Highly optimized embedding atom method potential for Pt-Cu alloys

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Abstract

We have developed an empirical and many-body type potential model for Pt-Cu alloys under the framework of the embedding atom method (EAM) formalism. This model can describe the structures and energies of clusters, bulk, surfaces, and defective systems of Pt-Cu alloy well. The test values of cohesive energies, surface formation energies, the formation energies of monovacancy defects, and surface adsorption energies are in good agreement with those predicted from *ab-initio* calculations. This demonstrates that the new model is able to handle complicated Pt-Cu alloy systems.

Keywords: embedding atom method; force matching; ab-initio calculations; Pt-Cu alloy

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1. Introduction

Currently, platinum is widely used in the chemical industry as electrocatalysts in full cells due to its high efficiency at hydrogen/hydrocarbon oxidation and oxygen reduction reaction (ORR) [1]. However, the high cost and some inherent defects such as CO poisoning prohibit the widespread use of platinum as a catalyst [2,3]. Current effort on developing anode catalysts toward commercialization is to lower the cost and improve the anti-CO poisoning performance. As a result, a number of alternatives to replace the pure platinum have been proposed. For example, various binary platinum-based alloy nanocrystal catalysts (NCs) and nanoparticle catalysts (NPs), such as PtCu [4–12], PtCo [13–15], PtNi [16–21], PtFe [22–24], PtPd [25–29], have been synthesized. Analysis of platinum-based alloy nanocatalysts suggests that they can not only reduce the cost, but also enhance the catalytic activity [4]. Of these platinum-based alloy catalysts, the Pt-Cu binary alloy has proven to be one of the most promising catalysts for redox reaction of methanol and formic acid [5, 8, 12]. Furthermore, the catalytic performance of Pt-Cu alloy has been found to depend on many factors, such as shape [8], composition [9, 12], and morphology [10,11]. In recent years, many experimental works have been devoted to investigating the catalytic abilities of Pt-Cu binary alloy NCs with various experimental techniques; whereas there are only very limited theoretical studies concerning Pt-Cu alloy [30–34].

The size of a Pt-Cu nanocrystal is on the order of nanometers (i.e. 1–20 nm), containing more than 10000 atoms. Therefore, it is a significant challenge to study such large-scale systems with the complicated structures at the *ab-initio* level, even with fast codes using density functional theory (DFT) like Vienna Ab-initio Simulation Package (VASP) [35,36], currently unfeasible. As we know, experiments provide the evidence of catalytic performance, but they cannot give the explanation of

catalytic mechanisms at the atomic level. Typically, the atomic structure information and the arrangement of Pt and Cu atoms with different Pt/Cu ratios have significant impacts on the catalytic abilities of Pt-Cu NCs. Therefore, to understand the mechanisms of enhanced catalytic performance at the atomic level, it is highly desirable to develop high-quality potential functions to study Pt-Cu NCs from the theoretical perspective. Compared with the first-principles potentials, which usually require huge computational cost and limited atom numbers, empirical potentials can fast handle large sized materials. In fact, there are various techniques for developing many-body types of potential, such as the Finnis-Sinclair (FS) model [37], the Tight-Binding (TB) approach [38], and the Embedding-Atom method (EAM) [39,40]. Of these models, the EAM potential is a popular framework of empirical potentials. Based on the modified EAM formalism, Onat and Durukanoğlu [39] developed a semi-empirical and many-body type model potential for Cu-Ni alloys. For the Pt-Cu system, Luyten et al. [40] reported new MEAM parameters for Cu, Pt, and Cu-Pt potentials, aiming to describe the segregation behavior in the Cu₃Pt surfaces. Although the potential successfully applies the investigations of surface segregation, its transferability needs to be improved to describe other Pt-Cu alloy systems correctly, such as cluster etc. To this end, we developed the EAM potential with good transferability for the Pt-Cu binary alloy system, which is a kind of classical atomic interaction and can easily handle the simulation system even containing millions of atoms.

In this work, we adopted the force-matching method [41] using the *potfit* package [42,43] to fit the EAM potential model. In this method, the potential functions were fitted to the reference database obtained from the *ab-initio* calculations. In our case, the forces on individual atoms, the cohesive energy of the system, and the stresses on the unit cells were used to fit a reliable potential. Moreover,

to improve the transferability of the EAM potential model, we performed various tests on some selected Pt-Cu systems during the fitting procedure. We only show the final optimized potentials and the test results.

2. Method

2.1 EAM potentials

The embedding atom method potential [44] is widely used to describe the atomic interactions in metals. Based on EAM theory, the total energy of an alloy system can be expressed in the general form of

$$E_{tot} = \sum_i E_i \quad (1)$$

$$\text{with } E_i = F_\alpha(n_i) + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \Phi_{\alpha\beta}(r_{ij}), \quad (2)$$

where the total potential energy of a system is defined as the linear summation of the potential energy of each embedded atom (E_i). The indices i and j represent the embedded atom and the neighboring atom, respectively. α and β are the element types of the i and j atoms.

