not influence the coupling, so the multiplicity of the BH$_3$ signals is as expected for BH$_3$ groups which are bound to the heterocycle.

Figure 2a shows the reductive stability of the neat ionic liquids BBH$_3$MIm and BMImTFSI as well as the corresponding electrolyte systems **E-B** and **E-H** on a stainless steel (SS) working electrode using magnesium metal as counter/reference electrode. Stainless steel was chosen as the material for the working electrode due to its cost-advantage with respect to the often used noble metal working electrodes, e.g., Pt working electrodes. Besides being more expensive, it was pointed out that

platinum metal may catalytically decompose BH$_4^-$ based electrolytes.[14] In contrast, BH$_4^-$ based electrolytes are not catalytically decomposed by stainless steel electrodes and also not corrosive towards stainless steel. For applications, we require negligible reactions and hence define reductive stability only for current densities below 0.025 mA cm^{-2} as indicated by a black dashed horizontal line in Figure 2a. The resulting reductive stabilities of the neat solvents are −1.29 V and −1.66 V vs. Mg^{2+}/Mg for BMImTFSI and BBH$_3$MIm, respectively. Similar to the reported stability vs. lithium metal,[30] BBH$_3$MIm also shows excellent stability vs. magnesium (enhanced stability compared to similar imidazolium ionic liquids). Applying the same stability criterion, the electrolyte system shows oxidative stability until 3.56 V vs. Mg^{2+}/Mg (cf. Supporting Information). At moderately positive potential vs. Mg^{2+}/Mg, the behavior of BBH$_3$MIm and **E–B** in linear sweep voltammetry (LSV) measurements is very similar, indicating reductive stability of the ZIL based electrolyte. Beginning at −0.61 V vs. Mg^{2+}/Mg and without any deviant behavior from BBH$_3$MIm, which would correspond to degradation of **E–B** upon the addition of magnesium borohydride, the reduction curve of **E-B** shows the expected steep decline commonly observed in the case of magnesium electrodeposition.[15,19]

In this study, neat BMImTFSI is surprisingly stable on the used stainless steel working electrodes;[32,18] however, Figure 2a reveals that the reductive stability of BMImTFSI is compromised by the addition of magnesium borohydride (**E–H**). This electrolyte system shows increased current over the whole voltage compared to the neat solvent and presents a significant reduction peak in LSV measurements prior to the typical steep decline related to deposition of magnesium. This behavior indicates chemical reactions in the electrolyte system at voltages which are not sufficient for magnesium electrodeposition and hence probably decomposition of the electrolyte. Such reactions are not observable in the zwitterionic liquid electrolyte system and indicate that **E–H** might not be suitable in magnesium electrochemistry.

In order to evaluate the application of **E–B** as an electrolyte system in magnesium batteries, cyclic voltammetry (CV) was performed. Figure 2b and c show the cycling behavior of both electrolyte systems on stainless steel versus magnesium counter/reference electrodes. The behavior of both systems at
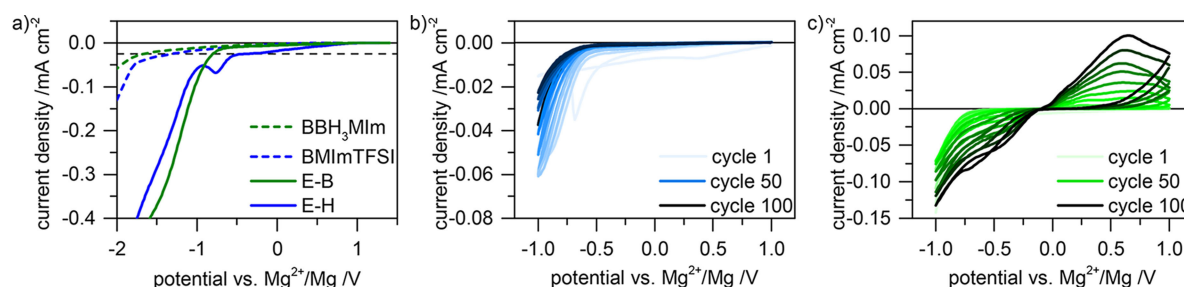

