Theoretically Relating the Surface Composition of Pt Alloys to Their Performance as the Electrocatalysts of Low-Temperature Fuel Cells

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Objectives

The main goal of this project is to gain fundamental knowledge about the relation between surface composition and catalytic performance of Pt alloy catalysts for oxygen reduction reactions (ORR).

Specific objective 1: Develop and improve a first-principles based multiscale computation approach to simulating surface segregation phenomena in Pt alloy surfaces.

Specific objective 2: Evaluate the surface electronic structure and catalytic activity of Pt alloy catalysts.

Specific objective 3: Relate the surface composition to the catalytic performance of Pt alloy catalysts.

Technical Barriers

To accomplish the research objectives, the PI needs to develop the modified embedded atom method atomic interaction potentials for Pt alloys, improve the atomistic Monte Carlo simulation method for simulating surface segregation process in Pt alloys, perform the density functional theory transition state calculations to determine the reaction energetics of the ORR on Pt alloy surfaces, and develop kinetic Monte Carlo simulation codes to evaluate the rate of the ORR on the Pt alloy catalysts.

Abstract

The project was launched on September 15, 2009. Over the grant period, we have accomplished all the research objectives proposed in the proposal. Specifically, we have developed and performed Monte Carlo (MC) simulations predicting the surface composition of a series of Pt binary and ternary alloy catalysts, carried out first-principles transition state calculations of the ORR on Pt and Pt alloy surfaces, developed and performed kinetic Monte Carlo (KMC) simulations predicting the activity for the ORR on Pt surfaces, and derived the relation between surface composition and catalytic activity for the ORR on Pt alloys. As a result of our study, ten research articles supported by this grant have been published in peer-reviewed journals.

Progress Report

Monte Carlo simulations on surface segregation in Pt alloys

Supported by this grant, my research group has successfully developed the modified embedded atom method (MEAM) atomic interaction potentials for Pt-Ni, Pt-Re, Pt-Mo, Pt-Co, Pt-Ti, Pt-Fe, Pt-Pd, Pt-V, Pt-Au, and Pt-Mn binary alloys and Pt-Ni-Co, Pt-Ni-Fe, and Pt-Pd-Ni ternary alloys. Furthermore, we performed the Metropolis Monte Carlo (MC) simulations to accurately predict the surface segregation phenomena and surface composition profiles in these Pt alloys after annealing in vacuum. In Fig. 1, we show the predicted surface composition profiles of three representative alloys using the developed MEAM potentials and the MC simulation method. For ordered Pt3Ti alloys (Fig. 1(b)), the Pt concentration in the outermost (111) surface layer exhibits an abrupt change around the stoichiometric composition (75 at.% of Pt) and reaches 100 at.% even if the bulk Pt concentration is just slightly above 75 at.%. In the annealed Pt-Ni (111) surface (Fig. 1(c)), the surface Pt concentration varies in an oscillatory fashion from the outermost surface layer to the bulk material and Pt enriches the outermost layer. Fig. 1(d) shows that the surface Pt concentration varies gradually with increasing Pt in the annealed Pt-Pd (111) surface and Pd will enrich the outermost surface layer. Our theoretical predictions are in excellent agreement with available experimental data.

Density functional theory transition state calculations of ORRs on the surfaces of Pt catalysts

In this project, we examined the influence of both ligand effect and structure effect on the reaction energetics of the ORRs on Pt-based electrocatalysts. To this end, we calculated the reaction energetics (including surface adsorption energy, heat of reaction, and activation energy) of the ORRs on Pt(111), Pt/Ni(111), Pt(100), and Pt/Ni(100) surfaces using the DFT method. With the DFT structure optimization calculations, we first identified the most stable sites for the seven ORR intermediates adsorbed on the Pt and Pt/Ni

(a)

(b)

(c)