The first term in Eq. (2) is the embedding energy of i atom, reflecting the interactions of atom i and its background electron charge density. For the embedding function $F(n)$, the original form was adopted from [45]:

$$F(n) = F_0 \left[\frac{q}{q-p} \left(\frac{n}{n_e} \right)^p - \frac{p}{q-p} \left(\frac{n}{n_e} \right)^q \right] + F_1 \frac{n}{n_e}. \quad (3)$$

It is based on the more general equation of Rose et al. [46]. The parameters p and q are real values, and n_e is the equilibrium density. Because the original form is numerically unstable with our optimization algorithms, we let $p \rightarrow q$ and chose $n_e=1$; Equation (3) reduces to the following form

$$F(n) = F_0[1 - \gamma \ln n]n^\gamma + F_1 n. \quad (4)$$

In the formula above, there are three free parameters F_0 , F_1 , and γ . We use the simplified form (4) in our potential model.

In Eq. (2), n_i is the host charge density, which is calculated as the linear summation of electron density contributions from the atoms within the cutoff radius (r_{cut}) except for the embedding atom itself.

$$n_i = \sum_{j \neq i} \rho_\beta(r_{ij}), \quad (5)$$

It is noteworthy that this charge density is only an empirical value: it does not represent the actual physical density.

Next, the electron transfer function $\rho_\beta(r_{ij})$ can be written as [47]

$$\rho_\beta(r) = \Psi\left(\frac{r - r_c}{h}\right) \frac{1 + \alpha_1 \cos(\alpha r + \varphi)}{r^\beta}. \quad (6)$$

This transfer function includes oscillations with four free parameters, α_1 , α , φ , and β . α_1 controls the amplitude of the oscillation, h serves the purpose of smoothing the potential, and α , φ , and β are the wave vector, the initial phase, and the factor of decay, respectively.

The second term of Eq. (2) is the pair interactions between atoms i and j separated by a distance r_{ij} . Here, the empirical oscillating pair potential (EOPP) [48], the classical Morse potential [49] and Lennard-Jones (L-J) potential [50] were chosen to perform test calculations. As a result, we find that the EOPP has a great flexibility on the description of atomic interactions in the Pt-Cu system. Therefore, the pair potential function with oscillations is adopted here, which can be expressed as

$$\Phi(r) = \Psi\left(\frac{r - r_c}{h}\right) \left[\frac{C_1}{r^{\eta_1}} + \frac{C_2}{r^{\eta_2}} \cos(kr + \varphi) \right]. \quad (7)$$

In the expression above, the parameters C_1 and η_1 control the short-range repulsion, and the parameters C_2 and η_2 are responsible for the damping of the oscillations with the frequency k . Also, this empirical oscillating pair potential had been successfully used in previous works on the ternary

intermetallic system [51,52] and other complex metallic alloy systems [53].

The cutoff function $\Psi(x)$ in Eq. (6) and Eq. (7) is defined as [51]

$$\Psi(x) = \frac{x^4}{1 + x^4} \quad (8)$$

for $x < 0$ and $\Psi(x) \equiv 0$ for $x \geq 0$. This function ensures that the potential function, as well as their derivatives up to the second order, approach zero smoothly at the cutoff distance r_c . In addition, both h and r_c are global parameters that have the same value in all functions. In our model, the cutoff radius r_c is set to be 6.0 Å through the entire fitting procedure.

All potential functions are used in the analytic forms. For a binary Pt-Cu alloy system, in total seven analytic functions are employed to determine the atomic interactions, including two embedding functions (F_{Pt} and F_{Cu}), two electron transfer functions (ρ_{Pt} and ρ_{Cu}), and three pair potential functions ($\Phi_{\text{Pt-Pt}}$, $\Phi_{\text{Pt-Cu}}$, and $\Phi_{\text{Cu-Cu}}$). On the other hand, the free parameters in the present potential functions include three parameters in the embedding function, four parameters in the transfer function, six parameters in the pair potential function, and one global parameter h . All these parameters are determined by fitting the potential energy surface of our considered Pt-Cu alloy systems such as the clusters, faced-centered cubic (fcc), artificial body-centered cubic (bcc) and simple cube (sc) structures.

2.2 Target systems for fitting

In order to improve the transferability of the EAM potential model, we considered a large number of reference configurations of Pt-Cu alloy in the potential fitting, including clusters, fcc crystals, artificial bcc and sc crystals. Of these reference configurations, most structures (Figures 1 and 2) were fully relaxed with *ab-initio* calculations, where the largest force acting on each atom was less than 0.01 eVÅ⁻¹. A few structures were relaxed under different strains (Figure 3).