Figure 2. a) Stability limits of the ionic liquids and the electrolyte systems as observed by linear sweep voltammetry. The horizontal dashed black line corresponds to 0.025 mA cm^{-2}. b) Cyclic voltammetry of the electrolyte system **E-H**. c) Cyclic voltammetry of the electrolyte system **E-B**. All voltammetry was conducted at 5 mV s^{-1} on a 316ss working electrode against a magnesium metal counter electrode. Changes of color shading from bright to dark in b) and c) indicate increasing cycle number. Cycles 1, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 are displayed.

negative potentials vs. Mg^{2+}/Mg is similar to the results of Figure 2a. In case of **E–B**, activity gradually increases at positive potentials vs. Mg^{2+}/Mg upon cycling until a notable peak is visible. This observation indicates the deposition and dissolution of magnesium albeit at a notable overpotential. To investigate the factors that determine stability and applicability for reversible magnesium electrodeposition, we compared CV experiments of **E–B** ($BBH_3MIm + Mg(BH_4)_2$) to similar electrolyte systems. When exchanging $Mg(BH_4)_2$ by $Mg(TFSI)_2$ as the magnesium salt dissolved in the ZIL, no activity at positive potentials vs. Mg^{2+}/Mg was observed in CV experiments (cf. Supporting Information), indicating the importance of $Mg(BH_4)_2$ as presented before.[15] The solvent is however just as important: Cycling of **E-H** ($BMImTFSI + Mg(BH_4)_2$) between -1 and 1 V vs. Mg^{2+}/Mg also effects flattening of the CV curve, and no activity at positive potentials vs. Mg^{2+}/Mg can be observed (Figure 2b), which might be attributed to the electrochemically instable C2 position between both nitrogen atoms in the imidazolium ring.[28,22] Surprisingly, also no reversible electrodeposition of magnesium was observed in an electrolyte made from $Mg(BH_4)_2$ and 1-butyl-2,3-dimethyl imidazolium bis(trifluoromethane)sulfonimide (BMMImTFSI), which is isostructural to **E–H** with the exception of a methyl group bound to the C2 position in the imidazolium ring (cf. Supporting Information). The protected neat ionic liquid BMMImTFSI previously showed similar reductive stability vs. lithium as BBH_3MIm.[30] The incapability of the electrolyte $BMMImTFSI + Mg(BH_4)_2$ for reversible electrodeposition of magnesium indicates instability of the TFSI anion as extensively discussed before[4,10,22,29] and also demonstrates the unique interplay of the ZIL and magnesium borohydride.

Motivated by the successful reversible electrodeposition of magnesium from **E-B** in CV experiments, we conducted galvanostatic cycling experiments using **E-B** in different setups (see Supporting Information for setups). Figure 3 compares the results of cycling **E-B** between a stainless steel working electrode (SS-WE) and a magnesium counter/reference electrode (Mg-CE) to the results of cycling between two magnesium electrodes (a,b and c,d, respectively). In both cases, a current density of 1 mA cm^{-2} was applied. Continuous deposition and dissolution of magnesium is achieved for several hundred cycles for both tests. Using a SS-WE, stable cycling was achieved after a brief conditioning period with an efficiency of approximately 96% for 245 cycles without changes of the cycle shape (all cycles shown in the Supporting Information). While the shape of galvanostatic deposition and dissolution curves changes beyond this cycle, the efficiency is unaffected and stays at 96% for more than another 100 cycles. In case of galvanostatic cycling on a Mg working electrode, stable deposition and dissolution behavior and high efficiency is achieved even beyond this at the same coulombic efficiency.

