

Assessing the Quality of Ionic Liquids Using Single Crystal Electrochemistry, Surface Science and Data Screening.

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Abstract

Ionic liquids (ILs) are used in numerous chemical, biological, and physico-chemical applications. Native impurities in the IL, however, often limit the interpretation of results or the applicability of these chemicals. Here, we present an electrochemical approach, where the quality of ILs is visualised with cyclic voltammetry using well-defined single-crystal electrodes. As an example, we study Au(111) in *N*-methyl-*N*-propylpiperidinium bis(trifluoromethane)sulfonimide ([MPPip][TFSI]), where different suppliers with different supplied purity and different pretreatments are considered. The importance of studying the quality of ILs after pretreatments is illustrated with additional X-ray photoelectron spectroscopy measurements. We also show that the storage conditions and time/age can have a significant impact on the amount of water and oxygen in the IL. The relevance of reporting metadata and the role of databases in elucidating benchmark systems is also discussed.

Introduction

Over the last decades ionic liquids (ILs) received an increasing interest in various research areas such as chemical synthesis, analytical chemistry, biology, and electrochemistry.^{1–7} However, possible contaminations natively present in the IL can significantly impact their properties as well as the interpretation of their behavior.^{8–17} Methods for assessing the quality of ILs have been suggested, *e.g.* nuclear magnetic resonance (NMR) spectroscopy for detecting organic solvents in the IL, which are, however, rarely performed prior to their use in experiments or applications.^{5,12,14} In this work, we present surface science and electrochemical techniques to explore possible qualitative differences between different batches of the same IL from different suppliers purified by various pretreatments.

Surface science tools requiring ultrahigh vacuum (UHV) conditions, such as X-ray photoelectron spectroscopy (XPS), are applicable due to the intrinsically low vapour pressure of ILs.^{14,18,19} Using ILs as electrolytes to study electrochemical processes at the solid — liquid interface allows studying processes at po-

tentials beyond the stability window of water (1.23 V).^{15,20–22} However, it was also shown that impurities can have a significant impact on the electrochemical properties.^{9,10} A common approach to studying such systems is cyclic voltammetry, where a current is recorded upon applying a triangular wave potential. The features in the current signal are a fingerprint of the investigated system, as shown extensively for aqueous electrochemical systems.^{23–27} In turn, when the electrode’s quality is well-known, possible changes in the electrolyte can be deduced,^{28–30} thus, making the electrode a sort of probe.

In this work, we exemplarily focused on the IL *N*-methyl-*N*-propylpiperidinium bis(trifluoromethane)sulfonimide ([MPPip][TFSI]), which we had previously used for different electrochemical studies.^{2,12,31–33} We studied batches purchased between 2017 and 2022 from two suppliers and with different supplied purity, summarised in Table 1). Additional information on the pre-treatments and evaluated water contents for the individual measurements presented in the manuscript and the SI are summarised in Table S1 of the SI.

Table 1: Overview on all batches of [MPPip][TFSI] and their type of electrochemical behaviour (see text for details). A detailed overview of the ILs used for the individual figures in this work can be found in Table S1.

Purchased	Supplier	Purity	Type
11.2017	Iolitec	99%	1
09.2020	Iolitec	99%	2
05.2021	Iolitec	99.9%	1
06.2021	Solvionic	99.9%	2
08.2022	Iolitec	99.9%	2

First, all batches were characterised by cyclic voltammetry using a well-defined Au(111) single crystal as working electrode. This electrode can be reproducibly prepared under various atmospheres, such as ultra-high vacuum, laboratory conditions, or in a glove box.^{25–27,34,35} The procedure for the electrode preparation and the experimental parameters for the following ex-