Clusters have large specific surface areas and novel electronic properties. Moreover, the complicated electronic and structural features of clusters are dependent on the size, component and composition. In the present database, we choose five different-sized clusters, which consists of 10, 20, 30, 40 and 80 atoms, respectively. Furthermore, there are 20%, 30%, 40%, and 50% Cu atoms for each size of cluster. In addition, for each element ratio in a sized cluster, four isomers with different Cu atom distribution were selected by a random method. Therefore, the summation of considered Pt-Cu alloy clusters is 80, containing five cluster sizes, four Pt/Cu ratios, and four isomers for each size and each ratio. The partial reference structures for Pt_nCu_m clusters are shown in [Figure 1](#).

For the periodic fcc phase, we construct a $2\times 2\times 2$ supercell containing 32 atoms. 16 structures of $Pt_{32-x}Cu_x$ ($x=6, 10, 13, 16$) Pt-Cu alloy were selected. Similarly, for the artificial bcc and sc phases, we construct eight structures as the reference configurations, respectively. The partial reference structures of fcc, artificial bcc and sc crystal are shown in [Figure 2](#). In addition, to produce the correct properties of strained Pt-Cu alloy systems, some reference structures with different strains need to be added in the database. To do this, we compress and expand the fcc lattice from 85% to 124%. As shown in [Figure 3](#), the 21 strained structures with the Pt/Cu ratio of 20/12 were chosen as the reference configurations. In these considered reference structures, the arrangement of Pt and Cu atoms is random.

In brief, the reference database contains 133 structures (80 clusters, 16 fcc, eight bcc, eight sc, and 21 fcc strained phases) with 4712 atoms, 133 cohesive energies, 14136 forces, and 798 stresses. These target quantities were obtained from the accurate *ab-initio* calculations. The calculations were carried out by the projector augmented wave (PAW) approach [\[54,55\]](#) with the generalized gradient approximation (GGA) implemented in the VASP code [\[35,36\]](#). The PW91 [\[56\]](#) exchange correlation

functional was considered in the calculations. Pt $5d^96s^1$ and Cu $3d^{10}4s^1$ were treated as valence electrons, and the cut-off energy of 400 eV was used for the plane wave. We considered spin-polarization effects for all the selected reference configurations and all the test calculations parts. To prevent any interaction between clusters, a vacuum region of 15 Å in the x , y , and z directions was created.

2.3 Fitting procedure

All the optimizations of EAM potential functions were performed using the force-matching method [41] with the *potfit* package of Brommer and Gähler [42,43]. In this method, the results obtained from *ab initio* calculations are used as reference data to adjust the parameters of a potential. The electron transfer function $\rho_\beta(r)$ and pair potential $\Phi_{\alpha\beta}(r)$ are defined between the minimum distance $r_{\min}$ and the cutoff distance r_c , while the effective range of the embedding function $F_\alpha(n)$ is determined by the electron transfer function. The initial value of $r_{\min}$ equals the smallest interatomic distance in the corresponding configuration. The cutoff distance of 6.0 Å includes the interaction of an atom with up to the fourth-nearest neighbors in the equilibrium system.

To obtain the reliable parameters, two different optimization algorithms were used to fit our analytic functions. They both minimize the summation of squares expressed by

$$Z = \sum \frac{(f - f_0)^2}{f_0^2 + \varepsilon_j} + \sum w_E \frac{(E - E_0)^2}{E_0^2 + \varepsilon_k} + \sum w_S \frac{(S - S_0)^2}{S_0^2 + \varepsilon_l}, \quad (9)$$

where f_0 , E_0 , and S_0 are respectively forces, cohesive energies, and stresses calculated by the *ab-initio* method, while f , E , and S are forces, cohesive energies, and stresses obtained from the present EAM potential. ε_j , ε_k , and ε_l have no physical significance, only a small quantity. The first optimization algorithm we used is the simulated annealing algorithm [57], which is one of the global searching methods for the minimum state. Afterward, a conjugate-gradient-like deterministic algorithm [58] is

performed on the optimization to obtain the more precise local minimum state.

For the practical application side, the transferability of EAM potential model is very important. Generally, transferability strongly depends on the number of selected reference structures. Better transferability requires more reference configurations, but it will introduce more error at the same time. Therefore, it needs a balance for the reference data and the accuracy. In Equation (9), w_E and w_S are weight factors for cohesive energy and stresses, respectively. They can significantly affect the fitting precise of the forces, energy, and stresses. After multiple test calculations, w_E and w_S were chosen to be 20000 and 8000, respectively.

