The breakthroughs in rechargeable lithium metal-anode-based batteries is still challenged by safety and performance limitations. Ionic liquid (IL)-based electrolytes are in consideration for increased safety but their moderate electrolyte performance and high costs still suppress their usefulness in Li metal-batteries. In an effort to deepen the understanding of the limited performance, galvanic corrosion as an electrochemical degradation process is herein identified as a contributing factor toward battery cell deterioration. Four different ILs, based on bis(trifluoromethylsulfonyl)imide in combination with the quaternary ammonium cations N-butyl-N-methylpyrrolidinium, N-methyl-N-propyl-pyrrolidinium, N-butyl-N-methylpiperidinium, and N-butyltrimethylammonium, respectively, are systematically investigated for such corrosive side reactions. The reaction pathways of this commonly neglected phenomenon are found to be both Hofmann-type and reductive eliminations. Supported by headspace-gas chromatography-mass spectrometry, the evolving gaseous reaction products are characterized. With zero resistance ammetry and Li electrochemical dissolution and deposition experiments, the dependency of galvanic corrosion on the presence of the galvanically coupled materials is elucidated. Variation of the lithium bis(trifluoromethylsulfonyl)imide concentration in the electrolytes is shown to influence the extent of detectable degradation products. Based on these findings, the necessity for more sophisticated electrode designs and electrolyte formulations is emphasized.

1. Introduction

The global aspiration to increase the sustainability of energy production and consumption patterns demands fundamental changes of our transportation and energy storage systems.[1] During recent decades, tremendous efforts were devoted toward the development, establishment, and improvement of electromobility.[2,3] Key requirements to render electromobility more competitive with conventional internal combustion technologies are commonly seen as improvements toward the battery.[4] Whereas the development of conventional lithium ion battery (LIB) technology is already well advanced, improvements toward properties such as energy density, sustainability, and safety remain highly desirable to encourage mass adoption of electromobility.[5] State-of-the-art LIBs typically contain different types of carbon (e.g., graphitic, hard, soft, or amorphous carbons) and/or silicon as negative electrode materials.[6–8] A shift toward lithium metal-based batteries (LMBs) is often considered a desirable option for improvements of overall cell capacities and energy densities due to its high specific capacity (3860 mAh g⁻¹) and low standard reduction potential (−3.04 V vs standard hydrogen electrode).[2,9] Nevertheless, the strong benefit of the electrochemical characteristics renders Li metal a key technology for the next evolutionary step of batteries which includes the combination of Li with other high capacity materials at the positive electrode side. Novel key technologies like the utilization...
of sulfur-based or sulfur-containing positive electrodes are under consideration as cheaper or more resource-conserving alternatives to conventional, transition-metal-based materials. Reactive ambient gases, such as O₂ and CO₂, can be used for energy storage through the reversible formation of Li₂O₂ and Li₂CO₃ in O₂ and CO₂ Li cells, respectively. The transition to cell chemistries with Li metal electrodes is challenged by the inhomogeneous electrochemical deposition and dissolution behavior of Li metal, leading to the formation of high-surface-area Li (HSAL), which imposes safety concerns. Further, safety issues arise from the volatility and flammability of conventional liquid electrolytes.

Room-temperature ionic liquids (ILs) are molten salts that can be used as an alternative solvent for organic solvents for various types of batteries. Consisting of anions and cations with delocalized charges and sterically demanding side groups and thus weak intermolecular interactions, ILs have an almost negligible vapor pressure. Therefore, issues related to the flammability or volatility of electrolytes are considered insignificant for such cell chemistries. Furthermore, positive influences on the homogeneity of the electrochemical dissolution and deposition of Li with less severe HSAL formation were reported.

Cations derived from quaternary ammonium (e.g., pyrrolidinium or piperidinium) ions in combination with imide-based anions are often chosen as representative ILs in electrochemical studies. In the literature, N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonylimide) (Pyr₁₄TFSI), among many others, combined with a Li containing salt, has been examined as IL-based electrolyte for the use in LMBs. The wide electrochemical stability windows of ILs are considered a major benefit, as they exhibit high (electro-)chemical stability against oxidative species at the positive electrode. Reductive degradation reactions of ILs, as implied by reduction potentials of quaternary ammonium ions in the range of 0.09–0.24 V versus Li/Li⁺, are usually decelerated through an initial, spontaneous formation of protective surface layers on the Li metal, as well as through solid electrolyte interphase (SEI) formation during initial charging and discharging cycles. The resulting surface layers consist of organic and inorganic degradation products of the negative electrode and electrolyte components.

