Chapter 11

Reaction pathways analysis and reaction intermediate detection via simultaneous DEMS and ATR-FTIRS

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ABSTRACT

A newly developed hyphenated technique, the combination of *in-situ* ATR-FTIRS, on-line DEMS, and electrochemical flow cell measurements, will be described and its potential for studies of electrocatalytic reactions relevant for fuel cell operation will be outlined. This method allows the simultaneous detection of adsorbed reaction intermediates (*in-situ* ATR-FTIRS), volatile reaction products (on-line DEMS) and the total Faradaic current (electrochemical measurements), at the same time, in a single experiment, under enforced and controlled electrolyte transport conditions. Important for kinetic studies, it also allows us to follow the adsorption process in electrolyte exchange transients at constant potential.

The potential of this method will be illustrated in different examples. CO uptake transients from CO containing electrolyte show the influence of the potential on the CO adsorption kinetics. Using isotope labeled CO, similar information can be obtained on CO_{ad} exchange, demonstrating rapid exchange for CO adsorbed on Pt even at room temperature. Third, adsorption/oxidation transients and potentiodynamic measurements of the oxidation of C_1 and C_2 molecules are presented and discussed, which illustrate the potential of this method for determining the dynamics, kinetics and mechanism of the adsorption and oxidation of small organic molecules, by combining the parallel information on the contributions of different reaction pathways (product analysis) and adsorbed reaction intermediates at different stages of the adsorption/reaction process and under different reaction conditions. Finally, future developments and prospects of this method will be outlined.

Keywords: Electrocatalysis, Adsorption Dynamics, Reaction Dynamics, Exchange, CO Adsorption, CO Oxidation, Formaldehyde Oxidation, Ethanol Oxidation, *in-situ* ATR-IR, DEMS

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