

Effects of Lattice Strain on Activities of Pt-alloy Electrocatalysts for PEMFC

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Introduction

Polymer Electrolyte Membrane fuel cells (PEMFC), a type of hydrogen fuel cells that runs at relatively low temperatures, convert chemical energy of a fuel directly into electrical energy with high efficiency and low emission. The conversion is catalyzed by noble metal catalysts at the anode and cathode of a PEMFC. At present, pure platinum is the most commonly used electrocatalyst materials for PEMFC. Pt alloys have shown activity improvements of up to 3 times over pure Pt. However, for fuel cells to be commercially feasible, the catalyst activity needs to be improved further by at least a factor of 4 times over pure Pt and need to maintain these activities over sustained periods of time. To design and discover catalyst with the required activity characteristics, we started by understanding the fundamental structure-activity relationships of binary and ternary Pt alloys as well as their activity-stability relationships. Electrocatalytic mass and specific activities were measured using rotating-ring-disk-electrode method while changes in catalytic particle composition, uniformity and size distribution before and after electrochemical testing were obtained using Energy Dispersive Spectroscopy (EDS), and X-ray Diffraction (XRD).

Materials and Methods

Catalysts were synthesized via the impregnation-freeze drying route using liquid Cu precursors and Pt/carbon electrocatalysts of about 30 wt% Pt. Cyclic voltammetry (CV) was conducted to determine catalyst surface areas. Linear sweep voltammetry (LSV) was conducted by sweeping the potential from 0.06 V to open circuit potential at a scan rate of 5 mV/s. The currents measured were corrected for mass-transport interference. Mass and specific activities were established at 900 mV /RHE. Energy Dispersive X-ray Spectroscopy (EDS) analysis, using JEOL JSM 6330F field emission SEM, was performed on catalysts before and after electrochemical analysis. Laboratory-source X-ray Diffraction (XRD) was conducted using a Siemens D5000 ($\theta / 2\theta$) Diffractometer (Bragg Brentano configuration, Cu K α source) equipped with a Braun Position Sensitive Detector (PSD). Synchrotron based XRD was conducted at SSRL. Composition estimates of the multiple phases of disordered face-centered cubic (FCC) were based on Vegard's law.

Results and Discussion

We will present structure-activity-stability relationships of Pt-Co and Pt-Cu binary electrocatalysts. For the former, we were able to identify the effects of ordering on the activity and stability of Pt-Co alloy phases. We found that ordered face center tetragonal Pt-Co phases

were more corrosion stable but less active for the electroreduction of oxygen than disordered face centered cubic ones.

For the latter, multiple phases and smaller particle sizes were observed when catalysts were annealed at 600 °C while single phase and larger particle sizes were seen in those annealed at 950 °C. Figure 1 shows the XRD profile of a PtCu alloy catalyst, annealed at 950 °C. In the figure, a shift in the main reflection of the PtCu alloy from profile (B) to (C) indicated Cu dissolution during electrochemical measurement. The de-alloying process created highly active Pt nanoparticle electrocatalysts. It was observed that de-alloying of base metal rich phases generally resulted in more active de-alloyed particles compared to base metal deficient ones. Comparing the compositional data from XRD with that from EDS suggested the presence of lattice strain in the catalysts upon base-metal dissolution. The presence of strain was further confirmed when they were subsequently relaxed by further annealing at higher temperatures. As shown in Figure 1, a shift in the main reflection of the PtCu alloy from (C) to (D) indicated strain relieve in the catalyst. Our experimental findings together with preliminary Density Function Theory (DFT) computations from our collaborator indicated that compressive lattice strain improves the electrocatalytic surface reactivity of Pt.

Significance

We are one of the first groups to have studied the structural changes of individual crystallographic alloy phase before and after electrochemical testing to such great detail. The use of synchrotron-based XRD also allowed us greater flexibility in the incident energy used. Furthermore, lattice strained Pt nanoparticle exhibited activities for electroreduction of oxygen which were previously unachieved. Finally, the combination of experimental and computational DFT data is a powerful approach for the relational design and discovery of improved fuel cell electrocatalysts.

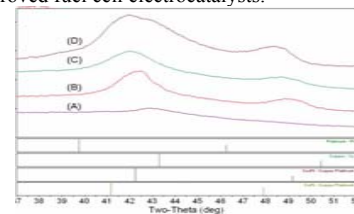


Figure 1. XRD data for PtCu (950°C) before and after electrochemical testing A) Background, B) PtCu powder, C) PtCu after electrochemical measurement, D) The same PtCu catalyst having been re-annealed after electrochemical measurement.

References

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