Phase Transitions at Electrode-Electrolyte Interfaces Interpreted As a Result of Finite-Size Effects

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A sudden deposition of a metallic (sub) monolayer on a crystalline electrode during underpotential deposition is associated with a phase transition on the electrode surface. The transition results in a steep jump in the electrode coverage and in a sharp spike in the electrode current. We present a statistical mechanical theory that can be used to obtain the jumps and spikes due to a *first*-order phase transition, interpreting them as a result of finite-size effects. We apply our theory to fit theoretical jumps and spikes to experiment with very good precision. In addition, using experimental data, the theory can determine microscopic properties of the electrode surfaces (such as its pollycrystaline structure or the interaction strength of depositied particles) and the phases involved in the associated transitions.