Insights into electrochemical reactions by differential electrochemical mass spectrometry

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A B S T R A C T

Differential electrochemical mass spectrometry (DEMS) has become an indispensable tool for not only qualitative and quantitative detection of volatile products or intermediates of continuous Faradaic reactions, but also determination of the amount of adsorbates (sub-layer or monolayer) at different electrode surfaces by means of their desorption.

In the present review, we give a short introduction about the history of the combination of electrochemistry and MS (EC-MS), followed by a summary of the several types of DEMS cell that are applicable for different purposes. We present in detail the calibration of DEMS systems and their application in aqueous and non-aqueous electrolytes.

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1. Introduction

The online coupling of an electrochemical cell to mass spectrometry (EC-MS) has proved useful in the identification of intermediates or products of the electrochemical reactions, leading to the ability to do qualitative and quantitative analysis and mechanistic studies of redox reactions. In 1971, Bruckenstein and Gadde [1] were the first to detect electrochemically generated gaseous products qualitatively by *in-situ* EC-MS using a hydrophobic porous electrode with a time constant of about 20 s. In 1984, Wolter and Heitbaum [2,3] improved the vacuum system of the EC-MS and reduced the delay time of detection, in order to use EC-MS for quantitative studies (current efficiency and kinetic information). Thus, the MS signal of the volatile species became proportional to its rate of formation instead of the accumulated product; this explains the term differential EC-MS.

In a typical differential EC-MS (DEMS) experiment, the ion current corresponding to given species of interest is simultaneously recorded with the Faradaic electrode current during the potential scan (cyclic voltammogram), yielding so-called MS cyclic voltammograms (MSCVs). Other electrochemical techniques, such as potentiostatic [4,5] or galvanostatic [6] and even pulsed voltammetry for short time (1 s) [7], have also been combined with DEMS.

2. Types of DEMS cell

In order to detect species that are produced at an electrode surface by MS, they have to be transferred from the electrolyte phase to vacuum. Fortunately, for aqueous systems [2] and also some organic electrolytes with a high surface tension {e.g., propylene carbonate (41.1 mNm^{-1}) [8] and dimethyl sulfoxide (DMSO) (43.5 mNm^{-1}) [9,10]}, the separation of the electrolyte from the vacuum can be achieved using porous Teflon membranes. Due to their hydrophobicity, the liquid does not penetrate the pores, whereas dissolved gaseous and other volatile species readily evaporate in them. The critical pore size depends on the surface tension of the liquid and the contact angle between the liquid and Teflon. For water, it is $r < 0.8 \text{ μm}$ [2]. A typical Teflon membrane (e.g., Gore-Tex) is 75 μm thick and has a nominal pore width of 20 nm with a porosity of 50%. The Teflon membrane is usually supported by a glass or steel frit. Different types of working electrode, such as lacquer, sputter-deposited, supported nanoparticles, smooth and massive, were used for DEMS. Several cell types have been described, as reviewed in detail { [11–13] and references therein}.

In the conventional cell, the electrocatalyst layer (e.g., Au) is deposited onto the Teflon membrane with a typical thickness of 50 nm (Fig. 1A). The metal-sputtered electrode can also be used as a gas-diffusion electrode [9]. A typical cell for these electrodes is shown in Fig. 1B. The response time for an electrochemical experiment was determined to be about 0.1 s [14]. When using volatile reactants (e.g., oxidation of CO or reduction of O_2), it must be kept in mind that the electrochemical reaction and evaporation are competing processes.

For the use of massive electrodes for DEMS (e.g., single-crystal electrodes), the thin-layer cells of Fig. 1C and 1D were developed [15–17]. In Fig. 1C, volatile species produced at the massive electrode (with a diameter of 1 cm) diffuse through a 50–100-μm thick electrolyte layer within 2 s to reach the vacuum system through the Teflon membrane.

Two capillaries serve as electrolyte inlet and outlet and as a connection to the reference electrode (RE) and the counter electrode (CE). This cell is well suited for desorption experiments under stagnant conditions. The main disadvantage of this cell is that a considerable part of the product formed close to the outlet of the cell is transported out of the thin-layer volume before it can reach the Teflon membrane during the continuous flow of electrolyte. A modification of a thin-layer cell is described [18].

