Observation of the Potential of Minimum Mass and Its Importance to Hydrogen Electrochemistry

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The electrochemical quartz-crystal nanobalance (EQCN) is a very sensitive research tool that can detect micro- and nanogram per cm² interfacial mass changes at the electrode surface although in many cases the data interpretation is complex [1,2]. The mass detection limit can be further enhanced by recording several mass vs. potential transients, under exactly the same experimental conditions and in the same potential limit, followed by their averaging and filtering. This way, the mass detection limit can be increased to ca. 1 ng cm^{-2} [3]. One can monitor minute mass changes associated with such interfacial phenomena as surface-oxide growth, hydrogen and anion adsorption. The Pt/H2SO4 system is often treated as a model one in surface-electrochemical research owing to its understanding. In this contribution, we report new results on the application of EQCN to research on the underpotential deposition of H (UPD H) and hydrogen generation. We perform an analysis of the interfacial mass responses of the Pt/aqueous H₂SO₄ system as a function of the applied potential and relate such gathered results to our knowledge of the Pt/aqueous H2SO4 interface. We present new data that demonstrate the interfacial mass changes brought about by the extension of the applied potential towards negative values (E $< E^{o}_{HER}$). They indicate that the interfacial mass passes through a local minimum at a potential that is different from the potential of zero total charge (*pztc*, where pztc ≈ 0.38 V [4]). This local mass minimum is referred to as the potential of minimum mass (pmm) and in the case of the Pt/0.5 M aqueous H_2SO_4 system pmm = 0.045 V. We interpret the results in terms of H_{UPD} adsorption on Pt, anion adsorption, Pt-water and Pt-H_{OPD}-H_2O interactions. The results show that the hydrophilic-hydrophobic properties of the Pt electrode are significantly modified by the H_{UPD} adsorption. Namely, the Pt electrode undergoes transition from a hydrophilic to a hydrophobic surface as H_{UPD} becomes adsorbed, thus modifying the Pt-H_{OPD} and Pt-H₂O interfacial interactions.

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