

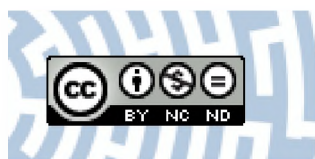


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Influence of experimental conditions on the electrochemical window. Case study on bis(trifluoromethylsulfonyl)imide-based ionic liquids

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ABSTRACT

Ionic liquids (ILs) are often selected as electrolytes in various devices, such as batteries, capacitors and sensors, because of their chemical stability, non-flammability, low volatility, high electrical conductivity, low melting point, high thermal stability, and wide electrochemical window (EW). The width of the EW of an IL depends on the cation type, the water content, the electrode material, and the chosen specific current density used to measure it. In this work, the EWs of four ILs containing the common and stable bis(trifluoromethylsulfonyl)imide anion and triethylsulfonium, 1-(2-hydroxyethyl)-3-methylimidazolium, 1-methyl-1-propylpiperidinium and 1-butyl-1-methylpiperidinium cations were investigated by linear sweep voltammetry in order to analyze their electrochemical stability toward reduction and oxidation at polycrystalline platinum, gold and glassy carbon disc electrodes under anhydrous conditions. Specific current densities of $0.1 \text{ mA}\cdot\text{cm}^{-2}$ or $1 \text{ mA}\cdot\text{cm}^{-2}$ or the linear fitting method were used for the systematic comparison of the EWs obtained from each dataset. The results indicate the dependence of the EW width of each IL on the electrode material and, more importantly, on the chosen specific current density. In this paper, we present new insight into some of the difficulties encountered during determination of the EW for ILs.

1. Introduction

The importance of ionic liquids (ILs) in electrochemistry continues to increase [1–4]. The key factors that influence the applicability of ILs in electrochemistry are their chemical stability, non-flammability, low volatility, high electrical conductivity, low melting point, high thermal stability, low (or high) viscosity, and wide electrochemical window (EW). Generally, the EW is the range of potentials in which the electrode is perfectly polarizable and no appreciable current flows [5]. However, what exactly is the EW? Various approaches have been used to determine EWs by applying different criteria such as specific current density cutoff [6] or the linear fitting method [7], e.g. based on the elimination of capacitive currents [8] and, as a result, strikingly different values can be obtained. The problem of EW determination has been discussed many times in the past, and is especially important now in the area of supercapacitors, where porous electrodes exhibit different behavior to non-porous ones. This issue is serious, but many authors do not provide information about the method used for EW determination. In fact, there is no established approach or recommendation for EW determination and thus the EWs reported in the literature are often not comparable. Our

work shows that measurements using two different specific current densities, i.e. based on the constant values to equal $0.1 \text{ mA}\cdot\text{cm}^{-2}$ or $1 \text{ mA}\cdot\text{cm}^{-2}$, or the linear fitting method, lead to significant differences between the resulting EW values.

The EWs of four aprotic ILs sharing a common bis(trifluoromethylsulfonyl)imide ([NTf₂]⁻) anion were investigated by linear sweep voltammetry (LSV) to analyze their electrochemical stability toward reduction and oxidation at polycrystalline platinum, gold and glassy carbon disc electrodes. The [NTf₂]⁻ is a relatively large, complex, fluorinated anion which is stable to hydrolysis and can exist in two conformational states: *cis*- and *trans* [9–11]. Although the [NTf₂]⁻ anion is known to be hydrophobic and is chemically stable in the presence of water [12], ILs containing this anion still absorb water from the atmosphere. The water content must therefore be controlled. The chosen ILs have previously been recognized as promising electrolytes and solvents. Triethylsulfonium bis(trifluoromethylsulfonyl)imide [S₂₂₂][NTf₂] has been used as an electrolyte in lithium metal batteries [13,14], supercapacitors [15–18] and for the oxygen reduction reaction [19]. 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [HOEMIm][NTf₂] has found application in electrochemical sensors

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[20]. 1-methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide [MPPP][NTf₂] has been tested as a gel polymer electrolyte [21], as an electrolyte for lithium deposition [22,23] and in supercapacitors [24,25]. Furthermore, some Li-ion batteries [26], Li-O₂ batteries [27] and supercapacitors [28] make use of 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide [BMPP][NTf₂]. These applications are possible only due to the electrochemical stability of these ILs at extremely oxidative and reductive potentials.