(d)
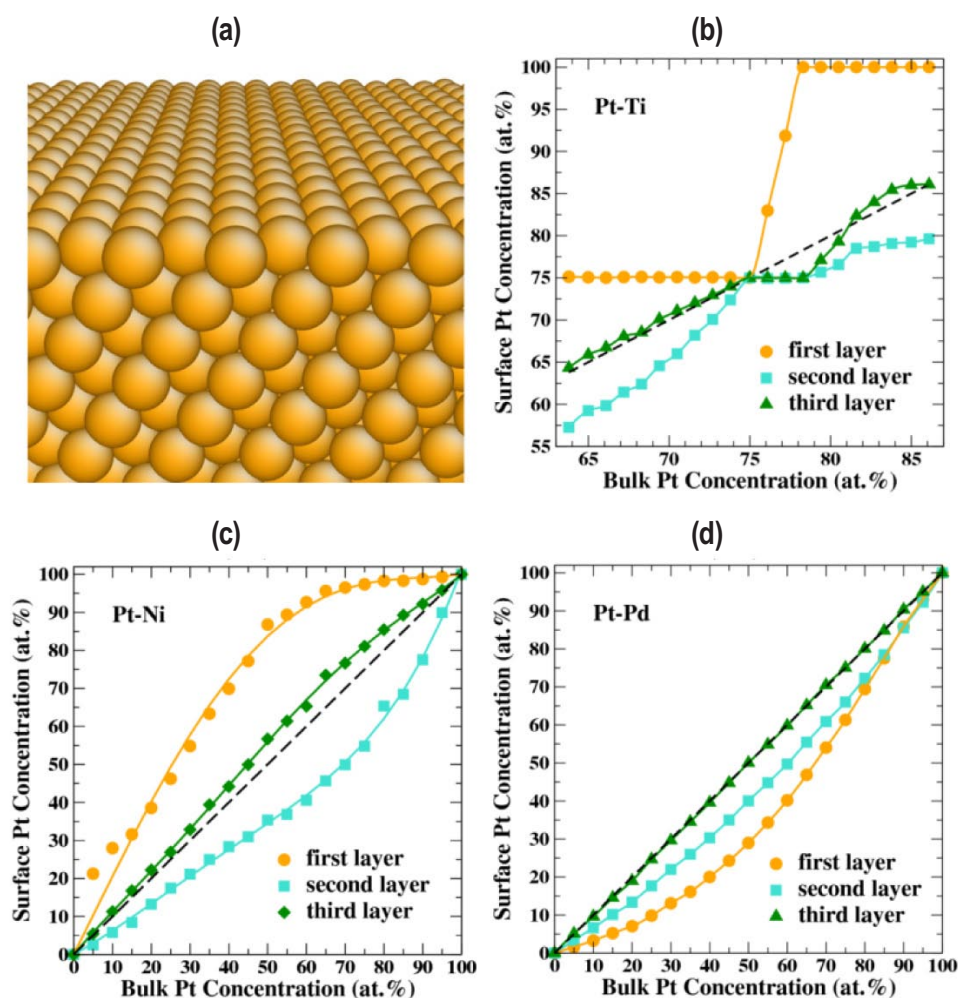
FIGURE 1. (a) Atomistic structure of the (111) surface of alloys with face-centered cubic lattice. Predicted chemical composition (expressed in atomic concentration of Pt) in the three outermost layers of the annealed fcc (111) surface of (b) Pt-Ti, (c) Pt-Ni, and (d) Pt-Pd alloys. In (b), (c), and (d), the black dashed lines indicate where surface compositions are equal to overall bulk compositions.

surfaces. Then, we constructed the initial and final states of various ORR elementary steps on the Pt and Pt/Ni surfaces using these lowest-energy configurations and determined the corresponding transition states using the climbing image nudged elastic band method. In Fig. 2, we show the atomic structures for the ORR elementary steps on the Pt(100) surface attained in our DFT calculations. Furthermore, we calculated heat of reaction and activation energy for all the elementary steps of the ORRs on the Pt(111), Pt/Ni(111), Pt(100), and Pt/Ni(100) surfaces. In this study, we predicted that the rate-determining step for the ORR is the OH hydrogenation reaction with activation energy of 0.80 eV on the Pt (100) surface, the O hydrogenation reaction with activation energy of 0.79 eV on the Pt (111) surface, the OH hydrogenation reaction with activation energy of 0.79 eV on the Pt/Ni (100) surface, and the O2 hydrogenation reaction with activation energy of 0.15 eV on the Pt/Ni (111) surface. Since a low activation energy for the rate-determining step