The pair potential function $\Phi_{\alpha\beta}(r)$ for each element pair, the transfer function $\rho_{\beta}(r)$, and the embedding function $F_{\alpha}(n)$ of each element are the target functions of potential fitting. The fitted functions of our EAM potential model for the Pt-Cu alloy system are shown in Figure 4, in which (a), (b), and (c) are the pair potential functions, transfer functions, and embedding functions, respectively. Obviously, the pair potentials and the transfer functions go to zero when the distance between two atoms is larger than 6.0 Å. It is therefore reasonable to choose a cutoff distance of 6.0 Å to truncate the interaction between any two atoms in a Pt-Cu alloy system. All the parameters from fitting for the present EAM potential model are summarized in Table 1. Figure 5 demonstrates that the average error per atom of cohesive energies calculated by the present EAM potentials is ~0.014 eV/atom compared to the *ab-initio* calculations. It is noted that the configurations with relatively large error (the largest being 0.06 eV/atom) are mostly highly activated states such as the small-sized clusters and those with large strains. On the contrary, the average error for the large-sized clusters and the crystalline phases is much smaller.

3. Test results and discussion

To validate our EAM potential model obtained by the fitting procedure, we performed some test calculations on the cohesive energy, surface formation energy, monovacancy defect formation energy, and surface adsorption energy for various structures of the Pt-Cu alloy, such as bulk, surfaces, defective bulk, defective surfaces, and interfacial case. Not all test structures participated in the fitting procedure and were relaxed by the EAM potential model for energy calculations.

3.1 Bulk structure

The structural properties of Pt-Cu alloy crystals are very important for their application. Therefore, it is necessary to assess the accuracy of our EAM potential model on the bulk Pt-Cu alloy. To do so, a $2 \times 2 \times 2$ fcc supercell containing 32 atoms was constructed, in which the Pt and Cu atoms distributed randomly according to the Pt/Cu ratio of 22/10, as shown in [Figure 6](#). For the crystal structure, our predicted equilibrium lattice constant is 7.811 Å, being very close to the value of 7.793 Å calculated at the *ab-initio* level. Here, the cohesive energy of the Pt-Cu alloy with different strains is the focus of the test calculations. The cohesive energies as a function of the lattice constant scale are shown in [Figure 7](#), in which the strain range is from 85–121% of the lattice constant. Clearly, the cohesive energy curve obtained from our EAM potential model is in fairly good agreement with that from the *ab-initio* calculations. This suggests that our EAM potential model can well describe the atomic interactions in the case of compression, equilibrium, and expansion for Pt-Cu binary alloy crystal structures.

3.2 Surface structures

We computed the surface formation energies using our EAM potential model, and compared them

to those from the *ab-initio* calculations. To this end, six different surfaces were constructed, including three typical low-index surface (100), (110), and (111). All the surface models are composed of Pt and Cu atoms with the Pt:Cu ratio 2:1; the arrangement of Pt and Cu atoms in the bulk and the surface is random. According to the definition of the surface formation energy

$$E_{surf} = \frac{E_{slab} - E_{bulk}}{2S}, \quad (10)$$

where E_{slab} and E_{bulk} are the total energy of slab and bulk corresponding to the structures shown in [Figure 8](#), respectively, and S is the surface area of a slab; the surface formation energies of the six different surfaces were calculated. As listed in [Table 2](#), the EAM potential model that predicted the surface formation energies agree well with those from the *ab-initio* level, indicating that our model can handle the surface property of Pt-Cu alloy. Additionally, the analysis of surface formation energies suggests that the atomic arrangement on the Pt-Cu alloy surface has little impact on the surface stability.

3.3 Monovacancy defects

Commonly, point defects exist in realistic materials, which usually affect some physical and chemical properties of the materials. Here, the monovacancy defect as an example was studied. Likewise, three low-index surfaces of Pt-Cu alloy and a $2 \times 2 \times 2$ fcc supercell were constructed, in which the arrangement of Pt and Cu atoms is random and the Pt:Cu ratio is 2:1. As shown in [Figure 9](#), for the surface model, the monovacancy site is located in the first layer by removing a Pt or Cu atom, respectively. For the bulk phase, the monovacancy site is generated randomly in a supercell with 32 atoms. The formation energy of a monovacancy defect is calculated as:

$$E_{defect} = E_{atom} + E_{defect} - E_{perfect}, \quad (11)$$

where E_{atom} represents the total energy of a free Cu or Pt atom, E_{defect} and $E_{perfect}$ are the total energy

of a slab or bulk of Pt-Cu alloy with or without a monovacancy defect. The monovacancy defect formation energies of the considered defects obtained from our EAM potential model together with those from the *ab-initio* calculations are listed in Table 3. Obviously, our calculated monovacancy defect formation energies are qualitatively consistent with those calculated by the VASP code. This test result suggests that our EAM potential model can also handle the defective systems of Pt-Cu alloy well, such as defective bulk and defective surfaces.