2. Experimental

2.1. Materials

The four ILs under study were purchased from IoLiTec (Germany); the brief specification provided by the vendor is presented in Table 1. Because the purity of samples is one of the crucial conditions in electrochemical investigations, samples comprising a few cm³ of the ILs were specially dried and deoxygenated prior to carrying out measurements in glass apparatus under vacuum (about 1 Pa) at 373 K, far below its decomposition temperature [29–32] for 5 h, and saturated with Argon 5.0 gas after cooling. After this procedure, the water content was below 15 ppm for each sample (as determined by Karl Fischer coulometry, using a SI Analytics Titrator TitroLine® 7500 KF trace).

2.2. Experimental techniques

All electrochemical measurements were performed using an Ametek Solartron Analytical ModuLab XM ECS potentiostat–galvanostat in a three-electrode configuration. Mineral® flat disc electrodes ($\phi = 1.5$ mm) made of either glassy carbon (GC), polycrystalline gold (Au) or polycrystalline platinum (Pt) were selected as working electrodes, a coiled platinum wire was used as the counter electrode (with a surface area about 20 times larger than that of the working electrode) and polished silver wire (99.99%) adopted as a quasi-reference electrode. The electrodes were polished using a Methrom Autolab polishing kit for solid-state electrodes. Next, the electrodes were rinsed with acetone and dried in a stream of argon. Linear sweep voltammetry was used in the electrochemical stability investigations from 0 V in positive and negative directions in individual experiments, each time on clean electrodes. The potential was scanned from 0 V to –4 V and from 0 V to +4 V vs. Ag at a scan rate of 10 mV·s^{–1}. This wide potential range is sufficient for registration of any electrochemical activity of the ILs studied here, and the low scan rate provides low capacitive currents. The experiments were stopped if the anodic or cathodic currents reached 100 mA·cm^{–2}. After registration of electrochemical stability, ferrocene was used as an internal standard (10^{–4} mol·L^{–1}), and the ferrocenium/ferrocene redox

Table 1
Specification of the ILs used.

IL	CAS number	Assay NMR %	Cation IC %	Anion IC %	Halides ppm	Water ppm
[S ₂₂₂][NTf ₂]	321746–49-0	>99	99.9	99.8	<100	86 ^a 110 ^b 10 ^c
[HOEMIm][NTf ₂]	174899–86-6	>99	>99	>99	<100	51 ^a 280 ^b 13 ^c
[MPPP][NTf ₂]	608140–12-1	>99	99.9	99.9	<100	84 ^a 44 ^b 7 ^c
[BMPP][NTf ₂]	623580–02-9	>99	99.9	99.9	<100	53 ^a 165 ^b 11 ^c

^a Declared by the supplier.

^b Water content determined by us in the commercial samples.

^c Water content determined by us after the drying procedure.

couple potential was determined by taking the average of the oxidation and reduction potentials at the maximum (minimum) of the corresponding peak. Measurements were carried out under isothermal conditions (293 ± 1 K). The glass vessel used in the measurements was dried at an elevated temperature under an Argon 5.0 gas stream. During the measurements, laminar argon gas flow was used to reduce the possibility of atmospheric influence.