For quaternary ammonium cations, possible reductive side reactions with pristine Li are understood as a combination of reductive eliminations and Hofmann-eliminations, which could be proven by both simulations and analytical studies. Degradation products of such cations are typically alkanes, olefins, and tertiary amines. Hofmann-eliminations with intramolecular ring-openings leading to amines with olefinic side chains were also reported. Degradation reactions of typical imide anions, such as bis(trifluoromethylsulfonylimide) (TFSI⁻) or bis(oxazolylmethyl)pyrrolidinium (FSI⁻), lead to the release of fluorinated species, often yielding surface layer compositions with high contents of inorganic compounds such as LiF.

Recent studies highlighted the relevance of galvanic corrosion phenomena at the current collector-electrolyte phase boundaries, e.g., for Li powder-based electrodes. Galvanic corrosion is caused by the immersion of a galvanic couple of two electronically connected electron conductors, like metals with different oxidation potentials in an electrolyte. For LMBs, galvanic coupling can occur at the interface between the Li metal electrode and the current collector (typically Cu) or metal cell housing (typically stainless steel) through contact of both with the electrolyte. In such cases, Li as the metal with the lower oxidation potential can be oxidized, whereas at the other metal, reduction reactions take place. In the case of Li and a current collector material that does not insert Li or “alloys” with Li, the electrons from the oxidation of Li can be transferred through the current collector toward its phase boundary with the electrolyte, where reductive electrolyte degradation reactions can take place. Such reactions also lead to pit formation at the Li surface.

Galvanic corrosion in the context of electrochemical energy storage was previously only investigated for a few systems, e.g., for the combination of powdered Li electrodes with conventional carbonate or dioxolane electrolytes. In our recent study, forced galvanic corrosion was abused to amplify the amount of detectable decomposition products of only one IL (Pyr₁₄TFSI), but without further investigations of the underlying corrosion mechanism. Thus, we herein present a systematic study of the occurrence and the extent of galvanic corrosion of Li electrodes in the context of IL-based electrolytes. For this, TFSI⁻-based ILs with four quaternary ammonium cations of varying ring size and alkyl chain length (Scheme 1), namely N-butyl-N-methylpyrrolidinium (Pyr₁₄⁺), N-methyl-N-propylpyrrolidinium (Pyr₁₃⁺), N-butyl-N-methylpiperidinium (Pip₁₄⁺), and N-butyltrimethylammonium (N₁₁₁₄⁺) were investigated for their corrosion behavior with galvanic couples of Li in combination with copper (Cu), nickel (Ni), or stainless steel, as well as in dependency on the LiTFSI concentration in the electrolytes. Degradation products were identified with headspace-gas chromatography-mass spectrometry (HS-GC-MS), whereas the extent of degradation was correlated with the Coulombic efficiencies (CEs) of the Li electrodeposition and -dissolution, and corrosion currents I_{corr} obtained from zero resistance ammetry (ZRA).

### 2. Results and Discussion

In this study, stacks of Li electrodes and electronically conductive materials were prepared to mimic the occurrence of galvanic couples within LMBs. In contrast to reference stacks prepared with a nonconductive boPET-foil, prolonged immersion of these stacks in the investigated ILs led to strong discolorations of the liquid phases. These discolorations ranged from yellowish to brownish and were perceivable for all combinations of ILs with the respective galvanic couple materials Cu, Ni, and stainless steel (Figure S1, Supporting Information), but not for the reference stacks, where the ILs remained colorless (Figure S1, Supporting Information). In addition to the color changes, changes to the surface morphology of the Li were
recognizable, which was further investigated by scanning electron microscopy (SEM).

In Figure 1, the occurrence of pit formation at the Li surface is depicted for galvanic couple stacks from different combinations of materials subsequent to prolonged immersion in pure N\textsubscript{1114}TFSI. Cu (Figure 1c) led to the most pronounced surface deterioration of the Li, as evident from the formation of rather deep 3D voids in the surface whereas general pit formation behavior could be observed for all three investigated coupled metals and all four ILs. To a lesser extent, with fewer and less pronounced morphological changes, pit formation could as well be observed for galvanic couple stacks with Ni and stainless steel (Figure 1a,b). Notably, Li dissolution was evident originating from the edges of the foil as well as from the planar side. Pit formation was exclusively observed at the Li, while no morphological changes of the galvanic couple metals (Ni, Cu, or stainless steel) were observable.

For a galvanic couple stack with a nonconductive polymer foil instead of a conductive metal (Figure 1d), no morphological changes of the Li surface occurred. Thus, chemical reactions leading to corrosion of the Li electrodes only take place for stacks with electronically conductive materials (namely galvanic couples) and are explicitly promoted by the conductivity of the materials in contact with the Li. However, both pit formation and discoloration are inhibited, if sufficient amounts of LiTFSI are added to the ILs prior to immersion (Figures S2 and S3, Supporting Information). Since these dissolved transition metal ions would presumably be reduced to metal deposits on the Li surface due to the very low oxidation potential of Li\textsuperscript{+}\,[35] energy-dispersive X-ray spectroscopy (EDS) scans of the Li electrodes were conducted as an additional confirmation noninvolvement of such compounds (Table S1, Supporting Information). An overview of the overall applied analytical and electrochemical techniques in this study is presented in Scheme 2 to ease the understanding of the experimental setup.

