Supporting Online Information

Dealloying of Cu₃Pt (111) Studied by Surface X-ray Scattering

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This supporting information contains:

Oxygen reduction reaction (ORR) electrocatalytic activity of dealloyed $Cu_3Pt(111)$ and comparison to that of pure polycrystalline Pt (Figures S1) as well as detailed electrochemical measurements.

Oxygen reduction reaction (ORR) electrocatalytic activity of dealloyed $Cu_3Pt(111)$ and comparison with that of pure polycrystalline Pt

The oxygen reduction activities of single crystal $Cu_3Pt(111)$ dealloyed at 700 mV (vs. Ag/AgCl, calibrated as 0.930 ±0.005 V vs. the reversible hydrogen electrode (RHE)) and polycrystalline pure Pt in 0.1 M $HClO_4$ are shown in Figure S1a. The currents were measured at a rotation speed of 1600 rpm and normalized by the geometric area. There is a positive shift of 78 mV in the half-wave potential of dealloyed $Cu_3Pt(111)$ as compared to pure Pt, which shows that dealloyed $Cu_3Pt(111)$ is more active than pure Pt. Cyclic voltammetry (CV) of dealloyed $Cu_3Pt(111)$ and pure Pt in Ar-saturated solution is shown in Figure S1b. The electrochemical surface areas (ECSA) of dealloyed $Cu_3Pt(111)$ and pure Pt were determined from the charge of H adsorption/desorption. The ECSA of dealloyed $Cu_3Pt(111)$ (6.24 cm^2) is about 17.8 times that of pure Pt (0.35 cm^2). The roughness factors (RF, ratio of ECSA to geometric surface area) for dealloyed $Cu_3Pt(111)$ is 12.4, which shows that a very rough surface is formed on dealloyed $Cu_3Pt(111)$ due to leaching of Cu.

The details of ORR electrocatalytic activity measurements are described below.

Electrochemical measurements

After surface X-ray scattering measurement, single crystal $Cu_3Pt(111)$ dealloyed at 700 mV (vs. Ag/AgCl) was cleaned by ultrapure water and was transferred to the disk of a rotating disk electrode assembly as described in Ref 1. Briefly, the single crystal sample was protected by a drop of ultrapure water and placed face down on a polypropylene film covered with a thin film of water. Then it was mounted to the disk position of an insertable rotating disk electrode assembly (Pine Instruments) and subsequently immersed into 0.1 M $HClO_4$ solution under a potential control of 0.050 V (vs. RHE) in a electrochemical cell. The electrochemical measurements were conducted in a standard three-electrode

electrochemical cell at room temperature. A Pt-foil was used as the counter electrode, and a Ag/AgCl reference electrode was used in a double-junction reference chamber. The potential of the Ag/AgCl reference electrode was calibrated versus RHE. All potentials reported in this electrochemical catalytic study refer to that of RHE in order to compare our results with others reported. The electrolyte was 0.1 M $HClO_4$ solution prepared from double-distilled $HClO_4$ (70%, Sigma Aldrich) and ultrapure water (Millipore, 18.2 MΩ cm). Pure polycrystalline Pt electrode (Pine Instruments) was measured for comparison. The geometrical surface area of $Cu_3Pt(111)$ disk electrode and pure Pt electrode exposed to the electrolyte was 0.503 cm^2 and 0.196 cm^2, respectively. The working electrode potential was controlled with a potentiostat (Gamry Instruments, Reference 600).

The electrolyte was deaerated by purging high-purity Ar gas into the electrolyte for at least 30 mins before electrochemical measurement. Cyclic voltammetry (CV) with a scan rate of 50 mV/s was collected on the dealloyed single crystal $Cu_3Pt(111)$ and pure Pt sample to determine the platinum electrochemical surface area (ECSA). The platinum ECSA was determined by the mean integral charge of the hydrogen adsorption and desorption regions after double-layer correction and using 210 μC.cm$^{-2}_{Pt}$ as the conversion factor assuming 1 H atom is adsorbed to 1 Pt atom. The roughness factor (RF) was obtained from the ratio of ECSA to the geometric surface area (SA$_{geometric}$, 0.503 cm^2 for $Cu_3Pt(111)$ and 0.196 cm^2 for polycrystalline Pt)

$$RF = ECSA/SA_{geometric} \tag{1}$$

The oxygen reduction reaction (ORR) electrocatalytic activity of the dealloyed $Cu_3Pt(111)$ and pure Pt was studied with RDE using a rotator (AFMSRX, Pine Instruments). The electrolyte was purged with high-purity O_2 gas for at least 30 mins to ensure O_2 saturation. Linear sweep voltammetry (LSV) measurements during oxygen reduction were performed in O_2-saturated 0.1 M $HClO_4$ by sweeping the potential from 0.05 V anodically to 1.0 V at 20 mV·s^{-1} with the electrode rotated at 400, 900, 1600 and