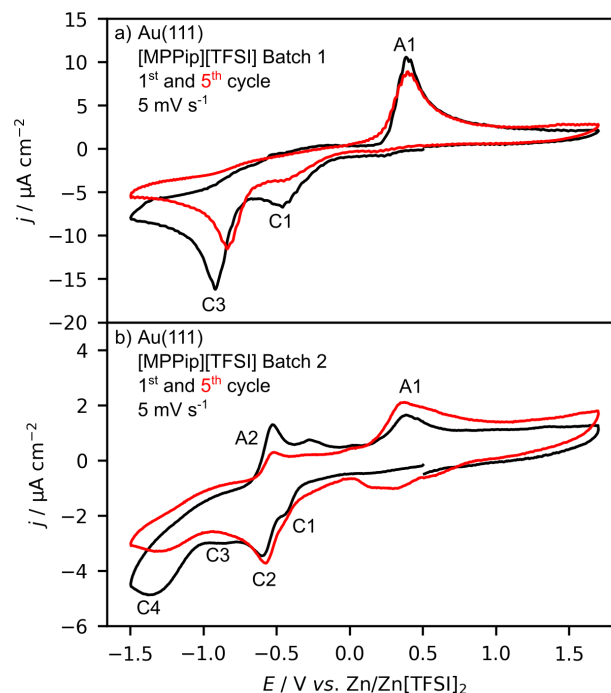


Figure 1: CVs for Au(111) recorded in two different batches (a: batch 1, b: batch 2) of [MPPip][TFSI]. The first potential cycle is shown in black, and the fifth in red. The CVs were recorded at a scan rate of 5 mV s⁻¹ from a starting potential of 0.5 V scanning to negative potentials first.

periments are summarised in the Experimental Section of the Supporting Information.

For all investigated batches, two distinct electrochemical behaviours were observed in the CVs for Au(111). The cyclic voltammograms (CVs) recorded at a scan rate of 5 mVs^{-1} in two different batches of this IL are shown in Figure 1a and b, covering a potential range from -1.5 V to 1.7 V (all potentials throughout this work are given *versus* the $\text{Zn}/\text{Zn}[\text{TFSI}]_2$ reference electrode). The black and red curves show the first and fifth cycles, respectively. CVs for the other batches are provided in the SI in Figure S1. The respective behaviour for each batch is provided in Table 1.

Comparing the observed behaviour (type I or II) for each batch with their respective properties (*i.e.*, purchase date, supplier or labeled purity), unfortunately reveals no correlation. For example, type I was observed for different supplied purities, and type II was observed for ILs of both suppliers. For the following qualitative discussion, only the most essential differences between both behaviours are highlighted, a more detailed discussion can be found in Ref. [REF-Rxiv]. The features in the CVs for batch 1 show approximately five times higher current densities than those for batch 2. The peaks C1, C2, and A1 (see Figure 1) are observed in both cases. Peak A1 only appears when the potential is decreased in the negative-going scan into the region of peaks C1 and C2. For batch 2, additional peaks C2, C4, and A2 are observed. Peak A2 is only observed when the lower potential limit is extended at potentials more negative than peak C2.

The differences between the batches are likely caused by traces of impurities natively present in the ILs. Impurities can interact differently with the surface and species in the electrolyte, changing, in the worst case, the system's electrochemical response. A common issue is site-blocking (poisoning), which can, for example, lead to

- lower overall current densities, such as in batch 2,
- the disappearance of certain peaks, such

as peaks C2 and C4, which are only apparent in batch 2,

- the appearance of new peaks caused by the adsorption of impurities from the electrolyte on these sites (peaks C2, C4, and A2 in batch 2), and
- additional reactions with species in the electrolyte (*e.g.*, electrolyte components, solutes, or solvated species).

Based on a more detailed evaluation of the charges passed in both scan directions during potential cycling, we can conclude that possible surface ad-/desorption processes involving a charge transfer occur concomitantly with other electrochemical reactions.[Ref-ChemRxiv] Thus, impurities deposited on the electrode can indeed act as catalytic sites for the conversion of species in the solution or act as a poison, changing the surface properties as well as reducing the catalytic activity of the substrate towards the reaction with species in the solution.

Previously, we investigated the purity of the as-received ILs with NMR and infrared (IR) spectroscopy,¹² which did not hint at impurities that could be resolved with these techniques. To elucidate other possible contaminants, we performed XPS measurements under UHV conditions, which are given and discussed in detail in the SI. The spectra for both batches are similar, and possible impurities could not be identified. Their concentration could, however, still be below the detection limit of the instrument. The relevance of using XPS to study the quality of the electrolyte will, nevertheless, be illustrated further below.