To further elucidate the reaction pathways of galvanic corrosion in the herein investigated experimental setup, gaseous reaction products of IL degradation were analyzed by HS-GC-MS. By this technique, compounds in the headspace over the immersion samples could be chromatographically separated and identified. Figure 2 shows chromatograms with degradation products for each of the investigated ILs with immersed Cu\textvert Li galvanic couple stacks. For both Pyr\textsubscript{14}TFSI and Pyr\textsubscript{13}TFSI, 1-methylpyrrolidine (Ia, IIa) was observed as a major degradation product. Both ILs share the same five-membered pyrroliidine-rings in their respective cations. In Hofmann-type elimination reactions, the likelihood of eliminating a certain alkyl-group from a quaternary ammonium depends on both the stability of the eliminated group and kinetic effects from intramolecular...
The Hofmann-elimination of alkyl-chains is initiated by a deprotonation in β-position. This renders the respective butyl and propyl groups of the Pyr\textsubscript{14}\textsuperscript{+} and Pyr\textsubscript{13}\textsuperscript{+} cations more prone to elimination than the methyl groups, leading to 1-methylpyrrolidine as the favored reaction product for these cations. For the piperidinium-based Pip\textsubscript{14}\textsuperscript{+} cation, the analogous reaction product by elimination of the butyl-group, 1-methylpiperidine (III\textsubscript{a}), was observed. The according Hofmann-elimination product of the N\textsubscript{1114}\textsuperscript{+} cation, trimethylamine, was detected at earlier retention times \(t_r\) due to its high volatility, as depicted in Figure S5 in the Supporting Information. Interestingly, also reaction products from intramolecular Hofmann-eliminations (I\textsubscript{c}, II\textsubscript{c}, and III\textsubscript{c}), as described for Pyr\textsubscript{14}TFSI in the literature\cite{29,34}, could be detected for Pyr\textsubscript{13}TFSI, but also for Pyr\textsubscript{14}TFSI and Pip\textsubscript{14}TFSI. This type of ring-opening reaction is plausible, as the pyrrolidinium and piperidinium rings of the IL cations presumably are prone to deprotonation in β-position. Namely, the ring opening products N-butyl-N-methyl-3-buten-1-amine (I\textsubscript{c}), N-methyl-N-propyl-3-buten-1-amine (II\textsubscript{c}), and N-butyl-N-methyl-4-penten-1-amine (III\textsubscript{c}) could be detected for Pyr\textsubscript{14}TFSI, Pyr\textsubscript{13}TFSI, and Pip\textsubscript{14}TFSI, respectively. Due to the comparably large molecular weights and the reactive double bonds, these three degradation products are of particular interest as potential precursors for the formation of polymers or other types of degradation products. Polymerization reactions could subsequently lead to gel-like residues, as occasionally observed in disassembled cells that were used to model galvanic corrosion processes. Alike, such residues potentially related to our findings were mentioned in the literature\cite{27}. Such gel-formation could negatively impact electrolyte viscosity and ionic conductivity and ultimately contribute toward cell deterioration.

Reductive elimination reactions are independent of β-deprotonation and can thus yield tertiary amines upon the elimination of methyl groups\cite{27}. With 1-butylpyrrolidine (I\textsubscript{b}) for Pyr\textsubscript{14}TFSI, N-propylpyrrolidine (II\textsubscript{b}) for Pyr\textsubscript{13}TFSI, N-butylpiperidine (I\textsubscript{ib}) for Pip\textsubscript{14}TFSI, and butyldimethylamine (IVA) for N\textsubscript{1114}TFSI, all according reaction products were found. Notably, reductive eliminations can also yield the N-methylated products I\textsubscript{a}, II\textsubscript{a}, and III\textsubscript{a} upon elimination of butyl- or propyl-carbanions, respectively. As these carbanions act as strong

![Scheme 2. Overview of the analytical and electrochemical tools used in this study.](image)