3.4 Surface adsorption

The structural properties of the surface are very important for the activity of a catalyst. In particular, the interaction that occurs on the surface or interfacial is the key to a catalytic reaction. Therefore, it is necessary to examine the interaction between a single atom and the Pt-Cu alloy surface using our model. Here, a single Cu atom was chosen as the adsorption atom, and the three layers (111) surface of Pt-Cu alloy containing 27 atoms was constructed, where the ratio of Pt:Cu is 17:10. We considered nine different adsorption sites (hcp1-hcp9) on the (111) surface of Pt-Cu alloy. The structure of surface adsorption model together with the nine different adsorption sites is shown in Figure 10. It can be seen from Figure 10 that, after full relaxation, the adsorption sites of hcp3, hcp5, and hcp7 move to the bridge site between two Cu atoms, namely B_CC1, B_CC2, and B_CC3, respectively. The adsorption energy of a Cu atom adsorbed on the surface site is calculated according to:

$$E_{ads} = E_{slab} + E_{Cu} - E_{slab+Cu}, \quad (12)$$

where E_{slab} and $E_{slab+Cu}$ are the total energies of the (111) surface of the Pt-Cu alloy without and with a Cu atom adsorption. In our calculations, the second and the third layers were fixed to represent the bulk phase of the Pt-Cu alloy, whereas the top layer and the adsorbed Cu atom were fully relaxed.

The initial adsorption height that defined the distance between the Cu atom and the first layer is 2.3 Å, which is the same value as the interlayer spacing. Furthermore, to avoid the interaction between the surface and its neighboring images, the surface was separated by a 15 Å vacuum layer in the z -axis direction. The surface adsorption energies obtained from the EAM potential model and *ab-initio* calculations are summarized in Table 4. Clearly, the adsorption energies of the Cu atom calculated by the EAM potential model are slightly larger than the *ab-initio* adsorption energies. The maximum error of adsorption energies is about 12% (or 12 meV/atom), which is slightly larger but can be accepted. This error may be due to the inaccurate energy of the adsorbed Cu atom obtained from EAM potential. We did not consider the pure Pt and Cu in the reference database. Therefore, the present potential could not handle the Cu and Pt atoms well. Overall, the EAM potential model can describe the interactions between Cu atom and Pt-Cu alloy surface with reasonable adsorption energies.

3.5 Monte Carlo simulations

It would be interesting to assess the performance of the EAM potential in the structure discovery, as this is often a very challenging task with *ab-initio* methods. To this end, we performed Monte Carlo (MC) simulations for Pt₂₄Cu₈ bulk alloy employing the presented EAM potential. The simulations involve 10^5 steps, since the bulk alloy consists of a few atoms (32). The structure with the lowest cohesive energy is shown in Figure 11, and the cohesive energies of Pt₂₄Cu₈ bulk isomers obtained from MC simulations and *ab-initio* calculations, respectively, are listed in Table 5. Top i , mid i , and tail i ($i=1-3$) represent the isomers with the stability from high to low. From Table 5, we can see that the trend of stability for Pt₂₄Cu₈ bulk isomers from MC simulations using current EAM potential is the same as that from the *ab-initio* calculations. This result indicates that the MC

combined with the EAM could be used to search for the low-lying isomers for a large Pt-Cu alloy system.

3.6 Cluster tests

Finally, to test the transferability of the EAM potential model, we performed test calculations for Pt-rich and Cu-rich clusters. Three isomers of the Pt-rich cluster ($\text{Pt}_{40}\text{Cu}_{10-1}$, $\text{Pt}_{40}\text{Cu}_{10-2}$, $\text{Pt}_{40}\text{Cu}_{10-3}$) and three of the Cu-rich cluster ($\text{Pt}_{10}\text{Cu}_{40-1}$, $\text{Pt}_{10}\text{Cu}_{40-2}$, $\text{Pt}_{10}\text{Cu}_{40-3}$) are randomly selected. The isomer structures for the Pt-rich and Cu-rich clusters are shown in [Figure 12](#), and the average binding energies per atom of these isomers obtained from the *ab-initio* and EAM calculations are listed in [Table 6](#). From [Table 6](#), the EAM potential overestimates the binding energy of 0.5% for Pt-rich clusters and 0.0–0.7% for Cu-rich clusters. The larger deviation (0.7 %) for the Cu-rich clusters could be due to the fact that no Cu-rich clusters were included in the reference set used for fitting.

4. Conclusions

We have developed a transferable EAM potential model for Pt-Cu alloy with the force-matching method, which fits the parameters to the reference database from *ab-initio* calculations. Our extensive tests illustrate that this model can reproduce the *ab-initio* values of the cohesive energies, the surface formation energies, the monovacancy defect formation energies, and the surface adsorption energies with high accuracy. We believe that our EAM potential model can handle the different structures of Pt-Cu alloy well, e.g. clusters, crystals, surfaces, and defective systems. Typically, this new EAM potential model can achieve structure optimizations of large-sized Pt-Cu alloy systems, such as nanocrystals, searching for the best structures with various compositions of Pt-Cu alloy NCs.