In the data analysis, two ways of determining of the EW were chosen. First, two different specific current densities, i.e. current per geometric electrode surface area (not to be confused with the electrochemical surface area, which depends on the roughness factor or porosity of the electrode) were applied. As mentioned by Mousavi et al. [7], current densities ranging from 0.01 to 5 mA·cm^{–2} are reported in the literature in connection with the determination of the EWs of ILs. A low current density of 0.1 mA·cm^{–2} was assumed to be more appropriate for critical applications like batteries and supercapacitors, where electrochemical degradation products can decrease energy efficiency and cycle durability [33]. However, it should be pointed out that experiments should be performed using the target electrodes [8,34,35]. A larger current density, 1 mA·cm^{–2}, was also chosen for study. This is the most common value in the literature [7] in situations where possible degradation products do not influence the device's efficiency, or in large-scale processes such as electrochemical synthesis or electrodeposition [36]. These two values were chosen because specific current levels are not established in the literature (see also the values shown in Table S1 in the Supporting Information), but they are close to the values reported by other researchers and are suitable for studying the influence of water and other impurities [12,37]. Secondly, the commonly used linear fitting method was used (intersection point of two straight lines, which represent the extrapolation of a non-faradaic current before onset and a faradaic current after onset of the electrochemical process on the current–potential curve). This method depends to a small extent on the potential range of the voltammogram used for fitting [7]. All the potentials referred to in our work have an accuracy of ± 50 mV.

3. Results and discussion

The electrochemical responses were measured for each of the 12 arrangements (IL–working electrode combinations) studied. At the low potential of the working electrode, before starting the electrochemical reaction, only non-faradaic currents were observed, related to the charging of the electrical double-layer at the electrode–electrolyte interface. This behaviour is observed on the voltammogram as a flat section of the curve. The faradaic process starts in a certain potential range, which is characteristic of the electrolyte composition and the working electrode material. Depending on the polarization of the working electrode, reduction occurs in the negative potential range and oxidation in the positive potential range. This is shown on the voltammogram as a steep section of the current–potential curve. The onset of the faradaic process starts without a sharp current increase. Therefore, it is necessary to define a criterion that makes it possible to identify the potential at which an electrochemical reaction starts, known as the anodic or cathodic limit [5]. The results of linear stripping voltammetry (LSV) measurements are presented for the common ILs [S₂₂₂][NTf₂] and [HOEMIm][NTf₂] in Fig. 1 and for [MPPP][NTf₂] and [BMPP][NTf₂] in Fig. 2. It can be seen from the voltammograms that the current–potential curves differ depending on the electrode material.

In the case of [S₂₂₂][NTf₂], undisturbed reduction and oxidation processes appear only at the GC electrode. At the precious metal electrodes, additional oxidation processes can be observed. These are probably related to impurities in the IL sample originating from the substrates used in the synthesis. The whole oxidation peak of the IL is not visible in this current density range but can be seen in the full-scale voltammogram in Figure S1 in the Supporting Information. In this case the GC working electrode is insensitive to these impurities. The reduction process starts at very similar potentials in the case of the GC