![Figure 2. HS-GC-MS-chromatograms of the four different ionic liquids Pyr\textsubscript{14}TFSI, Pyr\textsubscript{13}TFSI, Pip\textsubscript{14}TFSI, and N\textsubscript{1114}TFSI subsequent to immersion of Cu|Li galvanic couple stacks.](image)
bases, reductive elimination reactions can potentially even promote subsequent Hofmann-eliminations. For Pyr\textsubscript{14}TFSI and Pyr\textsubscript{13}TFSI, \textit{N}-dibutyl-\textit{N}-methylamine (I\textsubscript{d}) and \textit{N}-butyl-\textit{N}-methyl-\textit{N}-propylamine (I\textsubscript{Id}), respectively, were found as reaction products presumably from intramolecular reductive elimination reactions. As the analyte sensitivity of HS-GC-MS correlates with volatility, this method proves particularly useful for the analysis of IL degradation products due to the negligible vapor pressure of the initial ILs. Yet, this method is limited to volatile degradation products such as the amines found in this study. A hypothetical reaction product analogue to I\textsubscript{d} and I\textsubscript{Id} could be \textit{N}-butyl-\textit{N}-methyl-\textit{N}-pentylamine for the degradation of Pip\textsubscript{14}TFSI. The absence of this reaction product might suggest that the compound is either less likely to form or less volatile as anticipated from its comparably larger molecular weight. Due to the different chemical interactions of the degradation products with the ILs, the partitioning between liquid and vapor phase of the analytes may not be trivial to assess, as no internal standards were used in this study. Thus, quantitative assessments of corrosive reactions yield the best accuracy for systems of high chemical similarity. In the HS-GC-MS experiment depicted in Figure 3, the content of LiTFSI in IL-based electrolytes was varied and the resulting gaseous reaction products from galvanic corrosion were analyzed. Due to the inherent chemical similarity of the samples, as well as comparable immersion times of the galvanic couple stacks, the peak areas of the analyzed reaction products can be utilized to quantitatively assess degradative processes. Contrary, comparisons between the four individual ILs should not solely be based on HS-GC-MS data but rather be supported by electrochemical measurements.

In Figure 3, chromatograms for the degradation of Pyr\textsubscript{14}TFSI, Pyr\textsubscript{13}TFSI, Pip\textsubscript{14}TFSI, and N\textsubscript{1114}TFSI in dependency of the LiTFSI content are shown. The depicted \( t_r \) window between 1.7 and 2.0 min was chosen, as all four ILs show olefinic degradation products, allowing for a better comparability. Additional information about the assignment of peaks is given in Figure S5 in the Supporting Information. Figure 3a shows the degradation chromatograms for Pyr\textsubscript{14}TFSI, with two resolved peaks with \( t_r \) of 1.78 and 1.82 min, respectively. These two peaks were identified as the two butene isomers but-1-ene (Hofman-product) and but-2-ene (Saitzeff-product). However, the two compound structures were not further assigned to the two different peaks, as no internal standards were used to unambiguously distinguish between the two compounds. Still, the simultaneous presence of two different butene species indicates either a type of degradation yielding the two compounds in different ratios based on thermodynamic and kinetic factors or rather two different origins of the two species. Potentially, butene species could also be emitted from elimination reactions subsequent to the described ring-opening reactions. This claim is supported by the presence of albeit minor butene peaks for the degradation of Pyr\textsubscript{13}TFSI (Figure 3b), which does not include a butyl group in its structure. Analogously, the degradation of the ringless N\textsubscript{1114}\textsuperscript{+} cation (Figure 3d) only leads to a single butene peak at a \( t_r \) of 1.78 min in addition to the trimethylamine peak at 1.86 min. The presence of a minor pentene peak at a \( t_r \) of approximately 1.96 min for Pip\textsubscript{14}TFSI (Figure 3c) further supports this hypothesis.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** HS-GC-MS chromatograms for the four different IL Pyr\textsubscript{14}TFSI, Pyr\textsubscript{13}TFSI, Pip\textsubscript{14}TFSI, and N\textsubscript{1114}TFSI with different LiTFSI contents subsequent to the immersion of Cu/Li galvanic couple stacks.
However, corresponding reaction products for these hypothetical eliminations subsequent to ring-opening reactions, such as N-butylmethylamine and N-methylpropylamine, could not be identified in this study, possibly due to a high solubility in ILs or a very low retention on the GC column, leading to coelution with the injection peak. Of particular interest is the decreasing peak intensity upon increasing the LiTFSI content of the ILs. For each of the four ILs (Figure 3a–d), the intensities decrease until no more butene is detectable for the highest investigated LiTFSI content. As the peak intensity dependent of the amount of degradation products, it can be concluded that the extent of galvanic corrosion of Li is heavily dependent on the concentration of LiTFSI in the IL-based electrolyte. A correlation between degradation stability and LiTFSI content was reported in the literature only for Pyr14TFSI, but the reactivity of Pyr13TFSI, Pip14TFSI, and N1114TFSI appears to follow a similar pattern. During galvanic corrosion, electrons from the Li pass through the metal of higher electrochemical potential and enable reactions at the metal–electrolyte interface. Thus, the inhibition of galvanic corrosion by LiTFSI is presumably caused by either the formation of an effective, insulating interphase layer on top of the Cu or Ni, or through effects, e.g., related to the disturbance of ion pair or double layer formation at the interface, yet more elucidation by future studies is required.