Next to the stability of the system for many cycles and the high coulombic efficiency, the shape of the cycles is noteworthy. The experiment shows two distinct steps in both oxidation and reduction cycles, which may indicate that the zwitterionic liquid contributes to the reversible magnesium electrodeposition in terms of two consecutive one electron
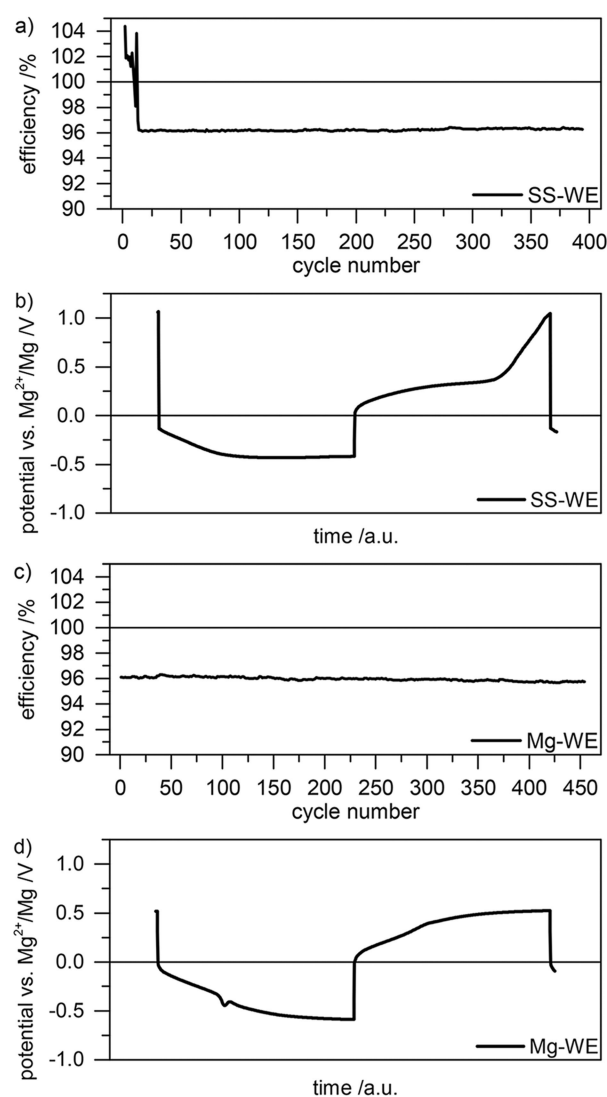

Figure 3. Results of galvanostatic cycling with a current density of 1 mA cm^{-2}. a), b) Cycling between a SS-WE and a Mg-CE; c), d) cycling between a Mg-WE and a Mg-CE. a), c) Efficiency vs. cycle number; b), d) shape of a typical cycle. More cycles are shown in the Supporting Information.

transfer steps. Similar results were obtained at different current densities, with the two-step deposition/dissolution process even clearer at higher current density (cf. Supporting Information), which reveals that the two-step process seems to be rate dependent. However, there is no clear trend of the capacity at which the step occurs with the charging/discharging rate. To emphasize this observation, potential as a function of charge for representative cycles is also summarized in the Supporting Information. We note that the two steps in oxidation and reduction cycles are most prominent when using SS-WEs, but they may also be observed when using Mg-WEs, as also highlighted in the Supporting Information. Investigations regarding the nature of the two step oxidation and reduction are ongoing. When using **E–H** instead of **E–B** as electrolyte system, no reversible cycling was achieved (cf. Supporting Information). This is in agreement with linear sweep and cycling

voltammetry as described above as well as with most literature results stating that magnesium cannot reversibly be electro-deposited and dissolved from imidazolium ionic liquids.[22,28] Consequently, no deposit from **E–H** could be analyzed, and we will focus on **E–B** in the rest of this study.

In order to obtain information about the type of deposit from the zwitterionic liquid containing electrolyte **E–B**, the cell used for galvanostatic cycling was subjected to a final deposition half cycle, and the deposit was subjected to scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Figure 4 compares the deposit from galvanostatic cycling experiments to the results obtained after a simple galvanostatic deposition step from **E–B** without prior extensive cycling. In both cases, a material with metallic shine is deposited on the working electrode. The deposit grew into the separator of the measurement cell during galvanostatic deposition and could be easily peeled off the electrode. We note that even though the measurement cells were opened inside an argon filled glove box, and SEM samples were prepared there, the samples were exposed to ambient air while transporting them to the electron microscope. Contaminations by atmospheric air could hence not be avoided. Consequently, the formation of a passivation layer on both samples must be assumed.

Indeed, carbon and oxygen can be detected next to magnesium in both cases, with the sample obtained after prolonged electrodeposition and dissolution cycles of magnesium showing significantly lower relative amounts of carbon and oxygen. We expect a thicker layer of magnesium on this electrode, which was cycled for several hundred times with a coulombic efficiency lower than 100 % and hence more deposited than dissolved material. The higher relative proportion of magnesium within the deposited material supports the assumption that carbon and oxygen signals in EDX measurements may result from atmospheric contamination. Additionally, we point to the conditioning phase during the first cycles of magnesium electrodeposition (Figure 3a), in which some minor decomposition of impurities from the electrolyte may happen. Such impurities may contribute to carbon and oxygen signals in EDX measurements, and as this conditioning phase is within the first deposition cycles, this may also explain why such signals are significantly more pronounced after only one

deposition cycle compared to several hundred deposition cycles. Boron was not detected in any EDX samples, again indicating electrochemical stability of the electrolyte. Overall, SEM and EDX experiments confirm successful electrodeposition of magnesium from the zwitterionic liquid electrolyte **E–B**. As expected, no deposit was observed from **E–H** as discussed above.

