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Enabling real-time detection of electrochemical desorption phenomena with sub-monolayer sensitivity

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ABSTRACT

Electrochemical reactions play an increasingly important role in sustainable energy conversion and chemical synthesis. Better understanding of catalytic mechanisms at electrode surfaces is thus important for the transition to a clean-energy economy, but is hindered by the difficulty of real-time detection of reaction products and intermediates during electrochemistry experiments. Herein, we present a new type of electrochemistry – mass spectrometry (EC-MS) based on a versatile gas inlet to vacuum fabricated onto a silicon microchip, and compare it to established techniques with focus on sensitivity, time response, and mass transport. The inlet system is able to capture reactant molecules directly from an electrode surface and pass them on to a mass spectrometer on a sub-second time scale with 100% collection efficiency for quantitative analysis with unprecedented sensitivity. The high sensitivity and fast time-response, coupled with well-characterized mass transport of both reactants and products in this setup enables sub-turnover resolution for analysis of electrochemical reactions. The technology and concepts presented here can serve as a platform to improve in-situ mass spectrometry in electrochemistry as well as other fields.

1. Introduction

A transition from fossil fuels to sustainable energy sources like wind and solar and sustainable chemical feedstocks like water, carbon dioxide, and biomass is strictly necessary to avoid catastrophic climate change [1]. This transition is bringing a drastic change in the global energy landscape, causing electrochemical and biochemical processes to play an increasing role [2–4]. In order to improve the economics of sustainable energy conversion and chemical synthesis, it is thus important to expand fundamental understanding of electrochemical and biochemical processes.

Electrochemical and biochemical processes are generally run in wet environments at or above ambient pressure, while the most versatile tool for identifying and quantifying the reaction products, mass spectrometry, requires high vacuum [5]. A wide range of sample introduction and ionization methods have been developed that are suitable for product identification and quantification by mass spectrometry after a batch reaction [6], but experiments investigating reaction kinetics and catalytic mechanisms in electrochemistry and biochemistry can be greatly facilitated by in-situ and real-time, i.e., second-timescale, product detection in a small reaction volume [7,8]. This underscores the need for fast, sensitive, and quantitative real-time delivery of reaction products from a liquid test environment to high vacuum [9]. As electrochemical experiments using modern instrumentation allow for finely controlled and near-instant experimental input and output in the form of electrode potential and electric current, electrochemistry – mass spectrometry (EC-MS) thus serves as a natural platform for the refining of real-time mass spectrometry methods which can then be adopted in other fields.

Membrane inlet mass spectrometry (MIMS), the earliest technique for studying dissolved analytes with mass spectrometry, which remains widely used in environmental and bio-analytical applications, was also applied to electrochemistry early on [10]. In MIMS, the liquid testing environment is separated from the

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vacuum of the mass spectrometer by a semipermeable polymer membrane. To protect the vacuum, the membrane must be thick enough to prevent excessive permeation of the solvent, but as the analyte also must diffuse through the membrane, this slows the response time, generally up to several minutes [11]. A much faster response time was later achieved by the use of a porous polytetrafluoroethylene (PTFE) membrane [12], but the correspondingly higher flux of solvent and analyte across the membrane necessitated a differential pumping stage, forming the basis of differential electrochemical mass spectrometry (DEMS), where the term "differential" emphasizes that the mass spectrometer signal represents a snapshot of the analyte concentration at the membrane [13]. DEMS has since been developed extensively, particularly through the work of Helmut Baltruschat and coworkers [14–16], and has become a widely used method in electrocatalysis research [17–20]. DEMS has proven especially useful in fundamental electrochemical studies, for example comparing the product distribution of a Faradaic process on different crystal facets [21–23]. A notable variation on DEMS, termed on-line mass spectrometry (OLEMS), developed by Marc Koper and coworkers [24–26] and now used by several groups [27,28], involves a small PTFE vacuum inlet at the end of a glass tube as an EC-MS probe, scaled such that the flux to the mass spectrometer is sufficiently small that no differential pumping is needed.

Much of the development in DEMS the past three decades has focused on the cell that interfaces the electrochemical experiment and the vacuum inlet. In the original DEMS experiments, the working electrode was sputtered onto the PTFE membrane of the vacuum inlet [13], giving the fastest possible time response but complicating construction of the interface and restricting the materials that could be studied. The advent of a stagnant thin-layer cell [14] made it possible to perform DEMS on smooth electrodes, but effects of solvent evaporation made it difficult to perform experiments in a controlled environment. This was remedied by the advent of a dual thin-layer flow cell in which the working electrode and vacuum inlet are in separate compartments [29]. This dual thin-layer flow cell also served as a platform for combining DEMS with other analysis methods such as electronic quartz crystal microbalance [29] and attenuated total reflection-infrared spectroscopy [30], but always with stringent requirements on the working electrode. A subsequent modification made it possible to choose working electrodes of various sizes in DEMS, including single-crystals [31], a flexibility also offered by OLEMS, though with a less well-defined geometry for mass transport [24]. Another design of a dual-layer DEMS flow cell focused on the electrode geometry, incorporating a counter electrode parallel to and separated from the working electrode by a membrane, though requiring specialized electrode geometries [32].