To simulate galvanic corrosion processes occurring in an LMB cell with a Li-based electrode, a current collector (Cu or Ni) and an IL-based electrolyte, external short-circuiting of Cu || Li and Ni || Li cells was performed, whereas the current flow from the Li to the corresponding counter electrode was measured. This procedure is referred to as ZRA, which has been proven helpful for the quantification of corrosion phenomena. In this study, ZRA was used to assess the $I_{\text{cor}}$ between a pristine Li foil and a counter electrode from Ni or Cu, respectively, for the four different ILs. In all cases, initial currents in the range of several mA were measured upon start of the ZRA experiment, followed by a rapid decline toward a steady current in the µA-range (Figure 4). According to our understanding, the comparably high initial current might be explained not only by galvanic corrosion but also by other spontaneous electrochemical processes occurring during the initiation of the experiment, such as double layer formation or the reduction of oxidized surface layers on the current collectors. However, these current contributions can be expected to be completed within short time periods (e.g., 120 s), after which galvanic corrosion is anticipated to be the main contributing factor toward the overall measured corrosion current $I_{\text{cor}}$. During the measurement period of 3 d, the corrosion currents followed a similar pattern for each of the four different ILs (Figure 4). Subsequent to the rapid initial drop as described above, $I_{\text{cor}}$ converged to a plateau-like region. As $I_{\text{cor}}$ originates from galvanic corrosive processes, the slow decline over the course of several days might be attributed to the depletion of involved reactants. Smaller differences in the plateau value of $I_{\text{cor}}$ were found for the four ILs. For the Ni || Li-cell (Figure 4), the N1114TFSI-based IL ($I_{\text{cor}}: 6.64 \mu A$ after 72 h) showed the highest $I_{\text{cor}}$, followed by Pyr14TFSI ($I_{\text{cor}}: 2.44 \mu A$ after 72 h) and Pip14TFSI ($I_{\text{cor}}: 1.59 \mu A$ after 72 h) with significantly lower values. The Pyr13TFSI-based IL ($I_{\text{cor}}: 0.68 \mu A$ after 72 h) showed the lowest values for $I_{\text{cor}}$ with Ni among the four investigated ILs.

![Figure 4](https://www.advenergymat.de) $I_{\text{cor}}$ versus $t$ plots of ZRA measurements of Cu || Li- and Ni || Li-cells for the four ILs Pyr14TFSI, Pyr13TFSI, Pip14TFSI, and N1114TFSI and their respective electrolytes with LiTFSI in a logarithmic scale. By integration of $I_{\text{cor}}$ over $t$, the overall corrosion charge $Q$ was determined, here shown as bars ($n = 3$). The initial 120 s of the ZRA experiment showed high currents from initial electrochemical processes presumably not related to galvanic corrosion and were thus excluded from integration.
ILs. Through integration of the $I_{\text{cor}}$ over time, the overall corrosion charge $Q$ was calculated for each IL. In Figure 4, the results of this procedure are shown on the right axis to give a more comprehensive overview about the reactivity of different cations. The findings underline that the reactivity of different cations with Li metal were influenced by their chemical structures. Such structure–property relationships can be expected, as each different side group of the quaternary ammonium ions is prone to elimination reactions to a varying degree. Ring substituents are generally inhibiting elimination reactions through decreased reaction kinetics compared to ring-free systems.[38] By steric effects, increased lengths of alkyl chain substituents can slightly decrease the extent of elimination reactions.[39] A similar course for $I_{\text{cor}}$—and thus for the galvanic corrosive reactivity of cations—was found for Cu||Li cells in the ZRA experiments. N1114TFSI ($I_{\text{cor}}$: 4.03 µA after 72 h) and Pyr13TFSI ($I_{\text{cor}}$: 4.79 µA after 72 h) showed values in a similar range, whereas Pip14TFSI ($I_{\text{cor}}$: 2.12 µA after 72 h) and Pyr13TFSI ($I_{\text{cor}}$: 2.34 µA after 72 h) show lower values for $I_{\text{cor}}$ (Figure 4). Overall, the $I_{\text{cor}}$ for the four ILs in the Cu||Li cells extend through a lower range of values in comparison to the use of Ni. The N1114+ cation is not ring stabilized, thus the mostly higher values for $I_{\text{cor}}$ match the expectations, as its reactivity appears to be highest among the four different cations. Comparing Pyr13+ and Pip14+, the expected stabilization through the larger ring substituent of Pip14+ is represented by consistently lower values for $I_{\text{cor}}$. For Ni and partially for Cu, $I_{\text{cor}}$ is lowest for the Pyr13+ cation, contradicting the premise of a decreased steric hindrance for the elimination reaction, as it should be less reactive compared to Pyr13+. However, the occurring elimination reactions are a combination of both Hofmann-type eliminations and reductive eliminations and the observed reactivities might be influenced by different parameters, e.g., the viscosity or electronic and ionic conductivity of the ILs. One other possible explanation for this unexpected reaction behavior is the stability of the carbanions involved in the reductive elimination reaction. Due to inductive effects, propyl-carbanions are more stable than butyl-carbanions,[40] which might lead to a higher reactivity of the latter, potentially resulting in increased rates of galvanic corrosion.