leads to high activity for the ORRs, our DFT results suggest that the catalytic activity for the ORR would be slightly higher on the Pt/Ni (100) than that on the Pt (100) surface, would be reasonably higher on the Pt (111) than that on the Pt (100) surface, and would be much higher on the Pt/Ni (111) than that on the Pt (111) surface. Our theoretical study provides a quantitative explanation to the experimentally measured trend of the ORR activity on the Pt and Pt-Ni (111) and (100) single crystals.

Correlation between surface composition of Pt alloys and catalytic activity for ORR

Supported by this grant, my research group has made great effort to establish the relationship between the surface chemical composition and the ORR activity of Pt alloy catalysts using both the first-principles DFT transition state calculation method and the kinetic Monte Carlo (KMC) method. In this research, we focused on studying the rate of
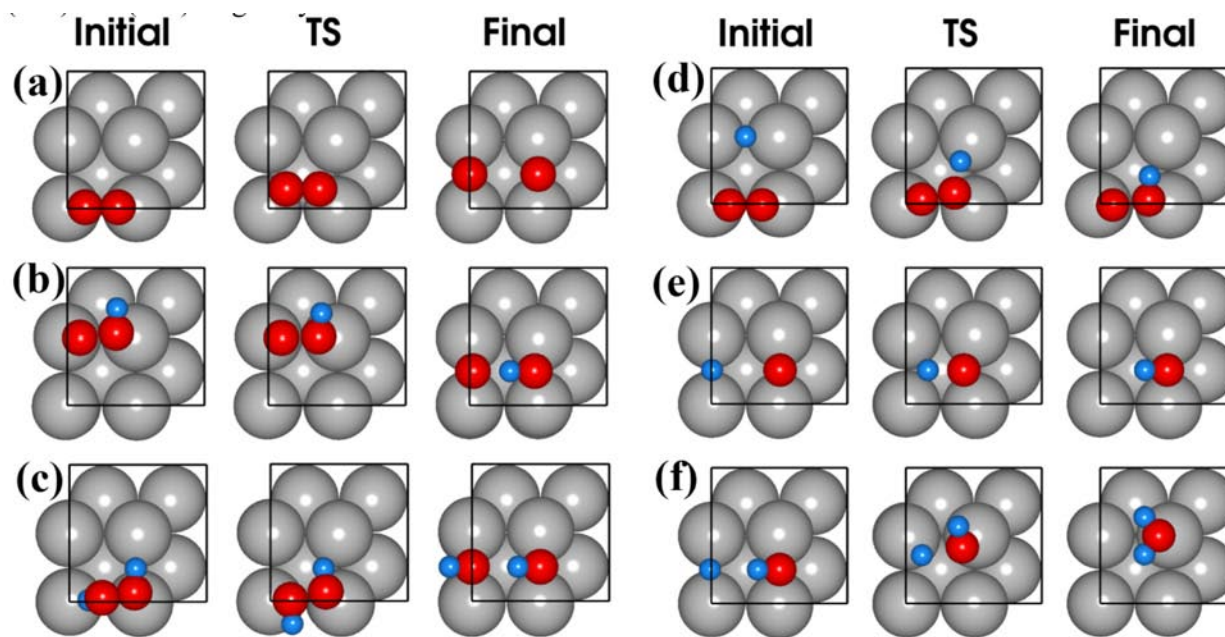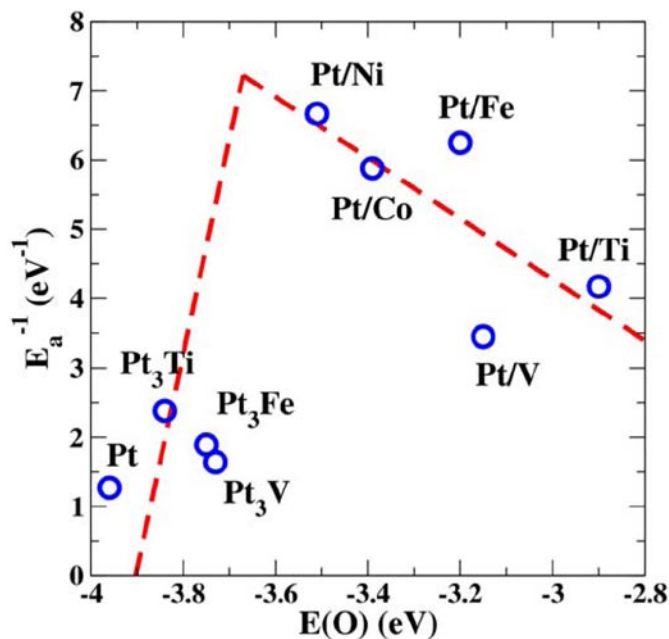
FIGURE 2. Atomic structures of the initial state, transition state, and final state for (a) O2 dissociation reaction, (b) OOH dissociation reaction, (c) H2O2 dissociation reaction, (d) O2 hydrogenation reaction, (e) O hydrogenation reaction, and (f) OH hydrogenation reaction on Pt (100) surface. In the figure, gray balls represent Pt atoms, red balls represent O atoms, and blue balls represent H atoms, respectively.