Impurities such as O_2 and water natively present in the IL, require different techniques to those presented above. The presence of O_2 can be determined by electrochemical methods, which is often demonstrated in studies where ILs are part of O_2 sensors.³⁶⁻³⁸ The common approach to determine the water content is Karl-Fischer titration.^{1,12,39,40} The removal of impurities, including oxygen and water, is, especially for electrochemical measurements, detrimental, as they can have a significant impact on the

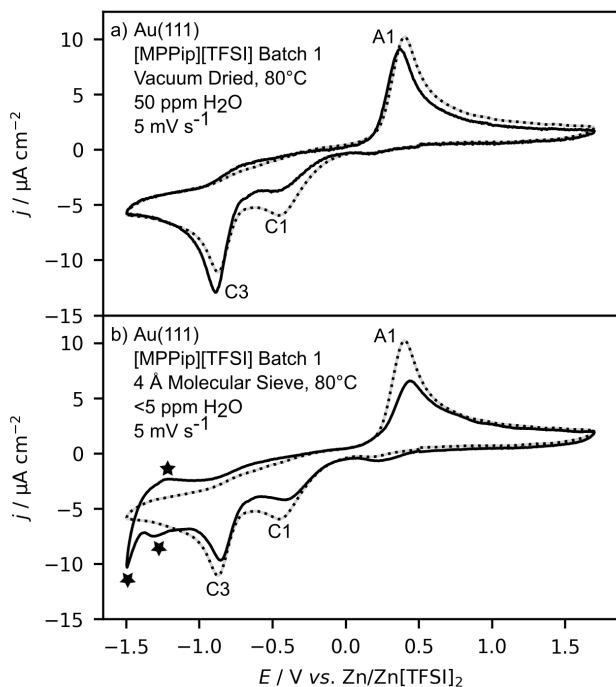


Figure 2: CVs for Au(111) recorded in batch 1 of [MPPip][TFSI] after the application of a) heat (80 °C) and vacuum and b) molecular sieve (4 Å), heat (80 °C) and vacuum. In comparison, the CVs for Au(111) in the as-received ILs are shown as dashed curves. The CVs were recorded at a scan rate of 5 mV s⁻¹ and a starting potential of 0.5 V scanning to negative potentials first. Star symbols denote additional features possibly related to Na (see text for details).

electrochemical properties and interfere with other processes studied on the electrodes.^{10,12-14} Typically, the amount of water and volatile impurities, in general, is reduced by drying the IL under vacuum conditions and elevated temperatures.^{5,41,42} Applying this approach to batch 1 reduces the water content from 75 ppm to 50 ppm. The value can even be reduced to less than 15 ppm, depending on the experimental setup used for drying (see Experimental section). The CVs for Au(111) recorded in the heat-treated and vacuum-dried IL (batch 1) and the as-received IL are shown in Figure 2 a) by solid and dashed lines, respectively. Overall, there are only minor differences between the CVs, except for a slight decrease of peak C1 after drying the IL. As shown elsewhere and described below, we suggest that peak C1 is unrelated to water but to O₂ (which is also related to peak A1). Hence, removing water apparently does not affect the electrochemical properties in pure ILs.

The ILs can be pre-treated with a molecular sieve to further reduce the amount of water and simultaneously remove other impurities.^{41,43} In this work, a molecular sieve with pore sizes of 4 Å was added to the IL before drying in vacuum at 80 °C. The CVs for Au(111) recorded in ILs after this pretreatment compared to those recorded in the as-received ILs are shown in Figure 2 b) with solid and dashed lines, respectively. The maximum current density of peak C1, related to O₂, decreases (see below). The reason for the decrease of peak A1 could so far not be determined.[ref-chemRxiv] More importantly, three additional faint features marked with stars appear at potentials more negative than -1.0 V in the negative- and positive-going scans. Two possibilities could rationalise the emergence of these features. First, the molecular sieve indeed removed some impurities which could block sites for other surface redox processes, or second, new impurities were introduced into the IL during the pre-treatment with the molecular sieve. A possible ion exchange of Na from the molecular sieve with cations from an IL was suggested previously by *Ntais et al.*, based on X-ray diffraction and Raman spectroscopy measurements.⁴⁴

To verify the hypothesis that new impurities were introduced (Na and/or others) we performed XPS measurements. The XP survey spectrum of an IL pre-treated by a molecular sieve is shown in the SI in Figure S3 by the blue line. The XP spectrum contains features related to Si, where the Si 2*p* region is highlighted in Figure 3a in blue. The grey line is the reference spectrum recorded on the as-received IL. In some cases, faint features of Na are observed as shown in the Na 2*s* region in Figure 3b in blue. Both Si and Na are components of the molecular sieve. To unambiguously verify the presence of Na, we polarised a polycrystalline Au electrode at -1.8 V for 2 h in an IL pre-treated with a molecular sieve to deposit possible Na contaminations from the IL,³³ *i.e.*, to increase the local concentration of Na compared to that in the IL. Subsequently, the electrode was removed and the Au surface was rinsed with acetone to remove the IL. The survey XP spectrum of the Au surface after this treatment is shown in Figure S4 in red. No signs for Si were observed on the electrode, but the Na 2*s* peak significantly increased, as shown in Figure 3b in red. Hence, the pre-treatment of an IL with a molecular sieve might not be the most suitable solution for further purification.

