

Hydrogen Evolution at a Single Supported Nanoparticle: Theoretical Analysis

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A first detailed theoretical analysis of the processes during proton reduction at a single supported Pd nanoparticle and subsequent detection of the evolved hydrogen by oxidation at an STM tip is presented [1]. Corresponding experiments have been recently performed as a local *in-situ* probe of nanoparticle reactivity [2,3]. The experimental method is illustrated in Fig.1.

A critical parameter of the suggested model is the rate of hydrogen desorption from the substrate surface. If this rate can keep up with the apparent reaction rates, the current transient will be determined by bulk diffusion of hydrogen in the electrolyte and by the kinetics of the tip reaction. However, if desorption rates are too small, adsorbed hydrogen will spillover from the Pd particle to the Au support. As the comparison to measured transients for different particle sizes reveals, the latter scenario is encountered for small particles (1 to 2 monolayers height) which exhibit high turnover rates and small desorption rates. In this case, a surface diffusion front will expand on the substrate surface, from where molecular hydrogen will be subsequently released. The substrate thereby provides a large area for the intermediate hydrogen storage. The fit of experimental data, Fig. 2, provides an estimate of the involved surface fraction and of the desorption rate from the support.

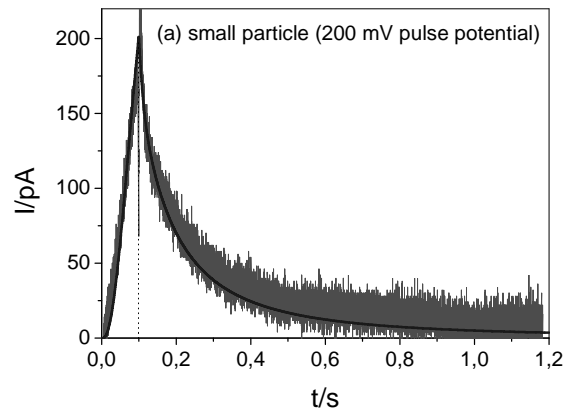


Fig. 2: Fit of experimental data (fluctuating curve) by the theory (smooth curve).

- [1] M. Eikerling, H. Kleine, J. Meier, and U. Stimming, *Z. Phys. Chem.*, accepted.
- [2] J. Meier, K.A. Friedrich, and U. Stimming, *Faraday Discuss.* **121**, 365 (2002).
- [3] J. Meier, J.K. Nørskov, and U. Stimming, in preparation.

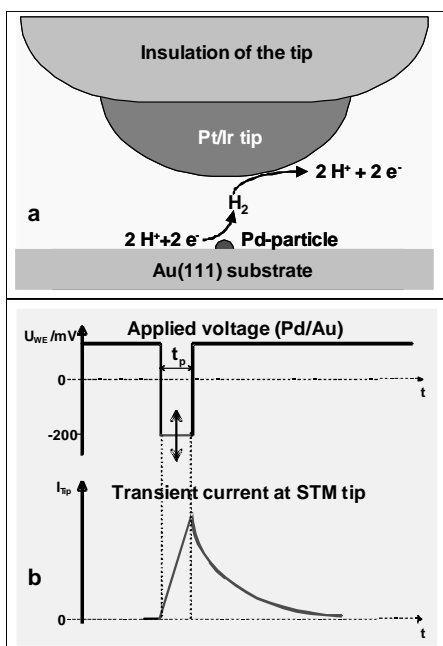


Fig. 1: Experimental method.