

Supporting Information for

Strain and Ligand Effects on the Catalytic Activity of Pt Alloys

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Pt-Ni/C alloy synthesis

Pt₃Ni alloy nanoparticles supported on carbon (Pt₃Ni/C) were synthesized using a wet impregnation method. The Pt/C (TEC150E, TKK) were dispersed in ultrapure water via magnetic stirring and sonication with an ultrasonic horn at 200 W. One minute of stirring followed by 5 minutes of sonication repeated three times was sufficient to fully disperse the catalyst. Upon obtaining a thoroughly mixed suspension, nickel nitrate hexahydrate, which was pre-dissolved in ultrapure water, was added in a 3:1 Pt to Ni stoichiometric ratio. Further mixing and sonication cycles were completed to ensure a homogeneous mixture and even dispersion of the nickel salt. The mixture was dried in a vacuum oven at 80 °C for 2-3 days.

The dry solids were recovered and ground into a fine powder as quickly as possible to reduce moisture uptake from the atmosphere. The precursor was subjected to a high temperature annealing protocol in a tube furnace (Lindberg/Blue M) to transform the sample from Pt particles coated with nickel nitrate into the desired Pt₃Ni alloy. During this process, the nickel salt was thermally decomposed, reducing Ni²⁺ to metallic nickel, and then the resulting mixture of Pt and Ni was alloyed. To complete this process, the temperature was ramped from room temperature to 400 °C over two hours while flowing 4% hydrogen in Ar. The temperature was held at 400 °C for 1 hour while purging with argon to prevent exposure to hydrogen at high temperatures, which would lead to sintering. After purging with Ar, the temperature was ramped to 800 °C in 1 hour and maintained for 4 hours in Ar.

Electrochemistry

Approximately 15 mg of Pt₃Ni/C were dispersed in a solvent consisting of 12 ml of water, 3 ml of isopropanol and 60 µl of 5% Nafion (Aldrich) by ultrasonic for 10 min. 10 µl of the suspension was deposited on the pre-cleaned glassy carbon substrate (RDE, Pine Instruments) and allowed to dry. Pt₃Ni//C was cycled between 0.05 and 1.2 V (vs RHE) for 20 cycles in a N₂ saturated 0.1 M HClO₄ solution. The extra Pt layers were deposited by galvanic displacement with Pt atoms of an underpotentially deposited (upd) Cu monolayer on the Pt₃Ni/C surface from a 50 mM H₂SO₄ + 50 mM CuSO₄ solution. The electrode covered with a Cu monolayer was rinsed and immersed in a 1.0 mM K₂PtCl₄ (Johnson Matthey) + 50 mM H₂SO₄ (GFS Chemicals) solution for about 2 min to displace the Cu with Pt. The catalysts with an extra Pt layer was rinsed with water and transferred into the electrochemical cell containing N₂ saturated 0.1 M HClO₄ solution. The catalysts were cycled between 0.05 and 1.2 V for 5 cycles at 100 mV/s and a final CV was recorded at 50 mV/s for ECA calculation. The oxygen reduction activity was measured in an oxygen saturated 0.1 M HClO₄ solution at 1600 rpm. This process was repeated on the electrode to increase the number of Pt layers and characterize their electrochemical behaviors. A reversible hydrogen electrode (RHE) was used as a reference electrode in the electrochemical measurement except in the Cu deposition, where an Ag/AgCl/KCl (3 M) leak-free electrode was used. All potentials are quoted with respect to the reversible hydrogen electrode (RHE). The kinetic currents for ORR at 0.9 V were calculated based on eq. 1:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} \quad (1)$$

where j and j_d are the measured current and limited current, respectively.

STEM characterization

The STEM EELS line scans were performed using a dedicated scanning transmission electron microscope, Hitachi HD2700C in the Center for Functional Nanomaterials. We have used a 1.3 Å probe with a current of 50~100 pA for EELS line scanning, which is a well-established method for detecting elemental distribution. [1,2] We have detected the Ni L_{2,3} edges (855 eV and 872 eV) and Pt M_{4,5} edges (2122 eV) from each EELS spectrum. After the alignment of the energy and background subtraction with the power law function, we have integrated signals with the energy windows of 850~1020 eV for Ni L_{2,3} edges and 2167~2357 eV for Pt M_{4,5} edges for their profiles. We have tested the results by using different energy windows for the integration. The EELS line-scan profiles of Ni and Pt were little affected by using different energy windows since we are interested in the relative distribution of Ni and Pt. The relative amounts of Ni and Pt are then normalized for their highest amount.