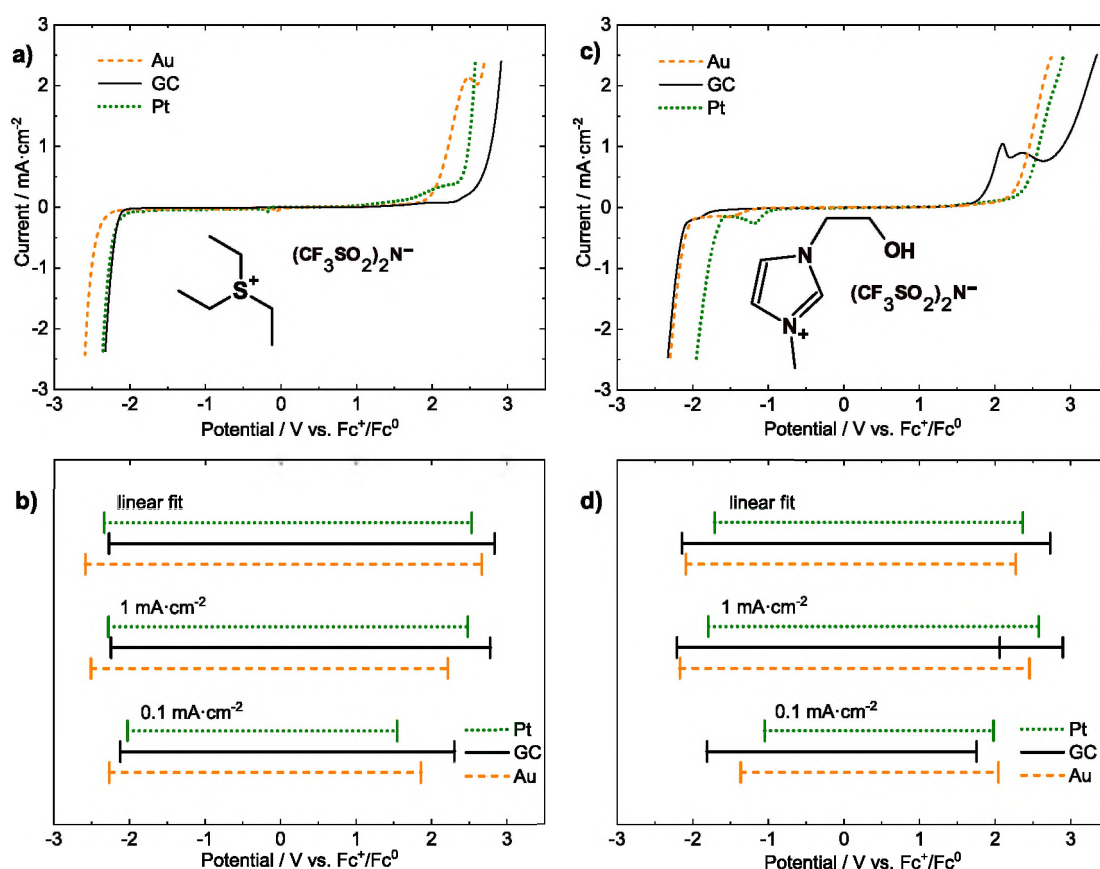


Fig. 1. Linear sweep voltammetry of (a) [S₂₂₂][NTf₂] and (c) [HOEMIm][NTf₂]; EWs of (b) [S₂₂₂][NTf₂] and (d) [HOEMIm][NTf₂] determined using three different criteria.

and Pt working electrodes but is shifted toward a more negative potential at the Au electrode. Comparing the size of the EW obtained using (i) the assumed lower cutoff current density $0.1 \text{ mA}\cdot\text{cm}^{-2} J_{0.1}$, (ii) the higher current density cutoff $1 \text{ mA}\cdot\text{cm}^{-2} J_{1.0}$, or (iii) the linear fitting J_{fit} method, it can be seen that the potentials determined from these criteria are different. Furthermore, two oxidation processes were registered in the case of [HOEMIm][NTf₂] before the oxidation process related to the decomposition of the IL (see Fig. 1c). Similarly, small reduction peaks appear before decomposition during the reduction of the IL, influencing the $J_{0.1}$ value. Considering each criterion, the EW determined with the Pt electrode is significantly smaller. Both [MPPPP][NTf₂] and [BMPP][NTf₂], which have similar chemical structures, show an electrochemical response during reduction (see Fig. 2), unlike previous research, where differences in reduction potentials are less apparent [31]. It is worth noting that each IL contains the same [NTf₂]⁻ anion. Regardless, the oxidation potentials differ by about 400, 100 and 160 mV for completely different [S₂₂₂][NTf₂] and [HOEMIm][NTf₂] and by about 500, 50, and 80 mV for piperidinium ILs for Au, GC and Pt working electrodes, respectively. The cathodic and anodic reduction potentials and corresponding EWs are reported in Table 2. Each of the investigated substances reveals a faradaic process unrelated to the potential limit of the IL on at least one working electrode material, but this is probably related to nonvolatile impurities in the commercial samples. Thus, for [HOEMIm][NTf₂], two J_{fit} values were determined, considering the first faradaic process and further decomposition current, significantly influencing the size of the EW.

Since the EW is not a physical constant, comparison of our values of the EWs with literature findings (see Table S1) is not straightforward due to the different measurement conditions and assumed criteria. There is good agreement between our results and the literature [38] for [S₂₂₂][NTf₂] in one case. However, only two sources of data are available.

