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Electrochemical Mass Spectroscopy for In-situ Liquid Phase Electron Microscopy

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Electrochemical energy devices convert small molecules in the atmosphere into higher-value products by coupling to renewable energy [1]. Electrocatalysts play a key role during those procedures as they can greatly promote the conversion process. Generally, the electrocatalyst performance, namely activity, durability, and selectivity, is determined by the structural parameters such as phase structure, size, exposed facets, chemical composition, microstrain, etc. Currently, various chemical and physical routes are well established to fine tune the above parameters and thus optimise the catalytic performance [2]. However, the electrocatalysts are subjected to dynamical change under working conditions. Real-time study of the structural dynamics of electrocatalysts and correlating it with the electrochemical performance are crucial to understanding the degradation mechanism and design advanced catalysts.

Liquid phase electron microscopy (LPEM) based on MEMS sample carriers provides the means to study the evolution of electrocatalysts morphology at the nanoscale with sub-microsecond scale temporal resolution [3, 4]. The electrochemical stimuli can be correlated with the observed structural changes, making operando studies possible. Until now, LPEM has mainly been used to study the structural dynamics, which is of importance to evaluate the electrocatalytic stability. Qualitative/quantitative analysis of the products during electrochemical reactions is highly desirable to fully understand the real-time chemical/electrochemical events as well as to judge the selectivity of the reactions [4]. Nevertheless, it is still a challenge to realize such analysis in the current available LPEM systems using an online mass spectrum method.

In this work, we successfully integrate the Stream Liquid Biasing system with the Si-microchip-based Electrochemical Mass Spectrometer [5]. Thanks to the on-chip flow capability of the Stream Nano-Cell [6, 7], the molecules generated in the Nano-Cell can be effectively delivered to and then captured by the mass spectrometer. As a proof of the concept, we employ hydrogen evolution reaction catalyzed by polycrystalline platinum electrode. The results show that the reaction products (hydrogen gas) can be directly detected and correlated with the electrochemical parameters. The liquid flow rate affects the product detection due to the mass transport in the liquid reaction and detection systems, including Nano-Cell, liquid tubing, and the MS cell. A direct flow control at the sample area is of vital importance for the product detection and MS performance. The time delay should be considered and calibrated to further evaluate the anticipated analyte collection rate based on the current measurement from the sample to the measured mass spectrometer signal. The current technique paves a new way to directly observe the structure-performance correlation of electrocatalysts under the real working conditions [8].

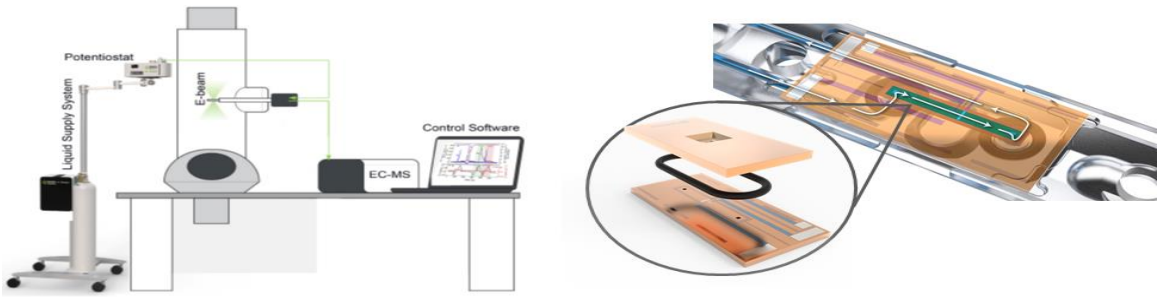

Figure 1. (Left) Schematic overview of the integrated Stream LPEM-ECMS system. (Right) Render of the Stream liquid biasing holder with an inserted Nano-Cell and a flow path of the liquid; the top chip is made transparent for observation. The inset shows the bottom and the top chips of the Nano-Cell with an O-ring.

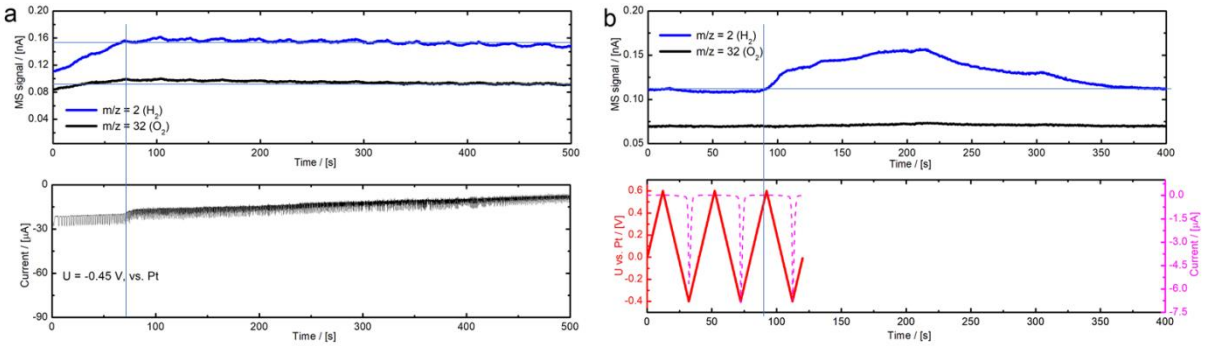

Figure 2. Real-time detecting the reaction products in the electrochemical electron microscopy system. (a) Demonstration of constant-potential (U = -0.45 V) electrolysis of water for 500 s. The lower panel shows the electrode current change versus time. The upper panel displays the ion currents for H_2 gas (m/z = 2, bule line) and O_2 gas (m/z =32, black line). (b) Demonstration of water electrolysis under cyclic voltammetry for 3 cycles with a potential range of -0.4 V to +0.6 V and a sweep rate of 100 mV s^{-1}. The lower panel shows electrode potential (red, left axis) and electrical current (magenta, right axis), while the upper one shows mass spectrometer signals for H_2 gas (m/z = 2, bule line) and O_2 gas (m/z =32, black line). The electrolyte of 0.5 M H_2SO_4 is flowed through the Nano-Cell and EC-MS with a rate of 8 uL min^{-1} by using the liquid supply system. All the potentials are shown vs. Pt pseudo-reference electrode.

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