DFT calculations

Tetrahedral particle model with 6 nm radius was generated from the bulk-like geometric model of Pt₃Ni alloy and pure Pt, by (111) plane cleavages. The models with up to four outer layers of Pt were generated by replacing Ni atoms in those layers by Pt atoms. Then we allow for geometric relaxation of particles using molecular dynamics with embedded atom method (EAM) potentials method, until equilibrium is reached and calculated forces on each atom are practically zero. The reported strain is calculated

from these equilibrium particle geometries at the outer (111) facets on the particles. The strain is calculated with respect to pure Pt particle, namely $(\langle d \rangle_{NL} - \langle d \rangle_{Pt}) / \langle d \rangle_{Pt} \times 100\%$, where $\langle d \rangle_{NL}$ and $\langle d \rangle_{Pt}$ are average inter atomic distances in 111 facets of particles with N layers of Pt and pure Pt particle, respectively. Such optimized surface geometries of {111} facets, in particular relative changes in interatomic spacing, are used to construct smaller surface models for computation of the oxygen binding energies using a first principles approach. The first-principles calculations are based on spin-polarized DFT using a generalized gradient approximation (GGA) [3] and the projector augmented wave (PAW) method [4] as implemented in the Vienna Ab-Initio Simulation Package (VASP).[5] The cutoff energy for the plane wave basis set was 400 eV, and the Brillouin zone was sampled using a Monkhorst-Pack sampling technique [6] with a 5 x 5 x 1 k-point grid for surface calculations. For surface models 8-layer slabs with a 2 x 2 surface cell separated by a 14 Å vacuum layer perpendicular to the surface were used, preserving particle geometry features. The oxygen adsorption energy (E_{ads}) was calculated based on the equation $E_{ads} = E_{sub+O} - E_{sub} - 1/2E_{(O_2)}$ where E_{sub+O} , E_{sub} and $E_{(O_2)}$ represent the energy of substrate with adsorbed oxygen, the energy of substrate alone, the energy of oxygen molecule in the gas phase.

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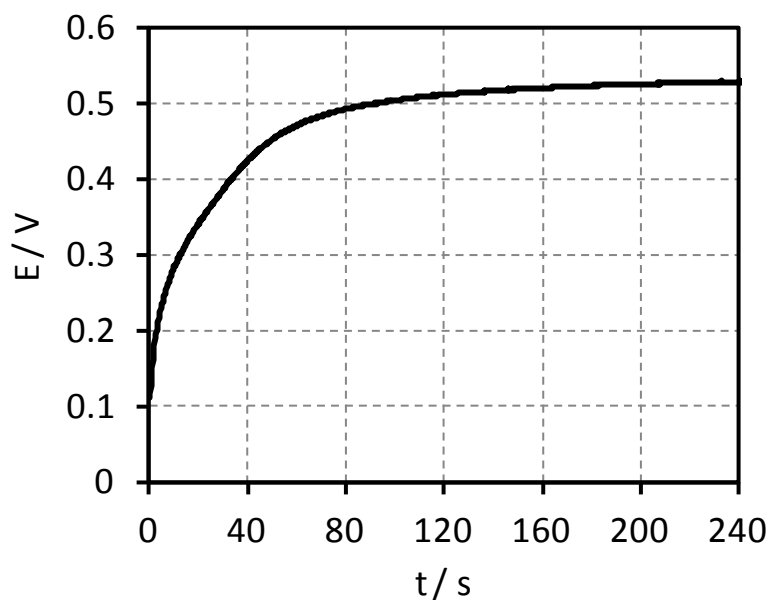


Figure S1. The open circuit potential (OCP) as a function of time during Cu-Pt displacement reaction in 1 mM K_2PtCl_4 + 50 mM H_2SO_4 solution. The potential is referred to Ag/AgCl.