Regardless of the different scan rates, there is a difference of about 100 mV in the EW. In the second case, the EW reported in this work is significantly larger, even when determined by the use of $J_{0.1}$ criterion. [HOEMIm][NTf₂] exhibits a considerably smaller EW than that reported in the literature [39]. It should be noted that [HOEMIm][NTf₂] shows similar size of EW with increasing specific current density as [EMIm][NTf₂] (4.3 V for $0.23 \text{ mA}\cdot\text{cm}^{-2}$ [40], 4.5 V for $0.5 \text{ mA}\cdot\text{cm}^{-2}$ [41], 4.2 V for $1 \text{ mA}\cdot\text{cm}^{-2}$ [6], and 5 V for $1 \text{ mA}\cdot\text{cm}^{-2}$ [42]). The most abundant data on EWs are available for [MPPPP][NTf₂] [23,31,43]. The EW determined -using the GC electrode is greater than the values reported in the literature. The EW obtained using the Pt electrode assuming $J_{0.1}$ is 500 mV smaller than the reported value [31]. There are no corresponding reported data for the Au electrode. Significant differences occur in EW width for [BMPP][NTf₂] [31,44,45], and there are again no available data for the Au EW.

There is a relationship between the electrode material and the reduction and oxidation potentials of the ILs. The reduction potential follows the sequence $\text{Au} \approx \text{GC} < \text{Pt}$ and the oxidation potentials follow the order $\text{GC} > \text{Au} \approx \text{Pt}$. The values of the EWs differ significantly depending on the working electrode-IL system and the applied criterion. However, the EWs determined at $0.1 \text{ mA}\cdot\text{cm}^{-2}$ with Au and GC are broader than the EWs determined with Pt. Unfortunately, at $1 \text{ mA}\cdot\text{cm}^{-2}$ this regularity disappears and, with linear fitting, a deviation is observed for [BMPP][NTf₂]. It is probable that if sufficiently pure ILs could be synthesized and examined, the regularity mentioned above could be successfully generalized.

Meanwhile, we have to consider the impurities in commercially available substances when planning experiments in which potential limits and EW play a leading role, such as lithium-oxygen batteries, supercapacitors or electrochemical synthesis. It seems that there are at least two approaches to this type of application. Firstly, proposing

