

Particle Size Effects in CO Monolayer Oxidation on Pt Nanoparticles - F. Maillard, M. Eikerling, O.V. Cherstiouk, E.R. Savinova, and U. Stimming (Technische Universitaet Muenchen)

It has been long recognized that catalytic and electrocatalytic properties of metal nanoparticles can differ dramatically from those of bulk materials (see e.g. [1] and refs. therein). We are however still far from a comprehensive understanding of how the size of a metal phase affects its electrochemical reactivity and even further away from being able to predict the reactivity of nanoparticles in various processes. Meanwhile, such a knowledge is vitally important for the development of the efficient electrocatalytic materials for various practical applications, including low temperature fuel cells, electrosynthesis and water remediation.

The present paper is aimed at the understanding of the relationships between the size of Pt nanoparticles and their electrocatalytic activity in CO monolayer oxidation. Anodic CO oxidation is a model electrochemical reaction of considerable practical relevance to proton exchange membrane fuel cells fed by reformat or methanol.

Over the past years an approach to prepare model Pt nanoparticles on non-porous carbon supports: glassy carbon (GC) and highly oriented pyrolytic graphite (HOPG) has been developed [2,3], which offers isolated Pt nanoparticles evenly distributed on the support surface. Armed with this experimental procedure, we explore CO monolayer oxidation at Pt nanoparticulated electrodes using stripping voltammetry, chronoamperometry and modelling.

We vary the Pt loading on the GC surface from 1.8 to 5.4 $\mu\text{g cm}^{-2}$ in order to change the square weighted mean particle size d from 1.7 ± 0.5 nm to 3.1 ± 1.2 nm.

We observe strong particle size effect in the CO monolayer oxidation for the particle size below 4 nm. This is demonstrated by the positive shift of the CO stripping peak and pronounced asymmetry and tailing of the current transients at constant potential towards longer time as the particle size decreases.

From the shape of the transients and weak dependence of the current relaxation on the electrode potential above the time of maximum for nanoparticles with $d < 3$ nm we conclude on the low mobility of CO_{ads} on the surface of small nanoparticles.

A mathematical model is proposed employing the active site concept in order to account for the experimental findings [4]. With a number of reasonable simplifications a full analytical solution is obtained, which allows a straightforward comparison of the theory with the experimental data. A good correspondence between experiment and theory is demonstrated. A single parameter controls the transition between reaction and diffusion limited regimes: the ratio between reaction rate times particle size and diffusion constant.

The model suggests restricted CO_{ads} mobility at Pt nanoparticles below ca. 3 nm size, with the diffusion

coefficient strongly dependent on the particle size, and indicates a transition towards fast diffusion when the particle size exceeds ca. 3 nm. The diffusion coefficient is estimated as $\sim 10^{-16}$ $\text{cm}^2 \text{s}^{-1}$ and $> 10^{-13}$ $\text{cm}^2 \text{s}^{-1}$ for ca. 2 nm and 3 nm nanoparticles respectively.

The average reaction rate per reactant site at the equilibrium potential is estimated as ca. 10^{-8} s^{-1} , which is in a good agreement with the value of the apparent intrinsic rate constant estimated by Koper et al for stepped Pt[n(111)x(111)] single crystals [5].

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