

Controlling electrocatalytic surface reactivity by lattice strain effects in de-alloyed Pt nanoparticles

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Introduction

Controlling the reactivity of catalytic surfaces is one of the most fundamental goals in catalysis research. In the area of electrocatalysis on multi-metal alloy surfaces, control of reactivity is achieved by bringing different metal atoms in atomic proximity; this proximity can cause electronic structure modifications of the surface atoms (electronic effects), geometric structure modifications of the surface atoms or ad-layers (geometric effects), or result in specific atomic ensembles with a specific functionalities (ensemble effects). All three fundamental effects modify the Gibbs energy of adsorption or activation of surface processes. Typically, when two or more metal atoms are in the top or second surface layer, electronic and geometric effects are strongly convoluted and not easy to separate.

The study of purely geometric effects on surface reactivity can be achieved by studying the reactivity of pure metals with varying amounts of lattice strain. Such an idealized material can be closely mimicked by particles consisting of a metal alloy core surrounded by a pure metal shell of varying interatomic distance (lattice strain). The preparation of such core shell structures with controlled amount of lattice strain in the metal shell has represented a big challenge.

Recently, our group has been developing an electrochemical de-alloying synthesis technique that enabled us to introduce controlled amounts of lattice strain into a pure Pt shell supported on a Pt-Cu alloy core. Catalytic reactivity measurements of the strained nanoparticles for technologically relevant reactions, such as the electroreduction of oxygen for hydrogen fuel cells, suggests that chemisorption energies of intermediate can be tuned by the amount of lattice strain of the Pt particles. A deliberate control of reactivity of such core-shell particles based on purely geometric effects has thus become possible.

Results and Discussion

We will report on the synthesis of lattice strain core-shell Pt particles by electrochemical de-alloying of base metal rich Pt alloy precursor electrocatalysts. Furthermore, we will discuss the theoretical basis of the de-alloying method and discuss the structure-activity-stability relationships of the resulting nanoparticles.

Specific alloy systems considered will be the Pt-Cu alloy system. We will present electrochemical Rotating Ring Disk Electrode (RRDE) activity measurements of de-alloyed Pt-Cu core shell particle catalyst and correlate these with synchrotron X-ray diffraction, X-ray

Photoemission, Small Angle X-ray scattering as well as SEM/EDX compositional data. XRD results suggest that the Pt-Pt interatomic distance of the de-alloyed Pt nanoparticles are shorter than normal, that is, that the Pt shell is in a state of compressive strain.

We will show experimental data that lattice strain Pt nanoparticles exhibit a previously unachieved activity improvement of about a factor of 5 compared to pure unstrained Pt for the electroreduction of oxygen in acidic electrolytes. This reaction occurs at the cathode of hydrogen fuel cells and is responsible for large portions of the power losses of a fuel cell. The most active alloy catalyst reported so far have shown activity improvements of about a factor of 3 compared to pure Pt.

In addition, a simple quantitative model for the average strain in core shell nanoparticles allowed us to estimate the lattice constant of the strained Pt shell quantitatively. Combining this with intrinsic Pt surface area based current density (kinetic activity) of the particle catalyst yielded volcano type reactivity curves.

We will also present DFT computational modeling results of the electrocatalytic surface reactivity of lattice strained Pt surfaces and compare these computational volcano curves to our experimental ones.

Significance

A new class of strained Pt core shell nanoparticles consisting of alloy cores and pure Pt shells have been synthesized and characterized for the electroreduction of oxygen. This class of electrocatalyst not only allows the study of purely geometric effects, which is usually difficult to study in surface alloys due to concurrent electronic modifications, but also showed previously unachieved activities for the oxygen catalysis. Since the identification of more active catalyst systems for this reaction is of prime importance in electrochemical energy conversion, these catalysts may potentially become very attractive in hydrogen PEMFC technology.

The notion of deliberate control of surface reactivity by lattice strain, combined with the synthetic strategy of introducing strain into metal lattices through rapid electrochemical de-alloying of certain selected sacrificial metals, may be relevant and of practical interest to tune the activity of other metals and catalytic reactions.