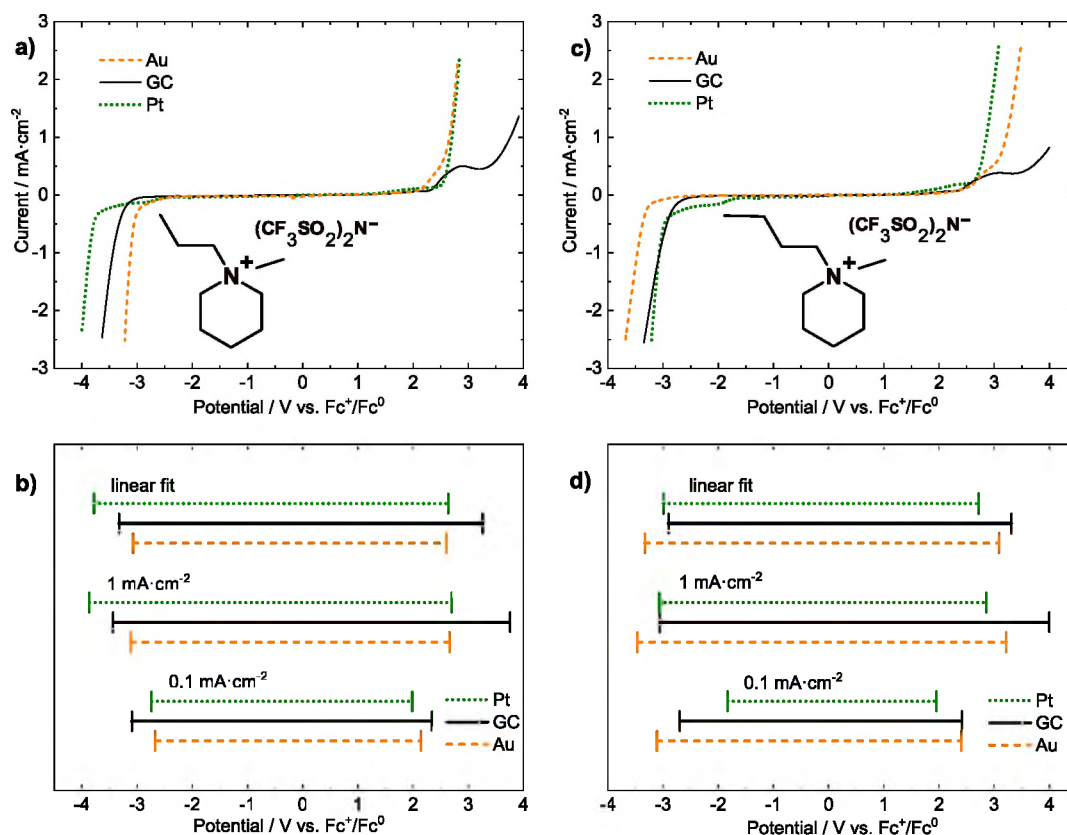


Fig. 2. Linear sweep voltammetry of (a) [MPPP][NTf₂] and (c) [BMPP][NTf₂]; EWs of (b) [MPPP][NTf₂] and (d) [BMPP][NTf₂] determined using three different criteria.

Table 2

The oxidation and reduction potentials and EWs of the investigated ILs determined using three different criteria. The maximum values of the EWs are shown in bold type.

[S ₂₂₂][NTf ₂]	IL											
	[S ₂₂₂][NTf ₂]			[HOEMIm][NTf ₂]			[MPPP][NTf ₂]			[BMPP][NTf ₂]		
	Working electrode material											
Au	GC	Pt	Au	GC	Pt	Au	GC	Pt	Au	GC	Pt	
Criterion	Reduction potential/V											
0.1 mA·cm ⁻²	-2.27	-2.12	-2.02	-1.37	-1.81	-1.05	-3.11	-2.70	-1.83	-2.67	-3.10	-2.74
1 mA·cm ⁻²	-2.51	-2.24	-2.28	-2.17	-2.21	-1.79	-3.47	-3.06	-3.07	-3.11	-3.44	-3.86
Linear fitting	-2.58	-2.27	-2.33	-2.09	-2.14	-1.71	-3.33	-2.90	-2.99	-3.07	-3.33	-3.78
Criterion	Oxidation potential/V											
0.1 mA·cm ⁻²	1.86	2.30	1.55	2.05	1.75	1.98	2.40	2.42	1.95	2.14	2.34	1.99
1 mA·cm ⁻²	2.22	2.78	2.48	2.45	2.06	2.58	3.22	4.00	2.86	2.66	3.76	2.70
Linear fitting	2.67	2.83	2.53	2.28	2.73 (2.90)	2.37	3.09	3.31	2.72	2.60	3.26	2.64
Criterion	EW/V											
0.1 mA·cm ⁻²	4.13	4.42	3.57	3.41	3.56	3.03	5.52	5.11	4.55	4.81	5.44	4.73
1 mA·cm ⁻²	4.73	5.02	4.76	4.63	4.27	4.37	6.69	7.06	5.92	5.77	7.19	6.57
Linear fitting	5.25	5.10	4.86	4.37	4.87	4.08	6.42	6.21	5.71	5.68	6.59	6.42
Δ _{max-min}	1.12	0.68	1.30	1.21	1.54	1.34	1.17	1.95	1.38	0.96	1.76	1.84

devices that work in the limited potential range, or secondly, broadening the potential range and examining the influence of the small faradaic currents encountered before the actual potential limit of the IL.

The EW is strongly affected by the water content and the humidity surrounding the working device. The influence of the water content on the narrowing of the EW was analyzed in detail by O'Mahony et al. [12]. Similar results were obtained by Döblinger et al. [37], who also observed the increasing contribution to the current from dissolved impurities as the water content increases. On a large scale, operation with ILs with a few ppm water content is not realistic due to the need for

extremely tightly fitting components, long drying times and special handling techniques.

