FINAL REPORT

Project Title:

SISGR: Theoretically relating the surface composition of Pt alloys to their performance as the electrocatalysts of low-temperature fuel cells

DOE Grant Number: USDOE DE-FG02-09ER16093

Project Personnel:

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Yearly Budget: \$220 K.

Period of Execution: September 15, 2009 to December 30, 2010

Year it Started: 2009

Research Goals and Specific 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 reaction (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.

Significant Achievements and Results: The project was launched on September 15, 2009. The research progress includes the development of the modified embedded atom method (MEAM) potentials for Pt-Co, Pt-Ti, Pt-Fe, and Pt-V bimetallic alloys, the Monte Carlo (MC) simulations of surface segregation phenomena in the (111) surfaces of (disordered) Pt-Ni, (disordered) Pt-Co, and (ordered) Pt-Ti alloys, the density functional theory (DFT) study of the transition states of ORR on pure Pt (111) and Pt-segregated Pt₃Ni, Pt₃Co, and Pt₃Fe (111) surfaces, and the DFT study of the effect of a third transition metal element on Pt surface segregation in Pt₃Ni and Pt₃Co (111) surfaces. The significant research achievements are: (a) we clearly explained how Pt atoms segregate to the outermost layer of ordered Pt₃Ti (111) surfaces combining both DFT and MC computation methods. Further, we found from DFT calculations that the Pt-segregated Pt₃Ti (111) surface could have better catalytic activity for ORR than pure Pt (111); (b) through extensive DFT calculations, we identified that as a third alloy component elements V, Cr, Co, Mo, Tc, Ru, W, Re, Os and Ir would further improve Pt surface segregation in the Pt₃Ni (111), and elements Ru, and Os would further improve Pt surface segregation in the Pt₃Co (111). At this moment, one manuscript (about surface segregation in Pt₃Ti (111)) has been submitted for review and three more manuscripts are expected to be submitted in this summer.

DOE Interests: A fundamental understanding of the relation between the surface composition and the catalytic activity for ORR of Pt alloys is important for developing low-cost, high-performance, and long-durability electro-electrodes for polymer electrolyte membrane fuel cells. This theoretical investigation is capable of providing guiding principles for the design and synthesis of multi-component Pt alloy catalysts. Moreover, the computational techniques developed in this project and the insights gained into the correlation of surface composition and surface electronic structures can be extended to study alloy catalysts for other chemical reactions and energy applications.

PROGRESS REPORT

Results Description

1. Develop modified embedded atom method potentials for Pt bimetallic alloys

Prior to this grant, I have developed modified embedded atom method (MEAM) potentials for Pt-Ni, Pt-Re, and Pt-Mo alloys. The developed potentials have been successfully used to predict the surface segregation phenomena in those alloys. Supported by this grant, my research group further developed the MEAM potentials for Pt-Co, Pt-Ti, Pt-Fe, and Pt-V alloys aiming at accurately predicting the surface segregation phenomena in those four Pt bimetallic alloys. In below, I list the calculated material properties using our developed MEAM potentials for the four Pt bimetallic alloys. For comparison, I also include the same materials properties calculated using density functional theory (DFT) method.

Table 1. MEAM results for Pt-Co alloys.

	MEAM	DFT-GGA
Properties of Pt ₃ Co (<i>L</i> ₁₂)		
Lattice constant <i>a</i> (Å)	3.842	3.897
Heat of Formation (eV/atom)	-0.074	-0.054
Properties of PtCo (<i>L</i> ₁₀)		
Lattice constant <i>a</i> (Å)	3.888	3.824
<i>c</i> (Å)	3.507	3.725
Heat of Formation (eV/atom)	-0.159	-0.079
Properties of PtCo ₃ (<i>L</i> ₁₂)		
Lattice constant <i>a</i> (Å)	3.662	3.667
Heat of Formation (eV/atom)	-0.094	-0.047

Table 2. MEAM results for Pt-Ti alloys.