3. Conclusions

In conclusion, for the first time we used a zwitterionic liquid electrolyte composed of an imidazol-2-ylidene borane and magnesium borohydride for reversible electrodeposition of magnesium. We also compared its electrochemical characteristics to an isostructural imidazolium bis(trifluoromethane)sulfonimide system. This similar ionic liquid, even in combination with magnesium borohydride, was however not suitable for magnesium electrodeposition, pointing to the importance of the zwitterionic liquid as solvent.

We investigated the zwitterionic liquid electrolyte by means of NMR spectroscopy and analyzed electrodeposition and reversibility of deposition/dissolution of magnesium from the electrolyte by means of voltammetric, galvanostatic, and microscopic techniques. NMR spectroscopy indicated strong, thermally reversible, intermolecular interactions within the electrolyte system based on the zwitterionic liquid and magnesium borohydride. The disruption of these interactions and the consecutive gain in entropy upon magnesium dissolution may be beneficial for magnesium electrochemistry. Electrochemical and microscopic characterization showed that the novel electrolyte system based on the zwitterionic liquid allows reversible plating and stripping of magnesium on a stainless steel (316ss) electrode for prolonged cycling at a high coulombic efficiency.

The zwitterionic liquid is easy and cheap to synthesize, stable, of low viscosity, and acts as perfect host for magnesium borohydride in electrolyte systems due to pronounced intermolecular interactions. Reversible electrodeposition of magnesium from the electrolyte indicates two consecutive one electron transfer steps. Together with the potentially highly ordered state of the electrolyte, this suggests a synergistic
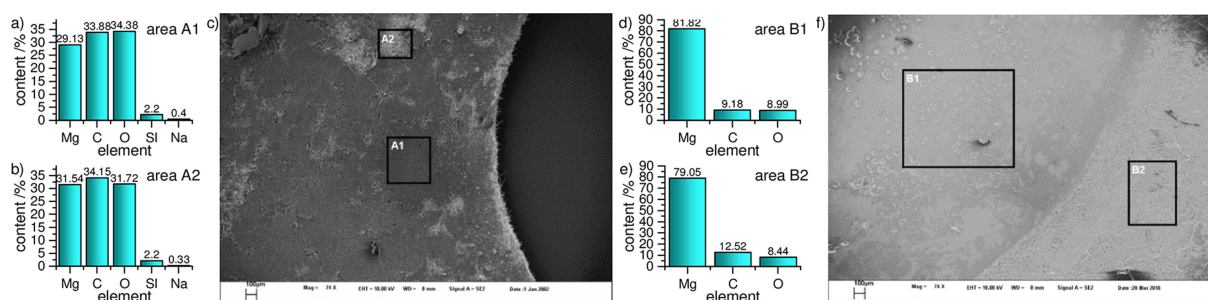
Figure 4. Scanning electron micrographs and results from energy dispersive X-ray spectroscopic analysis. a)–c) Deposit on stainless steel working electrodes after galvanostatic deposition of magnesium from **E-B** (no galvanostatic cycling). d)–f) Deposit on stainless steel working electrodes after galvanostatic cycling (Figure 3a,b) with a current density of 1 mA cm^{-2}.

effect created by the addition of magnesium borohydride to the zwitterionic liquid. Because of high stability, ease of synthesis, and reversibility of magnesium electrodeposition, this zwitterionic liquid based electrolyte is very promising to be applied in future magnesium batteries.

Supporting Information

The following file is available free of charge: experimental part; further ^{11}B and ^1H NMR spectra; method for measuring NMR spectra in bulk; electrochemical cell setup; oxidative stability of E-B; CV of different, similar, electrolyte systems; galvanostatic cycling at different discharging rate, on different substrates, and representative cycles; more SEM and EDX images. (PDF)

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

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