In the dual thin-layer flow cell (Fig. 1D), the electrochemical compartment is separated from an MS compartment [11,17]. The product species are transported from the upper compartment to the lower compartment through six capillaries (d = 0.5 mm) by constant flow of the electrolyte. With its small electrolyte volume (≈3.5 μL), this cell is well suited to continuous Faradaic reactions and also for the detection of adsorbates after their desorption, as the product concentration of desorbing species and thus the sensitivity for their detection are high. This flow cell can also be combined with an electrochemical quartz crystal microbalance (EQCM) [17] (also see below) or infrared (IR) spectroscopy. To do so, the working electrode is replaced by a quartz crystal or a prism with a thin layer of the electrode material for attenuated total reflection (ATR) [5,19,20]. Furthermore, the Teflon membrane in the bottom compartment may be covered by Au or Pt, thus serving simultaneously as a detection electrode like the ring in a rotating ring disc assembly [21].

In another approach, Kita and co-workers [22] used a hanging meniscus configuration for massive electrodes, using a pinhole as the gas inlet, located at the hemispherical end of a glass tube, covered by a Teflon film. Similarly, Wonders et al. [23] placed a small Teflon tip as inlet close to a bead single-crystal electrode in a hanging meniscus arrangement. This set-up has a long delay time of 10–15 s and does not allow working under convection.

A new approach combines the advantage of defined convection with the possibility to use small bead crystals in a hanging meniscus configuration, as shown in Fig. 1E [24]. A cone-shaped capillary is placed in the usual hanging meniscus very close to the bead electrode with a gap of about 200 μm. The electrolyte is sucked continuously through the gap and the capillary to the MS detection compartment and fresh electrolyte is injected into the cell at the same rate, in order to ensure a stable hanging meniscus at the electrode.

Recently, Abruna and co-workers described a double-band-electrode channel flow cell with an interface to the mass spectrometer between the working electrode at the electrolyte inlet and the detection electrode at the outlet [25].

In the wall jet geometry described by Scherson and co-workers [26], the working electrode is surrounded by a thin, porous Teflon cylinder, through which gaseous products are transferred to the vacuum of the MS.

3. Calibration of DEMS

Product-formation rates are monitored by recording the corresponding MS ion current, I_i. It is directly proportional to the incoming flow $J_i = dn/dt$ (mol s^{-1}) of that species i and therefore:

$$I_i = K° J_i \tag{1}$$

$K°$ contains all settings of the mass spectrometer and the ionization and fragmentation probability of the corresponding species. When the species is produced by a known electrochemical reaction (such as H_2 evolution or CO oxidation), J_i is given by the Faradaic current I_F corresponding to that process:

$$J_i = N I_F/(zF) \tag{2}$$

where z is the number of electrons, F is the Faraday constant and N is the transfer efficiency (i.e., the ratio of the amount of the species entering the vacuum system to the total amount of species produced).

When oxidizing adsorbed CO at Pt, the double-layer charging effects amount to 20% of the total oxidation charge even after background subtraction. The origin is mainly the different double-layer charge at a given potential with and without adsorbed CO [3,27,28]. N is less than 1 (at flow rate exceeding 1 μL/s) because a part of the species produced diffuses away from the electrode into the electrolyte and is not recovered at the membrane to the vacuum, so:

$$I_i = (K^*/z)I_F, \text{ with } K^* = K° N/F \tag{3}$$

When the current efficiency is less than 100%, I_F has to be replaced by its product with the current efficiency.

4. Applicable aqueous and aprotic electrolytes for DEMS

4.1. Aqueous electrolytes

4.1.1. Oxidation reactions at BDD

Boron-doped diamond (BDD) is an interesting electrode material because of the wide potential range even in aqueous electrolyte. One of the possible applications is for wastewater treatment. At the positive potential limit, OH radicals are formed and oxidize nearly every organic compound. DEMS is used here because oxygen