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References

- [1] E. Antolini, *Mater. Chem. Phys.* 78 (2003) 563.
- [2] C. Rice, R. I. Ha, R. I. Masel, P. Waszczuk, A. Wieckowski, T. Barnard, *J Power Sources* 111 (2002) 83.
- [3] H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang, D. P. Wilkinson, *J Power Sources* 155 (2006) 95.
- [4] H. Yang, L. Dai, D. Xu, J. Fang, S. Zou, *Electrochim. Acta* 55 (2010) 8000.
- [5] D. Xu, Z. Liu, H. Yang, Q. Liu, J. Zhang, J. Fang, S. Zou, K. Sunm, *Angew. Chem.* 121 (2009) 4281.
- [6] M. Oezaslan, P. Strasser, *J. Power Sources* 196 (2011) 5240.
- [7] F. Hasche, M. Oezaslan, P. Strasser, *ChemCatChem* 3 (2011) 1805.
- [8] L. Bromberg, M. Fayette, B. Martens, Z. Luo, Y. Wang, D. Xu, J. Zhang, J. Fang, N. Dimitrov, *Electrocatal.* 4 (2013) 24.
- [9] Y. Jiang, Y. Jia, J. Zhang, L. Zhang, H. Huang, Z. Xie, and L. Zheng, *Chem. Eur. J.* 19 (2013) 3119.
- [10] X. Huang, Y. Chen, E. Zhu, Y. Xu, X. Duan and Y. Huang, *J. Mater. Chem. A* 1 (2013) 14449.
- [11] X. Yu, D. Wang, Q. Peng and Y. Li, *Chem. Commun.* 47 (2011) 8094.
- [12] D. Xu, S. Bliznakov, Z. Liu, J. Fang, and N. Dimitrov, *Angew. Chem.* 122 (2010) 1304.

- [13] J. Zeng, J. Lee, J. Power Sources 140 (2005) 268.
- [14] H. Yang, J. Zhang, K. Sun, S. Zou, J. Fang, Angew. Chem. 122 (2010) 7000.
- [15] Z. Yu, J. Zhang, Z. Liu, J. Ziegelbauer, H. Xin, I. Dutta, D. Muller, and F. Wagner, J. Phys. Chem. C 116 (2012) 19877.
- [16] T. Deivaraj, W. Chen, J. Lee, J. Mater. Chem. 13 (2003) 2555.
- [17] B. Pawelec, S. Damyanova, K. Arishtirova, J. Fierro, L. Petrov, Appl. Cat. A 323 (2007) 188.
- [18] Y. Xu, S. Hou, Y. Liu, Y. Zhang, H. Wang, B. Zhang, Chem. Commun. 48 (2012) 2665.
- [19] K. Ahrenstorf, H. Heller, A. Kornowski, A. Broekaert, H. Weller, Adv. Funct. Mater. 18 (2008) 3850.
- [20] R. Mu, Q. Fu, H. Xu, H. Zhang, Y. Huang, Z. Jiang, S. Zhang, D. Tan, and X. Bao, J. Am. Chem. Soc. 133 (2011) 1978.
- [21] Y. Wu, S. Cai, D. Wang, W. He and Y. Li, J. Am. Chem. Soc. 134 (2012) 8975.
- [22] Z. Cai, Z. Lu, Y. Bi, Y. Li, Y. Kuang and X. Sun, Chem. Commun. 52 (2016) 3903.
- [23] D. Chung, S. Jun and G. Yoon, J. Am. Chem. Soc. 137 (2015) 15478.
- [24] H. Zhang, X. Liu and N. Zhang, Appl. Catal. B 180 (2016) 237.
- [25] Y. Lee, A. Ko, S. Han, H. Kim and K. Park, Phys. Chem. Chem. Phys. 13 (2011) 5569.
- [26] V. Petkov, S. Shastri, Phys. Rev. B 81 (2010) 165428.
- [27] H. Zhang, M. Jin, J. Wang, W. Li, P. Camargo, M. Kim, D. Yang, Z. Xie and Y. Xia, J. Am. Chem. Soc. 133 (2011) 6078.
- [28] A. Yin, X. Min, Y. Zhang and C. Yan, J. Am. Chem. Soc. 133 (2011) 3816.

