Microscopic Modeling of Current Spikes due to Phase Transitions at Electrode-Electrolyte Interfaces

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Underpotential deposition (UPD) is a phenomenon in which a metal ion deposits on a more noble metal electrode at more positive electric potentials than the one that causes bulk deposition. Thus UPD results in (sub)monolayer deposition. A sudden such deposition on a crystalline electrode is associated with a first-order phase transition at the electrode-electrolyte interface and is reflected in the associated voltammogram (the current versus voltage plot) as a sharp spike. We present a microscopic theory from which these voltammogram spikes can be obtained. We interpret a spike as a sum of the mutually shifted spikes of different heights and widths coming from the finite, differently sized and shaped crystalline domains formed on the electrode surface. Contrary to theoretical calculations using an infinite system or simulations using a small finite system, both of which give spikes much taller and narrower than the experimental ones, our theory has been applied successfully to fit the spikes in the voltammograms of the UPD of Cu on the (111) surface of a Pt or a Au electrode. A profound feature of the theory is that it provides explicit formulas relating the experimental parameters of a voltammogram spike (such as the area, position, height, and asymmetry) to the microscopic parameters of the statistical mechanical model used to simulate the deposition process. This can be used to gain, directly from experimental data, information about the phases and the transitions between them that are proposed to occur at the spike. This development is the object of our ongoing investigations.