ON-LINE DETECTION OF ELECTROCATALYTIC REACTION PRODUCTS: DIFFERENTIAL ELECTROCHEMICAL MASS SPECTROMETRY

Helmut Baltruschat

Institute of Physical and Theoretical Chemistry, Roemerstrasse 164, D-53117 Bonn, Germany
E-mail: baltruschat@uni-bonn.de

Volatile electrochemical reaction products can be detected on line by coupling a conventional mass spectrometer to the working electrode of an electrochemical cell, e.g. using the flow through cell shown in Figure 1. Using sufficiently fast pumping of the vacuum part, the partial pressure in the ion chamber and thus the ion currents are proportional to the flux $dn/dt$ of species into the vacuum chamber; this is the reason for the name "differential electrochemical mass spectrometry" (DEMS) [1]. The time constant for detection is only given by the time needed for convection and diffusion on the electrolyte side. Single crystal electrodes can be used. The use of small bead single crystals is also possible with the help of a new capillary inlet system.

The method cannot only be used for the qualitative identification of reaction products, but also for the quantitative evaluation of current efficiencies; this allows to gain information on side or parallel reactions. This will be demonstrated for the oxidation of methanol and ethanol at different catalyst surfaces. For ethanol, e.g., in some cases, the oxidation product is acetic acid, without formation of acetaldehyde as an intermediate. For the use in fuel cells, this is a problem, because acetic acid itself is not reactive. In other cases, acetaldehyde is the main product, which might slowly react further to CO$_2$. At room temperature, however, the current efficiency for CO$_2$ is negligible.

DEMS can also be used to characterize sub monolayer amounts of adsorbates on polycrystalline and single crystal electrode surfaces by means of their desorption. One possibility to achieve this is to oxidize a carbonaceous species to CO$_2$, which is quantitatively detected in the mass spectrometer. Many adsorbates can also be desorbed at certain potentials as such, or as the hydrogenated product, or by displacement with a second adsorbate, allowing a more direct characterization of the adsorbate.

The influence of the structure on the nano- and mesoscopic scale on electrocatalytic reactions will be demonstrated. In particular the role of monoatomic steps on reaction products is highlighted using vicinally stepped single crystal electrodes [2]. The role of co-catalysts for oxidation reactions is studied using ordered bi-metallic electrodes, which are obtained by decorating the steps of stepped single crystal surfaces. Decoration of steps of a Au crystal by Pd, on the other hand, leads to a regular arrangement of monoatomic rows of Pd atoms, onto which molecules can be adsorbed which would not adsorb on Au itself (cf. Figure 2).

Figure 1. Flow through cell for DEMS.

Figure 2. Model of Pd monoatomic rows at Au(332).

References