2500 rpm and O_2 gas purged into the solution at a rate of 1 L·min^{-1} through a 2 μm fritted tube (Ace Glass). The ORR polarization curves recorded from LSV measurements on both dealloyed $Cu_3Pt(111)$ and pure Pt at different rotation speeds all reached well-defined diffusion limiting currents (see the typical ORR polarization curves for dealloyed $Cu_3Pt(111)$ and pure Pt recorded at 1600 rpm in Figure S1). The faradaic current density, i.e., the current due to the oxygen reduction alone, was obtained by subtracting the capacitive current (the current measured from the CV under Ar) from the ORR data and then normalized by the geometric surface area (SA_{geo}),

$$j = -(j_{ORR} - j_{capacitive,Ar-CV})/SA_{geo} \tag{2}$$

The kinetic current density for the ORR was derived from the Koutecky-Levich equation:

$$1/j = 1/j_k + 1/j_d = 1/j_k + 1/(B\omega^{1/2}) \tag{3}$$

where j is the measured disk current density; j_k and j_d are the kinetic and diffusion limiting current densities, respectively; ω is the electrode rotation speed; B is a constant (determined from the slope of Koutecky-Levich plots), $B = 0.62nFD_{O_2}^{2/3}\upsilon^{-1/6}C_{O_2}$ where D_{O_2} is the diffusion coefficient of O_2 ($D_{O_2} = 1.93 \times 10^{-5}$ cm^2 s^{-1}), υ is the kinetic viscosity of the solution ($\upsilon = 1.009 \times 10^{-2}$ cm^2 s^{-1}), C_{O_2} is the concentration of O_2 dissolved in electrolyte ($C_{O_2} = 1.26 \times 10^{-3}$ mol L^{-1})[1,2], F is the Faraday constant, and n is the apparent number of electrons transferred in the reaction. The kinetic current density (normalized by the geometric surface area) was divided by the RF factor to obtain the ECSA normalized kinetic current density

$$j_{s,Pt} = j_k/RF \tag{4}$$

The ohmic resistances in the electrode contacts and electrolyte solution were assumed to be the same for dealloyed $Cu_3Pt(111)$ and pure Pt and were not included in the corrections. The specific activity was established from the ECSA normalized kinetic current density.

It should be noted that the measurements of ORR activity and CV are very fast (about 50 s for ORR activity and 40s for CV); thus, any additional dealloying of $Cu_3Pt(111)$ is negligible and can be ignored.

Referecnes

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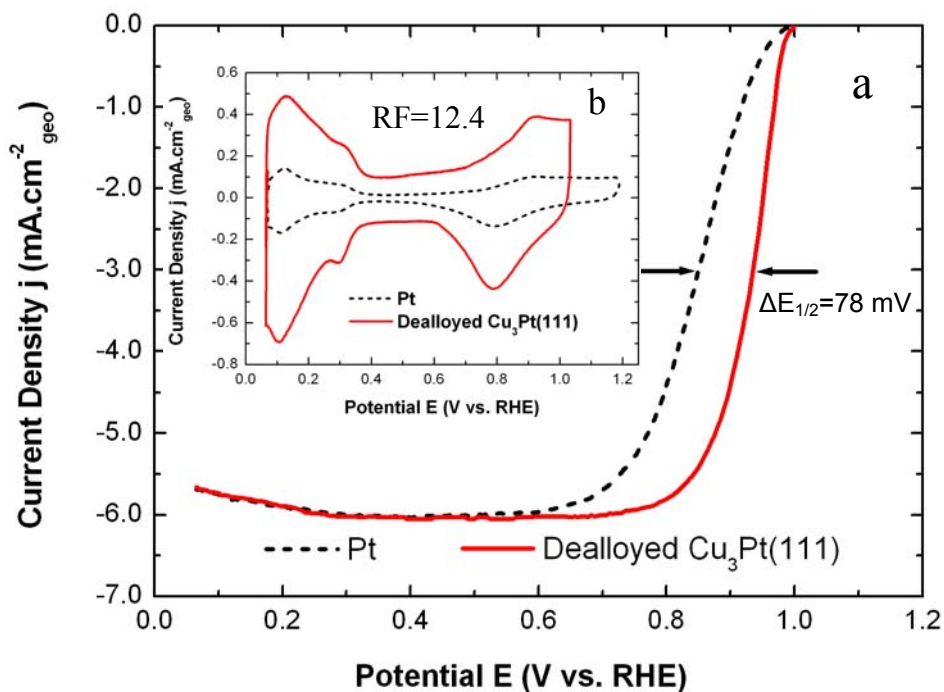2. Lide, D.R. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL,1995

Figure S1. a) Oxygen reduction currents measured on dealloyed $Cu_3Pt(111)$ and polycrystalline Pt at a rotation speed of 1600 rpm. Experiments were conducted in O_2-saturated 0.1 M $HClO_4$ at 298 K with a sweep rate of 20 mV/s. Arrows indicate the shift of half-wave potential between ORR polarization curves measured on dealloyed $Cu_3Pt(111)$ and polycrystalline Pt; b) Cyclic voltammetry of dealloyed $Cu_3Pt(111)$ and polycrystalline Pt. Experiments were conducted in Ar-saturated 0.1 M $HClO_4$ at 298 K with a sweep rate of 50 mV/s. $Cu_3Pt(111)$ was dealloyed at 700 mV (vs. Ag/AgCl, calibrated as 0.930 $\pm$ 0.005V vs.RHE).