	MEAM	DFT-GGA
Properties of Pt ₃ Ti (<i>L</i> ₁₂)		
Lattice constant <i>a</i> (Å)	3.956	3.956
Cohesive energy (eV/atom)	-0.614	-0.835
Bulk modulus (GPa)	255.23	235.74
Properties of PtTi (<i>L</i> ₁₀)		
Lattice constant <i>a</i> (Å)	4.004	3.990
Lattice constant <i>c</i> (Å)	3.912	3.898
Cohesive energy (eV/atom)	-0.906	-0.895
Properties of PtTi ₃ (<i>L</i> ₁₂)		

Lattice constant a (Å)	4.042	4.014
Cohesive energy (eV/atom)	-0.582	-0.495

Properties of PtTi₃ (A15)

Lattice constant a (Å)	5.013	5.027
Cohesive energy (eV/atom)	-0.857	-0.662

Table 3. MEAM results for Pt-Fe alloys.

	MEAM	DFT-GGA
Properties of Pt ₃ Fe ($L1_2$)		
Lattice constant a (Å)	3.854	3.924
Cohesive energy (eV/atom)	-0.408	-0.189
Properties of PtFe ($L1_0$)		
Lattice constant a (Å)	3.842	3.871
c (Å)	3.791	3.767
Cohesive energy (eV/atom)	-0.541	-0.227
Properties of PtFe ₃ ($L1_2$)		
Lattice constant a (Å)	3.791	3.740
Cohesive energy (eV/atom)	-0.374	-0.070

Table 4. MEAM results for Pt-V alloys.

	MEAM	DFT-GGA
Properties of Pt ₃ V ($d0_{22}$)		
Lattice constant a (Å)	3.926	3.903
c (Å)	7.855	7.909
Cohesive energy (eV/atom)	-0.406	-0.431
Properties of Pt ₃ V ($L1_2$)		
Lattice constant a (Å)	3.926	3.921
Cohesive energy (eV/atom)	-0.406	-0.371
Properties of PtV ($b19$)		
Lattice constant a (Å)	4.567	4.404
b (Å)	2.748	2.703
c (Å)	4.734	4.796
Cohesive energy (eV/atom)	-0.560	-0.535
Properties of PtV ($L1_0$)		
Lattice constant a (Å)	3.906	3.825
c (Å)	3.996	3.905
Cohesive energy (eV/atom)	-0.519	-0.533

Properties of PtV ₃ (A15)		
Lattice constant a (Å)	4.905	4.795
Cohesive energy (eV/atom)	-0.441	-0.419
Properties of PtV ₃ (L1 ₂)		
Lattice constant a (Å)	3.963	3.820
Cohesive energy (eV/atom)	-0.346	-0.223

2. Monte Carlo simulations of surface segregation in Pt bimetallic alloys

Using the developed MEAM potentials and the atomistic Monte Carlo (MC) method, we simulated the surface segregation process in the Pt bimetallic alloy surfaces. In our MC simulation method, series of configuration transformations (i.e., two atoms with different elements exchange their positions) were tried to an initially random Pt alloys until a thermostatic equilibrium ensemble was attained. The equilibrium Pt concentration in each surface layer was computed by averaging the values for those configurations in the equilibrium ensemble.

Figure 1. Calculated surface segregation profiles for (a) Pt-Ni (111), (b) Pt-Co (111), and (c) Pt-Ti (111) surfaces.

Our results above indicate that Pt would strongly segregate to the outermost layer of the (111) surfaces of Pt-Ni, Pt-Co, and Pt-Ti. Both Pt-Ni and Pt-Co have an oscillatory surface segregation profile. Distinct from them, Pt-Ti (near 75 at.%) has a pure Pt outermost layer and a Pt₃Ti (L1₂) crystal structure from the second layer and below.

3. Density functional theory calculation for oxygen reduction reaction on Pt bimetallic alloy surface

In order to understand the reaction pathway of oxygen reduction reaction (ORR) on Pt and its alloy surfaces, we have conducted DFT calculations on the adsorption and transitions of O₂, O, OH, and H₂O on Pt, Pt₃Ni, Pt₃Co, and Pt₃Fe surfaces. All calculations were done with software VASP, using the generalized gradient approximation (GGA) with PW91 functional, ultrasoft pseudopotentials, a plane-wave basis set with an energy cutoff of 400 eV, and a 4×4×1 Monkhorst-Pack k-point mesh for the integration within the Brillouin zone. The (111) surface of metal catalysts were constructed using a 2×2 unit cell. Our modeled surface slabs contained four

atomic layers (with atomic separations determined by the bulk lattice constant (3.991 Å) of pure Pt) and a 12 Å vacuum space in the [111] orientation. For Pt₃Ni, Pt₃Co, and Pt₃Fe (111) surfaces, we replaced the four Pt atoms in the second layer of pure Pt surface slab with Fe, Co or Ni atoms. Optimized atomic geometries were obtained through force-based energy minimization method until the force on each movable atom was less than 0.05 eV/Å. During structural relaxation, the bottom two layers of atoms were fixed at their positions. The reaction pathways for every micro-steps of ORR were searched by nudged elastic band method.