- [29] H. Zhang, M. Jin and Y. Xia, Chem. Soc. Rev. 41 (2012) 8035.
- [30] A. Chaves, G. Rondina, M. Piotrowski and J. Silva, Comput. Mater. Sci. 98 (2015) 278.
- [31] M. Abe, S. Mori, T. Nakajima, K. Hirao, Chem. Phys. 311 (2005) 129.
- [32] V. I. Avdeev, V. I. Kovalchuk, G. M. Zhidomirov, J. L. d'Itri, Surf. Sci. 583 (2005) 46.
- [33] J. Mejía-López, G. García, and A. H. Romero, J. Chem. Phys. 131 (2009) 044701.
- [34] P. Strasser, S. Koh and J. Greeley, Phys. Chem. Chem. Phys. 10 (2008) 3670.
- [35] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558(R).
- [36] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.
- [37] M. W. Finnis and J. E. Sinclair, Phil. Mag. A 50 (1984) 45.
- [38] P. F. Li and B. C. Pan, J. Phys.: Condens. Matter 24 (2012) 305802.
- [39] B. Onat and S. Durukanoğlu, J. Phys.: Condens. Matter 26 (2014) 035404.
- [40] J. Luyten, M. Schurmans, C. Creemers, B. S. Bunnik, G. J. Kramer, Surf. Sci. 601 (2007) 2952.
- [41] F. Ercolessi and J. B. Adams, Europhys. Lett. 26 (1994) 583.
- [42] P. Brommer and F. Gähler, Philos. Mag. 86 (2006) 753.
- [43] P. Brommer and F. Gähler, Modelling Simul. Mater. Sci. Eng. 15 (2007) 295.
- [44] M. Daw and M. Baskes, Phys. Rev. Lett. 50 (1983) 1285.
- [45] R. Johnson and D. Oh, J. Mar. Res. 4 (1989) 1195.
- [46] J. Rose, J. Smith, F. Guinea and J. Ferrante, Phys. Rev. B 29 (1984) 2963.
- [47] S. Chantasiriwan and F. Milstein, Phys. Rev. B 53 (1996) 14080.

- [48] M. Mihalkovič, C. Henley, M. Widom and P. Ganesh, Phys. Rev. B: Condens. Matter. 85 (2008) 1311.
- [49] P. Morse, Phys. Rev. 34 (1929) 57.
- [50] J. Jones, Phys. Status. Solidi 106 (1924) 463.
- [51] D. Schopf, P. Brommer, B. Frigan and H. Trebin, Phys. Rev. B 85 (2012) 054201.
- [52] M. Mihalkovič, C. Henley, Phys. Rev. B 85 (2012) 092102.
- [53] M. Mihalkovič, W. Zhu, C. Henley and R. Phillips, Phys. Rev. B 53 (1996) 9021.
- [54] P. Blöchl, Phys. Rev. B 50 (1994) 17953.
- [55] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
- [56] J. Perdew, Y. Wang, Phys. Rev. B 33 (1986) 8800.
- [57] A. Corana, M. Marchesi, C. Martini and S. Ridella, ACM Trans. Math. Softw. 13 (1987) 262.
- [58] M. J. D. Powell, Comp. J. 7 (1965) 303.

Figure 1. Partial reference structures of clusters. The four digits in the lower-right corner of each cluster represent the number of Pt and Cu atoms, respectively. For example, the digits 0802 mean that there are 08 Pt atoms and 02 Cu atoms. The orange balls and white balls are Cu atoms and Pt atoms, respectively. The isomers of these clusters are not shown in this figure.

Figure 2. Partial reference structures of fcc, artificial bcc and sc crystals. Similar to Figure 1, the four digits at the bottom of each structure represent the number of Pt and Cu atoms, respectively. Cu atoms and Pt atoms are represented by the orange balls and white balls, respectively. The isomer structures of these crystals are not shown in this figure.

Figure 3. Reference structures under strain from 85–124%. The Pt/Cu ratio is 20/12. The orange balls and white balls are Cu atoms and Pt atoms, respectively.

Figure 4. Plots of the seven potential functions of the EAM potential model for the Pt-Cu alloy system. (a) pair potential functions, (b) transfer functions, and (c) embedding functions.

Figure 5. Comparisons of EAM potentials energies with *ab-initio* energies.

Figure 6. Bulk model of Pt-Cu alloy for the fcc phase. The Pt/Cu ratio is 22/10. The orange balls and white balls are Cu atoms and Pt atoms, respectively.

Figure 7. Cohesive energy versus lattice constant scale.

Figure 8. Six different surface models for Pt-Cu alloy. The Pt:Cu ratio is 2:1. The orange balls and white balls are Cu atoms and Pt atoms, respectively.

Figure 9. Defect sites in bulk, surface (100), (110) and (111), respectively. The orange balls and white balls are Cu atoms and Pt atoms, respectively. The gray and black balls represent the second layer and the third layer atoms, respectively.