the ORRs on Pt-skin Pt-TM alloy (111) surfaces. Here, TM refers to transition metal element Ti, V, Fe, Co, and Ni. To this end, we determined all the surface adsorption energies, heats of reaction, and activation energies related to the ORRs on the Pt-TM alloy surfaces using the DFT calculation method. From our DFT data of activation energies, we have found that the ORR will favorably follow the peroxyl dissociation mechanism on the Pt and Pt3Fe (111) surfaces but adopt the peroxide dissociation mechanism on the Pt/Ti, Pt/V, Pt/Fe, Pt/V, Pt/Ni, Pt3Ti, and Pt3V (111) surfaces. For each modeled Pt catalyst surface, we found the activation energy for the rate determining step (denoted as "Ea"), which has the highest activation energy among all the elementary reaction steps within the preferred mechanism, of the ORR following the most preferable mechanism. Conceivably, the lower the value of Ea is, the higher the rate of the ORR would be. Consequently, we plotted in Fig. 3 the reciprocal value of Ea as a function of oxygen (O) binding energy on the Pt-based catalyst surfaces. In this way, we correlate the catalytic activity for the ORR with the surface electronic structure of the Pt-based catalysts.

FIGURE 3. Plot of calculated activity (1/Ea) for ORR as a function of O binding energy on Pt-based electrocatalyst surfaces.

Future Directions

As a continuation of this grant, the PI will investigate the metal dissolution process, Ostwald ripening, and coalescence sintering processes, and the adsorbate-induced surface segregation process of Pt-based catalysts using atomistic simulation techniques. Moreover, the PI will

theoretically correlate the change in metallic catalyst surface (such as, structure and composition) with the change in catalytic activity for electrochemical reactions related to renewable energy technology. In particular, we will simulate the structure evolution in Pt and Pt alloy nanoparticles

with diameters ranging from 1.5 nm (about 200 atoms) to 10 nm (about 30000 atoms) using the MEAM atomic interaction potentials, which are capable of accurately describing the surface and bulk structures of the catalysts. The structure evolution of metal catalysts is influenced by many interplaying effects (such as surface composition, crystal structure, morphology, particle shape, particle size, surface adsorbate, gas partial pressure, and temperature) and is closely related to the performance (such as activity and durability) of the catalysts. Consequently, this study is expected to fill the existing gap in our knowledge on how to better design and fabricate metallic catalysts in order to ensure their long-term catalytic activity.

Publication list (including patents) acknowledging the DOE grant or contract

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