In general, based on studies in other electrolytes, the following aspects might as well have to be considered for assessing the quality of an IL electrochemically. While it seems clear that the electrochemical response is related to the quality of the electrode^{23,45} and the electrolyte,^{23,28,29} the role of species dissolved from components which are in touch with the electrolyte (*i.e.*, cell, reference or counter electrode) must be considered.^{46–48} Also, note that in our case, the complete removal of water is presumably almost impossible since a water film can form on the Au(111) electrode after its preparation under laboratory conditions and during the transfer into the glove box.⁴¹

Aside from the additional features observed in the CV related to Na, the CVs did not significantly change upon removing water from the IL. In contrast, previous reports clearly illustrated the impact of water addition or removal on surface redox processes.^{15–17} However, for electro-

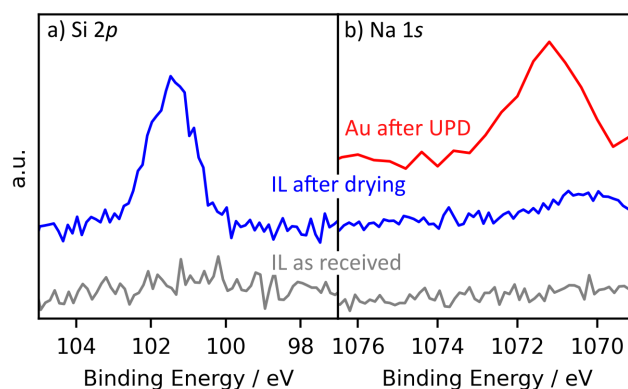


Figure 3: Detailed XP spectra of a) the as-received IL [MPPip][TFSI] (black) and the molecular sieve-dried IL (blue) in the Si 2*p* region and b) the as-received IL [MPPip][TFSI] (black) and the molecular sieve-dried IL (blue), and the poly-crystalline gold sheet after polarisation at -1.8 V in the molecular sieve-dried IL for 2 h (red) in the Na 1*s* region.

chemical processes in ILs which involve reactive species, such as metal deposition^{12,13} or oxygen reduction,^{10,49} water certainly has a critical influence.

Thus, to illustrate the role of water on the peaks observed in the CVs more profoundly, we added water to the IL and monitored the evolution of the electrochemical properties with time. For the following example, the water content of an IL was increased from 75 ppm to around 450 ppm. After storing the IL for five days in a closed container in a N₂-flooded glove-box, the amount of water was still 450 ppm. Interestingly, the CVs for Au(111) recorded in the IL containing additional water after 12 h, 2 days, and 5 days, which are shown in Figure 4, changed significantly. Here the first cycles are shown in Figure 4a and the fifth cycles in 4b with solid lines. For comparison, the CVs for Au(111) recorded in the as-received IL with a water content of approximately 75 ppm are shown with dashed lines. In the first measurement 12 h after the water addition, the first cycle (Figure 4a) shows a significant increase of peak C1 and a decrease of peak C3. At the same time, the positive-going scan does not show any significant changes. With longer storage times peak C1 in the first cycle (Figure 4a) decreases for the IL with an initial water content

of 450 ppm. After five days, the CV appears almost similar to that recorded in the as-received IL with a water content of 75 ppm. After five potential cycles, all CVs look almost identical except for that, which had an initial water content of 450 ppm and stored for 12 hours (Figure 4b). Hence, since the water content did not change over five days, water cannot be at the origin of the changes observed in the CVs after the different measurements. This means that a species that is either volatile or decomposed with time was introduced along with the water into the IL.

