A Novel Approach for Differential Electrochemical Mass Spectrometry Studies on the Decomposition of Ionic Liquids

D. Alwast[a], J. Schnaidt[b], Y.T. Law[a], R.J. Behm[a,b,*]

[a] *Institute of Surface Chemistry and Catalysis, Ulm University, Albert-Einstein-Allee 47, D-89081 Ulm, Germany*
[b] *Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, Helmholtzstr. 11, D-89081 Ulm, Germany*

ABSTRACT

We report on a novel differential electrochemical mass spectrometry (DEMS) set-up, which allows us the online detection of volatile products formed during potential induced decomposition of ionic liquids, and its application for elucidating the decomposition mechanism of the two ionic liquids (ILs) 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide ([BMP][TFSA]) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([EMIM][TFSA]) on polycrystalline Au electrodes. In the cathodic scan, the $[BMP]^+$ cation decomposes at potentials more negative than -1.0 V vs. Ag/AgCl by cleaving the butyl side chain, below -2.6 V also ring opening takes place. For [EMIM][TFSA] reduction, we find a decomposition product which based on its mass is compatible with a stable imidazolium radical appearing at -2.3 V, accompanied by its saturated derivative. In the anodic scan the $[TFSA]^-$ anion is decomposed first for both ILs, possible decomnposition products are discussed.

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1. Introduction

Ionic liquids (ILs) are considered to be promising electrolytes for future battery applications due to a number of favorable properties such as high ionic conductivity, very low vapor pressure, low flammability, and high thermal and electrochemical stability [1–5]. Since the electrochemical stability of ILs plays a key role for their use as battery electrolytes, it is interesting to study their electrochemical decomposition.

The electrochemical stability window, i.e., the potential difference between onset of the cathodic and anodic decomposition of the IL, is usually examined by cyclic voltammetry [6]. It is generally accepted that in most ILs the cathodic limit is determined by the onset of the reduction of the cation, while the anodic limit is set by the oxidation of the anion [6–13]. This conclusion is based on the comparison of the onset potentials for the anodic/cathodic decomposition of different combinations of cations and anions in ILs and on calculated values of the HOMO and LUMO energies [6,14,15]. Though appearing reasonable, direct experimental proof for this assignment is largely missing.

This general problem, which is highly relevant also for the understanding of more realistic battery systems, is topic of the present work, where we want to gain closer insight on the stability and decomposition behavior of ILs by *in situ* determination of the volatile products formed during the decomposition reaction. In a first step, we focus on the interaction of neat ILs with a Au electrode, in the absence of other electrolyte components or electrode materials such as Li, graphite, transition metal oxides. Differential electrochemical mass spectrometry (DEMS) is known as a powerful method for the online detection of volatile reaction products [16], but commonly used set-ups developed for aqueous electrolytes, where a porous, hydrophobic membrane serves as interface between the electrochemical cell and the differentially pumped vacuum system housing the mass spectrometer, are for several reasons not suitable for operation with ILs, among others because of the high viscosity of the ILs and the low permeability of the membrane for larger molecules. Furthermore, a flow cell set-up as developed and generally used in our institute [17] is inappropriate because of its high consumption of expensive IL electrolyte. Mass spectrometry set-ups developed for battery related research with non-aqueous electrolytes either use gas purging [18,19] or a leak valve [20] to transport the volatile products to the analysis chamber. We here report on the development of a new set-up, where we make use of the extremely low vapour pressure of the ILs. This allows us to operate without a separating membrane or any capillary inlet system, by placing the open electrochemical cell directly into the vacuum chamber of the mass spectrometer. This approach also offers the advantage of

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* Corresponding author.
  E-mail address: juergen.behm@uni-ulm.de (R.J. Behm).

characterizing the IL under "ideal" conditions, minimizing the effects of impurities such as water, oxygen or even nitrogen.

This set-up is employed to investigate the decomposition behavior of the two ILs 1-butyl-1-methylpyrrolidinium bis(tri-fluoromethanesulfonyl) amide ([BMP][TFSA]) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide ([EMIM][TFSA]) during potential scans on polycrystalline Au electrodes. [BMP][TFSA] is one of the most promising ILs for the use in batteries due to its especially wide electrochemical window and its hydrophobicity and stability against atmospheric influences, in particular against exposure to water vapor and air [21–24]. Before starting with the description of the DEMS set-up and the presentation and discussion of the results, we will briefly summarize the results of previous studies relevant for this work.