The influence of the LiTFSI concentration could also be observed in the ZRA experiments. For the Ni||Li-cells, LiTFSI-containing electrolytes based on Pyr14+ ($I_{\text{cor}}$: 0.73 µA after 72 h), N1114+ ($I_{\text{cor}}$: 5.86 µA after 72 h) and Pip14+ ($I_{\text{cor}}$: 0.99 µA after 72 h) showed significantly decreased values for $I_{\text{cor}}$ and thus lower tendencies to undergo galvanic corrosion. The only exception in this trend is the Pyr13+-based electrolyte, where an increased corrosion current was measured ($I_{\text{cor}}$: 1.24 µA after 72 h). In case of the Cu||Li-cells, corrosion currents decreased, with N1114+ ($I_{\text{cor}}$: 1.96 µA after 72 h) remaining the highest, followed by Pip14+ ($I_{\text{cor}}$: 1.13 µA after 72 h), Pyr13+ ($I_{\text{cor}}$: 1.03 µA after 72 h) and Pyr14+ ($I_{\text{cor}}$: 0.76 µA after 72 h). Overall, this decreased tendency for galvanic corrosion matches the results from the HS-GC-MS measurements, as a higher LiTFSI content appears to prevent galvanic corrosion to a certain extent.

An additional method to assess the extent of (corrosive) side reactions is the investigation of the CE of Li electrodeposition and -dissolution cycles. The value of CE is thereby determined by the ratio of electrochemically dissolved Li and previously electrochemically deposited Li. Hereby, a value of 100% would suggest ideal behavior under the absence of any side reactions. Results for the determination of CE for the Li electrodeposition and -dissolution on a) Ni and b) Cu current collector for the four different IL-electrolytes with the IL Pyr14TFSI, Pyr13TFSI, Pip14TFSI, and N1114TFSI and 5.6 wt% LiTFSI each. Data are derived from 100 cycles of 1 h of Li electrodeposition and -dissolution each (0.1 mA cm⁻² at 60 °C).

![Figure 5. Coulombic efficiencies (CEs) of the Li electrodeposition and -dissolution process on a) Ni and b) Cu current collector for the four different IL-electrolytes with the IL Pyr14TFSI, Pyr13TFSI, Pip14TFSI, and N1114TFSI and 5.6 wt% LiTFSI each. Data are derived from 100 cycles of 1 h of Li electrodeposition and -dissolution each (0.1 mA cm⁻² at 60 °C).](image-url)
For practical cells, minimized lithium contents are strived for, which would make any lithium losses through side reactions even more undesirable.

In the CE experiments, Pyr$_{14}^{+}$ shows the highest CEs for the electrochemical deposition of Li on Ni, closely followed by Pyr$_{13}^{+}$ and N$_{1114}^{+}$ (Figure 5a). At higher cycle numbers, the CE values converge toward a plateau with only negligible differences for these three cations. For Cu (Figure 5b), an analogous pattern in the CE values can be found; however, the differences between the three cations are less pronounced with only small deviations between the curves. Interestingly, the CE curve for Pip$_{14}^{+}$ consistently shows significantly smaller values compared to the other ions for both substrates. This behavior might be related to the poor cycling properties of the Pip$_{14}$TFSI-based electrolyte. Other possible explanations for the low CE values are a generally less effective SEI formation or a more expressed HSAL formation, leading to a higher Li loss in each cycle. This reveals limitations of the CE-method in terms of quantification, as it is most suited for the comparison of electrolytes with similar cycling properties.

Compared to the presented ZRA method, the determination of CEs provides the possibility to examine electrolyte degradation in a setup with electrochemical deposition and dissolution of Li. In addition to effects of galvanic corrosion, other side reactions and processes occur. In early cycles, such side reactions could, e.g., be SEI formation or other forms of spontaneous reactions of freshly deposited Li with electrolyte components, as no protective surface layer on the freshly electrodeposited Li is present. In later cycles, spontaneous reactions are expectedly more inhibited due to already formed surface layers. Thus, the effects of galvanic corrosion are partially overshadowed by other phenomena. The combination of the two herein used electrochemical experiments is advisable, as a deeper understanding of the proportions of different side reactions can thereby be achieved.