Before describing the vacuum inlet system and electrochemical cell behind our new version of EC-MS, we wish to introduce a conceptual framework motivating their design. The three components of a standard quadrupole mass spectrometer (QMS): (1) electron impact ionization (EI), (2) quadrupole mass separation, and (3) detection by a secondary electron multiplier (SEM); all require high vacuum to operate. Above a pressure of approximately $p_v^0 = 10^{-6}$ mbar, mass spectra become less reproducible and signals no longer respond linearly with the amount of analyte [5]. This sets a maximum flux of molecules into the vacuum chamber of the mass spectrometer, dependent on the pumping speed. With the turbo pump used in this paper, which has a pumping speed of $S_{\text{pump}} = 50$ 1/s, representative of standard turbo pumps for compact vacuum systems, the maximum desired flux into the vacuum chamber is

$$\dot{n}_v^{\text{desired}} = \frac{1}{RT} p_v^0 S_{\text{pump}} \approx 2[\text{nmol/s}] , \tag{1}$$

where R is the gas constant and $T = 298.15$ K is the absolute temperature. Considerations of the SEM and the EI filament longevity also encourage a maximum flux not much higher than this value [33].

In comparison, the production rate of gaseous analytes (hydrogen evolution on platinum, for example) under typical laboratory conditions (current density of $j^{\text{expected}} = -1$ mA/cm^2 and electrode area of $A_{\text{el}} = 0.2$ cm^2) happens to be

$$\dot{n}_{\text{el}}^{\text{expected}} = \frac{1}{-2\mathcal{F}} j^{\text{expected}} A_{\text{el}} \approx 1[\text{nmol/s}] , \tag{2}$$

where $\mathcal{F}$ is Faraday's constant. In other words, the expected analyte production rate during conveniently-scaled electrochemistry experiments happens to be on the same order of magnitude as the allowable influx to the mass spectrometer of a conveniently-scaled vacuum system. This implies that it should be possible to have 100% *collection efficiency*, i.e. $\eta = 1$, while maintaining an arbitrarily fast time response. Accepting this framework, a clear drawback of both DEMS and OLEMS becomes clear. Since the porous Teflon membranes employed allow a significant amount of solvent evaporation, the analyte will only make up a small portion of the influx to vacuum, and so the influx of analyte to the mass spectrometer must be kept below $\dot{n}_v^{\text{desired}} \sim \dot{n}_{\text{el}}^{\text{expected}}$. This is done either by differential pumping, as in DEMS, lowering the *vacuum collection efficiency*, η_v; or by limiting the total influx to vacuum, as in OLEMS, lowering the *membrane collection efficiency*, η_m. Either way, the overall collection efficiency $\eta = \eta_m \eta_v$ is lowered. The use of a flow cell also lowers the membrane collection efficiency, as some analyte escapes in the downstream flow [15].

To give a sense of how $\dot{n}_v^{\text{desired}} \sim \dot{n}_{\text{el}}^{\text{expected}}$ compares to the expected magnitude of transient surface phenomena interesting for surface characterization and electrocatalysis, the number of surface atoms in $A_{\text{el}} = 0.2$ cm^2 of Pt (111) is about 3×10^{14}, or 0.5 nmol. A monolayer desorption event lasting on the order of a second thus corresponds to a flux on the same order of magnitude as $\dot{n}_v^{\text{desired}} \sim \dot{n}_{\text{el}}^{\text{expected}}$. We refer to the ability to resolve and quantify less than one monolayer of gaseous products on a scale of seconds as *sub-turnover resolution*. In this paper, we present technology enabling sub-turnover resolution for gaseous analytes with 100% collection efficiency, together with full and fast control of dissolved gases at the working electrode. We also present methods for accurate quantification with this system and demonstrate a predictive mass transport model. We anticipate that the technology and concepts presented here will serve as a platform for further improvements in EC-MS, and eventually for in-situ mass spectrometry in other fields as well.

2. Technical

2.1. Membrane chip

Our strategy for achieving a fast and lossless transfer of dissolved gases from the liquid of the test environment to the high vacuum needed for mass spectrometry takes place in two steps. First, the liquid equilibrates across a perforated membrane with a microscopic gas-phase *sampling volume*, allowing any dissolved gases near the membrane to quickly evaporate. Second, gas in this sampling volume is continuously transported through a capillary to the vacuum chamber of the mass spectrometer. The membrane,