The EWs are also dependent on mass transport, the resistance of the electrolyte, and large capacitive currents in the case of porous electrodes, although for ideal systems (i.e. numerical simulations) the linear fitting method is not biased by electrolyte mass transport [7]. However, linear fitting does not provide a clear-cut value of the real, i.e. applicable potential limits. Some small electrochemical peaks could be overlooked at a sufficiently large current scale, which could drive the degradation of the electrode or poisoning of the electrolyte by its

decomposition products. For some of the electrolyte–electrode configurations, the electrochemical limit is almost not observed, as shown in Fig. 2c. The essential difference in the assumed criteria is whether only the pre-onset potential range is taken into account, or both the pre-onset and post-onset range. The wide potential range of the linear fitting methods could lead to the low current faradaic processes related to impurities present in the analyzed samples being overlooked.

A drawback of the specific current density criterion is its dependence on the scan rate and the concentration in the case of electrolyte solutions [7]. In conclusion, reliable and applicable values for the EWs of specific electrolyte solutions or ILs could be determined only for really pure substances. Therefore, a sufficiently low current density cutoff and low scan rates applied to diminish capacitive currents make it possible to operate within the non-faradaic current range, compared with the linear fitting method, which determines considerably higher EW values, including the initial region where the faradaic process starts. EWs determined by other researchers should be considered carefully as a clue in the search for suitable electrolytes. A detailed analysis of structure and properties should be carried out on a series of compounds from a single source [31], especially when the ILs supplied by vendors are not satisfactorily pure from the electrochemical point of view and change from batch to batch, particularly in water content. Classification of the electrochemical stability of ILs should begin with the exact determination of the residual impurities and thorough purification rather than the formulation of the criteria.

4. Summary

A consistent set of EWs is reported for four aprotic ILs using three different electrode materials under anhydrous conditions. There is some observed relationship between the electrode material and the potential limits. It is possible to overlook small parasitic faradaic currents when applying the linear fitting method and determining the intersection point when significant current flows occur during the electrochemical process. On the other hand, current density criteria are more convenient for the determination of the EW in cases when there is a low overall current related to the electrochemical reaction (see Figure S2) or electroactive impurities are present in the IL which could cause poisoning of the electrodes or consumption of the electroactive species. However, the linear fitting method describes EWs more generally, ignoring the faradaic reactions of some impurities. In our opinion, the criteria used in measuring the EW should be clearly quoted, as well as the scan rate, the type of working and reference electrode, and so on. The different criteria examined in this work, all commonly encountered in the literature, lead to large differences in EW width, typically c.a. 1 V and sometimes even 2 V, i.e. up to about 30% of the EW. Overstating the EW by 2 V could be a misrepresentation of a particular IL, which could appear to be a stand-out substance on this measure. As a result, the application of such ILs could be disappointing. A more detailed picture of the quality of the investigated sample could be obtained if the EW is reported next to the voltammogram as potential values at two or three specific current densities, e.g. $0.05 \text{ mA}\cdot\text{cm}^{-2}$, $0.1 \text{ mA}\cdot\text{cm}^{-2}$ and $1 \text{ mA}\cdot\text{cm}^{-2}$, even without additional chemical analysis. Although the EW is not a physical constant, it is more probable that suitable electrolytes for electrochemical devices such as batteries or ultracapacitors will be selected based on preliminary results, like EW, conductivity, etc. [46] than by the trial-and-error method. Therefore proper, precise reporting of EWs is desirable. The Au, GC, and Pt electrodes used in this study make it possible to repeat some experiments carried out by other researchers, but further investigation of the specific electrodes and ILs is also necessary. This work highlights the difficulties encountered in determining EWs and the need for some standardization in this area.

Declaration of Competing Interest

The authors declare that no competing financial interests or personal

relationships could have influenced the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.elecom.2021.107107>.

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