Based on the results of this study, the proposed mechanism of galvanic corrosion in IL-based electrolyte systems is schematically depicted in Scheme 3: During the reductive elimination reaction, an electron stemming from the oxidation of Li is transferred to the quaternary ammonium cation through the current collector, initiating the degradation reaction. This oxidation of Li can be considered the main cause of pit formation in the Li as described earlier for the SEM data. It is known from electrochemical dissolution experiments with Li, that the SEI layer (light grey, Scheme 3) on the Li is conductive for ions, yet is electronically insulating. Hence, a transmission of the Li$^{+}$ ions through the surface layer is possible, whereas the electronic current can only be transmitted through the current collector or generally, through a galvaniically coupled material, toward the corrosive electrolyte. The process of galvanic corrosion can occur without the application of external currents, e.g., also during shelf storage of cells, raising concerns for the long-term performance of affected cells. However, it could also be shown that the extent of galvanic corrosion can be decreased through increases in the LiTFSI content of electrolytes with the four investigated ILs. While the model systems in this study were designed to provide appropriate conditions for the examination of galvanic corrosion, cells produced in laboratory research or commerce might suffer from this phenomenon to a varying degree.

3. Conclusion

By this study, it was shown that galvanic couples of Li with Cu, Ni, or even stainless steel lead to galvanic corrosion when immersed in TFSI$^{-}$-based ILs with quaternary ammonium cations. Pit formation on the Li surface under the absence of externally applied currents was investigated by SEM. Concurrently, reduction products of the quaternary ammonium cations were analyzed by HS-GC-MS. Some of the arising decomposition products presumably can further react to gel-like or polymeric components and thus add to battery cell decay. It was shown that the decomposition behavior differs between the four investigated cations and indications of individual structure–property relationships were found. A combination of electrochemical methods for the quantification of degradation was presented, revealing distinct differences in terms of reactivity of the cations. The highest degree of degradation could be assigned to the noncyclic quaternary ammonium N$_{1114}^{+}$-ion, presumably due to a lack of ring stabilization. Comparison of the reactivity of galvanic couples in electrolytes with varying LiTFSI concentrations indicated that galvanic corrosion can effectively be suppressed if a certain threshold of dissolved LiTFSI is present. While this correlation prerequisites the use of elevated LiTFSI concentrations in cell applications, the underlying mechanism needs to be elucidated in future research.

While not all electrolytes do behave the same, this study will add to a better understanding of galvanic couple formation and its importance as a contributing factor for corrosive processes in electrochemical cells with IL-based electrolytes. Such galvanic couples of Li and another conductive metal might occur in laboratory or commercial battery cells if contact between current collectors and the electrolyte is not avoided. As pit formation could also be observed for galvanic couples with stainless steel and other electronically conductive cell materials, galvanic...
couple formation in cells might not be limited to current collectors but could potentially occur with metallic cell housing materials and others. To avert side reactions caused by galvanic corrosive processes in ionic liquid-based and other, e.g., organic solvent based-electrolytes, the following countermeasures (Scheme 4) are proposed: i) minimization of the interface area of electronically conductive materials (current collector materials and/or metal cell housing parts that are in contact with metallic Li) with the electrolyte, ii) use of sufficiently high conductive salt concentrations, iii) the use of electrolyte additives that create protective surface layers on Li metal and/or the current collector in the cell, and iv) protective surface layers coated on the Li electrode or the current collector material before immersion of these materials in the cell.

4. Experimental Section

Chemicals: N-Butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Py$_r$$_i$TFSI, 99.5%), N-methyl-N-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Py$_p$$_o$TFSI, 99%), N-butyln-N-methylpiperidinium bis(trifluoromethylsulfonyl)imide (Pip$_b$$_o$TFSI, 99%), N-butytrimethylammonium bis(trifluoromethylsulfonyl)imide (N$_{11}$$_{11}$TFSI, 99%) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, battery grade) were provided by IoLiTec (Germany). After predrying (10−2 mbar, 100 °C, 24 h), the ILs and LiTFSI were dried using a turbomolecular pump (Pfeiffer HiCube 80, 10−2 mbar, 100 °C, 48 h). The remaining water content of the ILs was <10 ppm, as determined by Karl-Fischer-Titration (C30S coulometric KF titrator, Mettler Toledo, USA). All experiments were conducted in dry room atmosphere with <20 ppm ambient humidity.