Figure 10. Model of surface adsorption (a) and nine different adsorption sites (b). The orange balls and white balls are Cu atoms and Pt atoms, respectively. The black balls represent the second layer atoms; the third layer atoms have not been shown in the (b). The ratio of Pt:Cu in the surface model is 17:10, and Cu atoms are distributed randomly.

Figure 11. Structure of $\text{Pt}_{24}\text{Cu}_8$ bulk isomer with the lowest cohesive energy.

Figure 12. Isomer structures for Pt-rich (a) and Cu-rich (b) clusters.

Table 1. Parameters for the EAM potential model with r in units of $\text{\AA}$ and $V(r)$ in eV. The global parameter r_{cutoff} is 6.0 $\text{\AA}$.

EOPP pair function							
pair	C_1	η_1	C_2	η_2	k	φ	h
Pt-Pt	30003.5298	12.4069	0.9449	1.0000	0.3400	0.8985	1.2134
Pt-Cu	27603.0050	13.4609	-6.4293	2.4930	0.3234	4.0675	1.2134
Cu-Cu	18412.0316	13.7946	3.4585	1.5999	0.0415	1.6001	1.2134
Transfer function							
element	α_1	α	φ	β	h		
Pt	-0.9950	0.9431	2.7263	1.7286	1.2134		
Cu	-0.3877	3.4719	2.4964	2.5835	1.2134		
Embedding function							
element	F_0	γ	F_1				
Pt	-4.2714	0.9332	0.0000				
Cu	-2.2682	0.7947	0.0012				

Table 2. Surface formation energies (in eV) of the six different surfaces for Pt-Cu alloy. The corresponding structures are shown in Figure 8.

E_{surf}	E_{100-1}	E_{100-2}	E_{110-1}	E_{110-2}	E_{111-1}	E_{111-2}
<i>ab-initio</i>	0.105	0.106	0.105	0.108	0.085	0.089
eam	0.099	0.109	0.106	0.106	0.089	0.098

Table 3. Monovacancy defect formation energy (in eV) for Pt-Cu alloy bulk and surface, respectively. The corresponding defective structures are shown in Figure 9.

	bulk				(100)surface			
	Cu1	Cu2	Pt1	Pt2	Cu1	Cu2	Pt1	Pt2
<i>ab-initio</i>	4.995	5.088	7.021	6.906	4.027	3.907	5.664	6.127
eam	4.889	4.837	7.221	7.032	4.020	4.214	6.009	6.080
	(110)surface				(111)surface			
	Cu1	Cu2	Pt1	Pt2	Cu1	Cu2	Pt1	Pt2
<i>ab-initio</i>	4.288	4.229	5.736	5.803	4.591	4.614	6.351	6.514
eam	4.073	3.989	5.626	5.907	4.479	4.483	6.361	6.202

Table 4. Adsorption energies (in eV) obtained from *ab-initio* and the eam potential model, respectively. The nine different initial adsorption sites are shown in Figure 10.

Initial sites	Relaxed sites	<i>Ab-initio</i>	eam
hcp1	hcp1	2.956	3.183
hcp2	hcp2	2.970	3.054
hcp3	B_CC1	2.860	3.200
hcp4	hcp4	2.970	3.054
hcp5	B_CC2	2.927	3.220
hcp6	hcp6	2.826	3.154
hcp7	B_CC3	2.860	3.200
hcp8	hcp8	2.826	3.154
hcp9	hcp9	3.025	3.043

Table 5. Cohesive energies of $\text{Pt}_{24}\text{Cu}_8$ bulk isomers obtained from MC simulations and *ab-initio* calculations.

system	eam (eV)	<i>ab-initio</i> (eV)
top1	-164.989	-164.563
top2	-164.977	-164.542
top3	-164.976	-164.575
mid1	-164.345	-164.113
mid2	-164.345	-163.876
mid3	-164.345	-164.088
tail1	-163.801	-163.691
tail2	-163.801	-163.691
tail3	-163.776	-163.744

Table 6. Average binding energies per atom of the isomers of $\text{Pt}_{40}\text{Cu}_{10}$ and $\text{Pt}_{10}\text{Cu}_{40}$ cluster from the *ab-initio* and eam calculations, respectively.

system	ab-initio	
	(eV/atom)	eam(eV/atom)
$\text{Pt}_{40}\text{Cu}_{10}$ -1	-4.254	-4.274
$\text{Pt}_{40}\text{Cu}_{10}$ -2	-4.279	-4.299
$\text{Pt}_{40}\text{Cu}_{10}$ -3	-4.267	-4.289
$\text{Pt}_{10}\text{Cu}_{40}$ -1	-3.227	-3.249
$\text{Pt}_{10}\text{Cu}_{40}$ -2	-3.225	-3.237
$\text{Pt}_{10}\text{Cu}_{40}$ -3	-3.241	-3.242