

**Current Spikes Due to Phase Transitions at Electrode-Electrolyte Interfaces:  
Effects of Finite Size and Surface Inhomogeneity**

Igor Medved<sup>C, S</sup>

*Department of Physics, Constantine the Philosopher University, Nitra, Slovakia  
Department of Materials Engineering and Chemistry, Czech Technical University,  
Prague, Czech Republic  
imedved@ukf.sk*

We present a statistical mechanical description of the current spikes associated with first-order phase transitions exhibited during under potential deposition (UPD). The latter is a phenomenon in which a metal ion is deposited on a more noble metal electrode, thus resulting in monolayer (or just a submonolayer) deposition. If such a deposition is sudden, within a narrow voltage range, it is reflected in the current versus voltage plot as a sharp spike and can be interpreted as a first-order phase transition at the electrode-electrolyte interface. Using 2D lattice gases to model UPD processes, it turns out that a current spike resulting from a single crystalline domain (representing an electrode surface) is much taller and sharper than an experimental spike. Our key idea is to use the fact that real electrode surfaces are not monocrystalline but composed of a large number of finite crystalline domains. Therefore, we consider the currents from all domains and interpret an experimental spike as a sum of the domain spikes. Since the domains are energetically inhomogeneous and of different sizes, the domain spikes are mutually shifted and of different heights and widths. Consequently, their sum can produce a spike that is much smaller and broader than the one from a single domain and can be successfully used to model an experimental spike. We apply our results to fit the experimental current spikes for the UPD of Cu on the (111) surface of a Pt and an Au electrode.