Preparation of Galvanic Couple Stacks and Immersion Experiments: As a model for galvanically coupled materials, stacks ("galvanic couple stacks") were prepared from Li (7 mm diameter, 500 µm thickness, battery grade, Albermarle, USA) and precleaned (with isopropanol, (Brenntag, Germany)) Cu (12 mm diameter, 50 µm thickness, Schlenk, Germany) or Ni (12 mm diameter, 100 µm thickness, 99.5%, Alfa Aesar, USA), respectively, by the application of pressure (1 MPa, 10 s, Polystat 200T, Servitec MaschinenService GmbH, Germany) between two siliconized biaxially oriented poly(ethylene terephthalate) (bopET) foils (PPi Adhesive Products, Germany). For immersion experiments, additional stacks were prepared using a typical stainless steel CR2032 housing material (stainless steel type 316L, 15.5 mm diameter), as well as a nonconductive reference from siliconized bopET foil (12 mm diameter). All galvanic couple stacks were individually immersed for 14 d in 1.5 mL of the respective ILs or the corresponding ILs with 5.6 wt% LiTFSI at 60 °C for increased reaction kinetics of the degradation.

Electrochemical Experiments: CR2032 coin cells with Cu/Li and Ni/Li two-electrode configurations were assembled using a six-layered poly(propylene) separator (FS 2190, 13 mm diameter, Freudenberg, Germany) soaked with 120 µL of the respective pure IL or an electrolyte based on the IL with a content of 5.6 wt% LiTFSI, respectively. ZRA experiments were conducted for periods of 72 h with a 6 h open-circuit voltage step prior to the experiment using a VMP-3 (BioLogic, France) at 60 °C and the ZRA data were denoised with a Savitzky-Golay filter. Analogously, CR2032 coin cells were assembled for electrochemical Li deposition and Li dissolution experiments. As electrolytes for these experiments, 120 µL of the respective IL with 5.6 wt% LiTFSI were used. Cycling was conducted in a battery cycler (Maccor Series 4000, Maccor Inc., USA) for 100 cycles in a temperature chamber (60 °C, KB 400, Binder, Germany) with 1 h of electrochemical dissolution followed by 1 h of electrochemical deposition at 0.1 mA cm−2 for each cycle.

Analytical Methods: SEM: The immersed galvanic couple stacks were retrieved from the immersion vessels and rinsed with 5 mL 1,2-dimethoxyethane (anhydrous, 99.5%, Sigma-Aldrich, UK). After the samples were dried, micrographs were obtained using an Auriga Crossbeam Workstation (Carl Zeiss AG, Germany) with a Schottky-type field emission gun and an EDS system (Oxford Instruments, UK). Images were recorded using an acceleration voltage of 3 kV (15 kV for EDS measurements) and an Everhart-Thornley (SE2) detector at a working distance of 5 mm.

HS-GCMS: For HS-GCMS measurements, galvanic couple stacks were immersed in 1 mL of the respective IL with varying LiTFSI concentrations (pure IL, 0.05, 0.10, 0.50, 1.00, and 5.6 wt%) in a gas-tight vial (20 µL) and stored at 30 °C in the autosampler prior to measurement. HS-GCMS measurements were conducted with a GCMS-QP2010 Ultra (Shimadzu, Japan) with assembled AOC-5000 Plus autosampler and a Supelco SLB-5 ms column (30 m x 250 µm x 0.25 µm). Data were analyzed using GCMS Postrun Analysis (Shimadzu) with integrated access to the National Institute of Standards and Technology 11 library. Carrier gas was Helium 6.0 (Westfalen Gas, Germany) at a 1.16 mL min−1 flow rate. Injection volumes of 500 µL of the gas phase were introduced via a gastight syringe at a 1:100 split at a liner temperature of 250 °C. The temperature program consisted of an initial heating step at 40 °C for 1 min, followed by a ramp to 60 °C at a rate of 3 °C min−1. Subsequently, the temperature was elevated to 260 °C at a rate of 30 °C min−1, then held for additional 2 min. The filament was operated at 70 V and the detector voltage was set relative to the respective tuning result (±1 kV).

ICP-OES: Subsequent to the immersion experiments, the supernatant liquid phase was diluted with 2% HNO$_3$ in water with a dilution ratio of 1:1000. ICP-OES was carried out using a Spectro ARCOS ICP-OES (Spectro Analytical Instruments, Germany) following a procedure described in ref. [42].

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors acknowledge the German Federal Ministry of Education and Research Bundesministerium für Bildung und Forschung for
the financial support within the project AMaLiS (03XP0125D). Further, the authors want to thank Verena Naber for the ICP-OES measurements shown in the Supporting Information.

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

batteries, galvanic corrosion, gas chromatography, ionic liquids, lithium metal batteries

Received: March 31, 2021
Revised: April 21, 2021
Published online: May 7, 2021

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