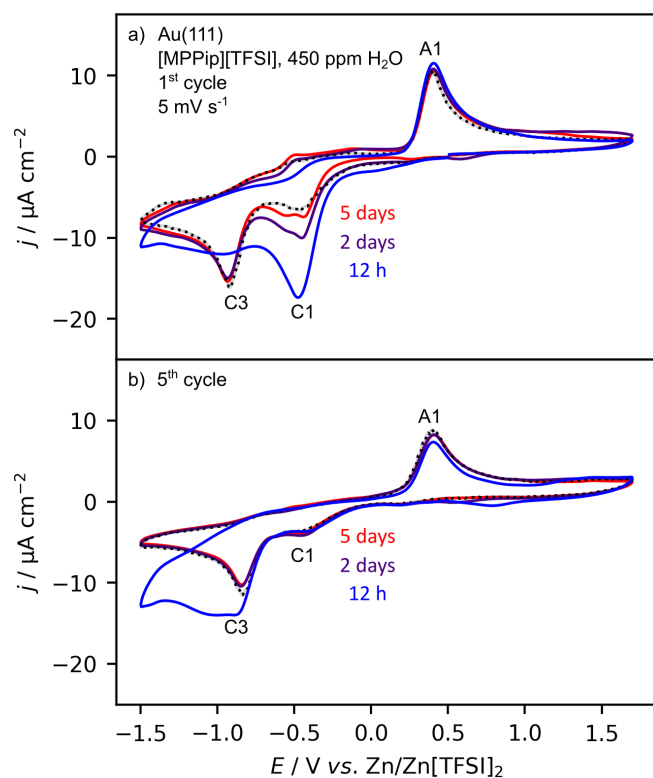


Figure 4: CVs for Au(111) recorded in batch 1 of [MPPip][TFSI] and a water content of approx. 450 ppm (solid lines) and a water content of 75 ppm a) 12 h, b) 2 d, and c) 5 d after the water content was increased to 450 ppm. Each first potential cycle is shown with a black curve, and each fifth with a red curve. The CVs were recorded at a scan rate of 5 mV s^{-1} and a starting potential of 0.5 V scanning to negative potentials first.

Based on our previous works with aqueous electrolytes, we are confident that the ultra-pure water added to the IL was free from

metal or hydrocarbon impurities. The non-deaerated water was, however, added to the IL under ambient atmosphere. The vial was evacuated of atmospheric gas before its transfer into the glove box. We suggest that O_2 dissolved in the IL is not removed by this treatment. Hence, peak C1 is possibly related to O_2 reduction. During the storage in the glove box, the amount of dissolved O_2 decreases with time, due to diffusion into the glove box atmosphere, which has O_2 contents lower than 0.5 ppm. A more detailed reasoning to attribute peak C1 to O_2 and possible reaction mechanisms for the reduction of O_2 on the Au(111) electrode in the presence and absence of water is discussed elsewhere.[REF-chemrxiv]

To mitigate the aforementioned issues, repositories containing appropriately annotated data obtained with different methods and starting materials and reported by various research groups would allow for determining benchmark systems. Currently, there are several approaches to developing ontologies and repositories in this research area.^{50–53} However, these do not yet provide a definite solution for reporting and storing the data from this work. Using literature data currently available in a database dedicated to CVs for single-crystal electrodes,⁵³ we compared CVs for Au(111) recorded in the herein investigated IL, which are shown in the Supporting Information (SI 2). The data from the repository show similar discrepancies to those illustrated in Figure 1. However, the origin of the discrepancies can not be inferred due to the limited number of database entries and possibly also missing metadata. Yet another issue for electrochemical measurements in non-aqueous electrolytes is that reference electrode potentials cannot simply be adjusted to each other, making a comparison even more tedious. Approaches are currently being explored to mitigate this issue.^{54,55}

In this work, we demonstrated the use of well-defined single-crystal electrodes (Au(111)) for assessing the quality of ionic liquid electrolytes ([MPPip][TFSI]). Using cyclic voltammetry, we measured different electrochemical behaviours for batches of the same IL, where the behaviour was independent of the supplier and the sup-

plied purity. We also exemplified that surface science techniques requiring UHV conditions are a great addition to the analytical toolbox for studying the purity of ILs. Here, we demonstrated with XPS measurements that molecular sieves might not be suitable for drying an ionic liquid since Na and Si are transferred during this process in the IL. Finally, after adding water to the IL, the electrochemical properties changed over time due to a slow decay of O₂ in the IL. In total, our study clearly illustrates the necessity of using ILs with different LOT numbers and/or from different suppliers. Even though it might seem obvious, detailed reporting of the purity of the electrolyte before and after a pretreatment is mandatory to avoid misinterpretation of the results.

CRedit Statement

M.-K. Heubach: Conceptualisation, Data Curation, Formal Analysis, Investigation, Visualisation, Writing – Original Draft Preparation. J. Bansmann: Investigation. A. K. Engstfeld: Conceptualisation, Supervision, Writing – Review and Editing, Data Curation,. T. Jacob: Resources, Supervision, Writing – Review and Editing.

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Conflict of Interest

There are no conflicts to declare.

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