A. Molecule adsorption calculations

Figure 2 shows the possible surface sites for (a) O₂ adsorption and (b) for O, OH, and H₂O adsorption on the (111) surface of the catalysts. In Table 5, we give the calculated lowest adsorption energy (in unit of eV) for O₂, O, OH, and H₂O adsorbed on Pt, Pt₃Ni, Pt₃Co, and Pt₃Fe (111) surfaces. The adsorption energy is the energy difference between the optimized adsorption structure and isolated components (surface and adsorbate molecules).

Figure 2. Schematic structures of various molecule adsorption sites on (111) surface.

Table 5. Calculated molecule adsorption energies on the (111) surfaces of Pt and its alloys.

Materials	O	OH		H ₂ O	O ₂
	Fcc	bridge	top	top	tbt
Pt	-3.967	-2.400	-2.384	-0.287	-0.655
Pt-Ni	-3.502	-2.142	-2.153	-0.237	-0.277
Pt-Co	-3.378	-2.219	-2.217	-0.261	-0.274
Pt-Fe	-3.191	-2.099	-2.098	-0.225	-0.186

B. Transition state calculations

We have performed transition state calculations for ORR on Pt, Pt₃Ni, Pt₃Co, and Pt₃Fe (111) surfaces to determine the required energy barrier for each micro-step in the reaction.

(1) O₂=O+O

Figure 3. Calculated transition process of $O_2=O+O$.

In this step, an adsorbed O_2 molecule is split into two O atoms on the surface of catalysts. Our DFT calculation results of the corresponding transition energy barriers are: 0.67 eV on Pt (111), 0.87 eV on Pt-segregated Pt_3Ni (111), 0.91 eV on Pt-segregated Pt_3Co (111), and 1.01 eV on Pt-segregated Pt_3Fe (111).

(2) $O+H=OH$

Figure 4. Calculated transition process of $O+H=OH$.

In this step, an adsorbed O atom reacts with an adsorbed H atom to form OH on the surface of catalysts. Our DFT calculation results of the corresponding transition energy barriers are: 0.86 eV on Pt (111), 0.64 eV on Pt-segregated Pt_3Ni (111), 0.52 eV on Pt-segregated Pt_3Co (111), and 0.44 eV on Pt-segregated Pt_3Fe (111).

(3) $OH+H=H_2O$

In this step, the reaction immediate OH atom reacts with an adsorbed H atom to form H_2O on the surface of catalysts. Our DFT calculation results of the corresponding transition energy barriers are: 0.11 eV on Pt (111), 0.07 eV on Pt-segregated Pt_3Ni (111), 0.12 eV on Pt-segregated Pt_3Co (111), and 0.10 eV on Pt-segregated Pt_3Fe (111).

Figure 5. Calculated transition process of $\text{OH}+\text{H}=\text{H}_2\text{O}$.

4. Density functional theory study of the effect of a third transition metal element on Pt surface segregation in Pt_3Ni and Pt_3Co (111) surfaces

In this work, we used DFT method to search a third transition metal element that is capable of further promoting Pt surface segregation for Pt_3Ni and Pt_3Co (111) surfaces. To this end, we have calculated the energy difference between non-segregated surface [Figs. 6(a), 6(b), and 6(c)] and Pt-segregated surface [Figs. 6(d), 6(e), 6(f), and 6(g)]. Based on this definition, negative Pt surface segregation energy implies that Pt would segregate to the outermost layer of the alloy surfaces. The more negative the Pt surface segregation energies are, the more strongly Pt segregates to the surface. All the 3d, 4d, and 5d transition metals have been examined in this effort. In Fig. 7, we present our preliminary calculation results. Results refinement and manuscript drafting are still on-going.

The Pt surface segregation energy in Pt_3Ni (111) is calculated to be -0.399 eV. After adding a third transition metal atom, we found in Fig. 7(a) that elements V, Cr, Co, Mo, Tc, Ru, W, Re, Os and Ir led to even lower Pt surface segregation energies. This result suggests that the existence of these elements improve Pt surface segregation to the Pt_3Ni (111).