Assuming that decomposition of [BMP][TFSA] at too high cathodic potentials proceeds via reduction of the [BMP]$^+$ cation which takes up an electron, Kroon et al. performed quantum chemical calculations to calculate the stability of the resulting [BMP] radical [15]. They found that the radical is not stable and decomposes into a smaller radical and a neutral fragment. The calculated relative energies of possible decomposition products, relative to that of the initial molecule, indicated that the formation of methylpyrrolidine and of a butyl radical is the most probable initial decomposition step. Two additional decomposition routes, which are also possible based on their energetics, were the formation of a dibutylmethylamine radical via ring opening or of a butylpyrrolidine and of a methyl radical. Such products were indeed found by *ex situ* GC-MS after extensive decomposition of [BMP][TFSA] on glassy carbon electrodes [15]. In contrast, Howlett et al. concluded from electrochemical and IR spectroscopic measurements that the [TFSA]$^-$ anion in a comparable IL (1-propyl-1-methylpyrrolidinium, [PMP][TFSA]) is reductively decomposed already at potentials positive of the onset of massive [PMP]$^+$ cation reduction [25]. They proposed a decomposition mechanism based on *ab initio* calculations. Furthermore they found that the [TFSA]$^-$ reduction depends sensitively on the water content of the IL. Endres et al. also observed cathodic peaks before the onset of massive [BMP][TFSA] decomposition [11,12], which according to Howlett et al. [25] were also due to [TFSA]$^-$ decomposition. From *in situ* STM measurements, Endres et al. concluded that the [TFSA]$^-$ breakdown products are loosely adsorbed on the Au surface and soluble in the IL [12]. Markevich et al. [26] concluded from stepwise electrochemical decomposition and IR measurements of the volatile reaction products after each step that the decomposition of the cation as well as the anion takes place at cathodic potentials. However, it is unclear, if and how a separation between the products formed at the CE and the WE was achieved. It is well known, that impurities influence the stability of ILs [27–31]. The influence of especially water and oxygen traces on the stability of [BMP][TFSA] towards cathodic decomposition was studied in more detail by Randström et al. employing cyclic voltammetry [32,33]. While in the presence of water traces similar features in the voltammogram were observed according to Endres et al. and Howlett et al. [11,12,25], the former authors did not find any voltammetric features indicating the reduction of the [TFSA]$^-$ anion in pure and dry [BMP][TFSA] before the onset of massive electrolyte decomposition [33]. Furthermore, comparing measurements performed under N$_2$ or Ar purging and measurements under vacuum they found that even the presence of N$_2$ leads to an additional cathodic process [32].

To gain more insight into the correlation between structure and reactivity, we also investigated the decomposition of a closely related second IL, which contains the same anion but a different cation. We chose [EMIM][TFSA], which in contrast to [BMP][TFSA] has an aromatic, imidazolium based cation. Investigations of Xiao et al. on Pt and Kroon et al. on Au working electrodes (WEs) in a

comparable aromatic IL (1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF$_4$]), using NMR spectroscopy for product analysis, led to the conclusion that reduction of [BMIM]$^+$ results in the formation of the related carbene and molecular hydrogen ($^1/_2$ H$_2$) [34], or via a disproportionation reaction in the above carbene and the related hydrogenated species [15]. In addition, Kroon et al. showed by quantum chemical calculations that a [BMIM] radical formed in the first reduction step would be stable in vacuum [15].

In the following we will first describe the new experimental set-up and the experimental procedures in chapter 2. This will be followed by the discussion and comparison of the decomposition behavior of [BMP][TFSA] (Section 3.1) and [EMIM][TFSA] (Section 3.2), demonstrating the insight accessible from such kind of measurements.

2. Experimental

2.1. Experimental set-up

The electrochemical cell, shown as enlarged cross-section in a circle at the bottom of Fig. 1, consists of a disk-like Kel-F cell body (diameter 4 cm) with 3 holes (diameter 0.5 cm) drilled into the body. While two holes are only drilled partly through the Kel-F and are therefore closed at the bottom, the central hole is drilled completely through the cell body and open at both sides. The outer holes will accommodate the reference electrode and the working electrode, respectively, forming the WE-compartment and the RE-compartment, while the counter electrode will be placed
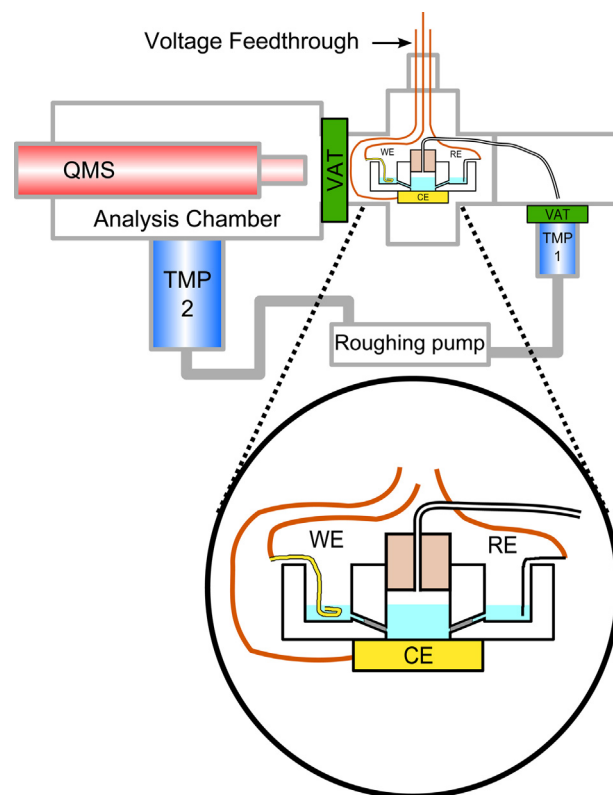

Fig. 1. Schematic drawing of the DEMS set-up. The electrochemical cell is directly placed inside the vacuum chamber. The working electrode (WE) consists of a Au wire, the reference electrode (RE) of a Ag/AgCl wire. The mass spectrometer (QMS) is placed inside the analysis chamber which is pumped by a turbomolecular pump (TMP 2). The gaseous products of the counter electrode (CE) are separated by a capillary which is capped on the compartment of the CE and leads directly to a turbomolecular pump (TMP 1).