Mesoscopic Transport Effects in Electrocatalytic Reactions

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Transport effects may not only influence the rate of electrocatalytic reactions, but also the product distribution. The underlying effects were studied under well-defined reaction and transport conditions, using nanostructured Pt/glassy carbon electrodes, which consist of regular arrays of electrocatalytically active Pt nanostructures on a planar glassy carbon substrate. The effect of varying the density of the Pt nanostructures or the electrolyte flow rate on the reaction characteristics and product distribution was investigated for apparently simple electrocatalytic reactions such as CO oxidation, methanol oxidation or oxygen reduction. It is shown that reducing the Pt coverage leads to an increase of the relative amount of the reaction intermediates. Similar effects are obtained for increasing the electrolyte flow rate. The results are discussed on a molecular scale in terms of the ‘desorption – re-adsorption – reaction’ model which we had introduced recently (Y.E. Seidel et al., Faraday Discuss. \textbf{140}, 167 (2008)).

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