Figure 6. Schematics of the atomic structures of various Pt_3Ni and Pt_3Co (111) surfaces. Purple balls represent Pt atoms, blue balls represent Ni (in Pt_3Ni (111)) or Co (in Pt_3Co (111)) atoms, and green balls represent a third transition element atom.

Figure 7. Calculated Pt surface segregation energies when a third transition metal atom is present in the surface of (a) Pt₃Ni (111) and Pt₃Co (111).

The Pt surface segregation energy in Pt₃Co (111) is calculated to be -0.626 eV. After adding a third transition metal atom, we found in Fig. 6(b) that elements Ru and Os led to even lower Pt surface segregation energies. This result suggests that the existence of these elements improve Pt surface segregation to the Pt₃Co (111).

Objectives for the Next Year

- (1) Develop MEAM potentials and perform MC simulations to predict the surface segregation phenomena in bimetallic (PtPd and PtAu) and ternary (PtFeNi, PtFeV, PtTiNi, PtNiAu, and PtCoNi) alloys.
- (2) Screen possible Pt ternary alloys using DFT calculations to find those candidates that have strong Pt surface segregation and desired *d*-electronic structure.
- (3) Develop and apply kinetic Monte Carlo method to directly predict the reaction rate for ORR on the Pt alloy catalysts using the DFT calculated transition state energies as inputs.
- (4) Set up experimental facility that fabricate and test Pt alloys catalysts in order to validate our theoretical predictions. (Note: no extra funding is requested from DOE for this effort. The PI will invest his own start-up funding.)

Special Recognitions Received by the PI

None yet.

Statement of Unspent Funds

No unspent fund is expected by the end of this grant period.

Pending and Current Support

Current Supports:

1.
Project/Proposal Title: Theoretically relating the surface composition of Pt alloys to their performance as the electrocatalysts of low-temperature fuel cells
(*This Grant*)
Source of Support: DOE, Basic Energy Sciences
P.I.: Dr. Guofeng Wang, IUPUI
Co-P.I.'s (if any): N/A
Total Award Amount: \$660,000
Total Award Period Covered: 09/15/2009 – 09/14/2012
Location of Project: Indiana University Purdue University Indianapolis
Person-Months Per Year Committed to Project: Acad: 0.0 Sumr: 1.0

2.
Project/Proposal Title: Nanosegregated Catalysts with Ultra-low Platinum Loading
Source of Support: DOE, Energy Efficiency & Renewable Energy
P.I.: Dr. N.M. Markovic, Argonne National Laboratory
Co-P.I.'s (if any): Dr. Guofeng Wang, IUPUI
Total Award Amount: \$6,550,000
Total Award Period Covered: 10/01/2009 – 09/30/2013
Location of Project: Argonne Lab & IUPUI
Person-Months Per Year Committed to Project: Acad: 0.0 Sumr: 1.0

3.
Project/Proposal Title: Battery Safety and Early Failure Detection Project
Source of Support: Navy, Crane Division
P.I.: Prof. A. Hsu, IUPUI
Co-P.I.'s (if any): Dr. Guofeng Wang, IUPUI
Total Award Amount: \$4,500,000
Total Award Period Covered: 10/01/2009 – 09/30/2012
Location of Project: Indiana University Purdue University Indianapolis
Person-Months Per Year Committed to Project: Acad: 0.0 Sumr: 1.0

Pending Grant Support:

None at this moment

Publication Since September 15, 2009

(1) From This Grant:

“Modeling Surface Segregation Phenomena in (111) Surface of Ordered Pt₃Ti Crystals”, Jun Zhong, Zhiyao Duan, and Guofeng Wang, submitted to the Journal of Chemical Physics.

“Density Functional Theory Study of the Effect of a Third Transition Metal Element on Platinum Surface Segregation in Pt₃Ni (111) surfaces”, Yuhua Zhang, Zhiyao Duan, Chan Xiao, and Guofeng Wang, to be submitted.

(2) From Other DOE Grants:

(3) From Other Sources:

“Unraveling oxygen reduction reaction mechanisms on carbon-supported Fe-phthalocyanine and Co-phthalocyanine catalysts in alkaline solutions”, R. Chen, H. Li, D. Chu, and G.F. Wang, *Journal of Physical Chemistry C*, 113 (2009) 20689-20697.

Multi-Year Publication from this Grant

None yet.