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Oxygen Chemistry on Transition Metals: First-principles DFT and Monte Carlo Studies

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Oxygen Chemistry on Transition Metals: First-principles DFT and Monte Carlo Studies

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Abstract

Electro-chemical and thermo-chemical processes occurring at multi-phase interfaces are the basis of many devices facilitating conversion between forms of energy including solar, electrical, and chemical in a number of devices from fuel cells to batteries. Large electric fields, high potential bias and inherent inaccessibility of these interfaces to many conventional experimental probes contribute to an absence of fundamental insight into mechanistic behavior of chemical species and interfacial environment. Modern first-principles tools including Density Functional Theory (DFT) can be used to study these interfaces from a first-principles approach and provide insight for molecular transformations. In our studies we also coarse-grain DFT calculations with the Cluster Expansion (CE) and extend quantum-mechanical ab-initio information to larger systems and include environmental factors such as temperature, partial pressure of oxygen, and surface morphology (undercoordinated step and edge sites). We investigate two case studies: recharge cycle of lithium/oxygen batteries and oxygen on a metal surface in ethylene epoxidation.

ACKNOWLEDGMENTS

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NOMENCLATURE

CE	Cluster Expansion
CV	Cross-validation score
CLS	Core-level Shift
DFT	Density Functional Theory
ECI	Effective Cluster Interactions
FCC	Face-centered Cubic crystal structure
GCMC	Grand Canonical Monte Carlo
GGA	Generalized Gradient Approximation
GPAW	Grid-based Projector Augmented Wave method
HCP	Hollow Close-packed crystal structure
MC	Monte Carlo
MMC	Metropolis Monte Carlo
PW91	Perdew-Wang exchange correlation functionals
XPS	X-ray Photoelectron Spectroscopy

1. INTRODUCTION

This report summarizes the major accomplishments and methods of our work performed during the three-year Excellence in Engineering Fellowship sponsored by Sandia National Laboratories at the University of Michigan.

1.1. Evaluation of Catalytic Performance of Lithium/Oxygen Battery Catalysts

Lithium/oxygen batteries are secondary batteries, which store chemical energy reversibly in the form of lithium peroxide. During charging, the use of a catalyst facilitates oxygen evolution; in the absence of a catalyst the lithium peroxide formation is irreversible. Using first-principles Density Functional Theory (DFT) calculations we studied elementary step mechanisms of this process with the goal of determining the underlying chemistry and identifying descriptors that could drive the design of catalytic materials with improved performance.

1.2. Establishing the Connection between the Geometric and Electronic Structure of Oxygen Species

Oxygen can adsorb to catalytic surfaces in different states (i.e. electrophilic, nucleophilic, neutral) and drive both desired and undesired reactions.^[1] The electronic fingerprints of these states are easy to identify using the shift in the binding energy of their core electrons but the exact geometry (e.g. surface oxygen, oxygen adsorbed at undercoordinated step/edge sites) remains unclear. Our ultimate objective is to establish a direct connection between the geometric and electronic structure of surface oxygen species on Ag (silver) surfaces under relevant catalytic conditions and how it relates to chemical and catalytic activity.

We began analyzing this problem by attempting to establish a link between the geometric and electronic structure of atomic oxygen species on Ag surfaces using DFT calculations and Monte Carlo simulations. Establishing such a link is critical for the characterization of various oxygen species that exist on the surface of Ag during catalytic oxidation reactions. At this point the geometric structure of the relevant, catalytically active oxygen atoms on Ag surfaces is unknown. Various structures have been proposed based on the analysis of the electronic fingerprint associated with active oxygen atoms. The insight is critical for understanding the origin of the surface reactivity of silver surfaces in oxidation reactions.

First we report the computational methods and models used including Density Functional Theory, Cluster Expansion, and Monte Carlo simulations. We discuss the application of Density Functional Theory to predicting core-level shifts using the complete screening approximation. Next we discuss some of the results obtained for Lithium/Oxygen batteries including energetics

of a proposed mechanism and a new model system for future studies that addresses some of the shortcomings of this model. We also discuss results from the coarse-graining of Density Functional Theory calculations using the Cluster Expansion method and show some preliminary results of a Monte Carlo simulation of oxygen on a silver surface. We present some preliminary work of calculating the core-level shifts of some surface and bulk silver/oxygen structures.

2. METHODS

2.1. Density Functional Theory

Density Functional Theory (DFT) was used to obtain the ground-state electronic energy and electronic structure information of individual model systems. Density Functional Theory numerically solves Schrödinger's equation to obtain electronic structure information and the ground-state electronic energy with relatively economical computational difficulty while maintaining reasonable accuracy. The electronic energy can be used to study elementary steps of chemical reactions as well as construct phase diagrams. The effects of finite temperature can be accounted for by adding entropic effects in Eq. 1:

$$\Delta G = \Delta E_{DFT} - T\Delta S + pV \quad (1)$$

It has been shown that the term pV is small and fairly constant for adsorbates on metal surfaces, so Eq. 1 simplifies to Eq. 2:

$$\Delta G = \Delta E_{DFT} - T\Delta S \quad (2)$$

The entropic contribution $T\Delta S$ can be calculated either from standard thermodynamic tables or from *ab-initio* analysis. Electro-catalytic systems such as batteries, fuel cells, and electrolyzers operate under potential bias. This can be accounted for by correcting for the free energy of charged species under a potential bias, relative to a reference potential in Eq. 3:^{[2], [3]}

$$\Delta G = \Delta G(0) + nF(U_{REF}) \quad (3)$$

Second-order effects from electric fields at the surface can be calculated with DFT; these effects are small and have been neglected in this study.^[4] DFT calculations were performed using both the GPAW^[5] and Dacapo^[6] computer codes in the Atomic Simulation Environment.^[6] Dacapo is a mature implementation of DFT using the ultrasoft pseudopotential plane wave method with the generalized gradient approximation (GGA-PW91). GPAW is a real-space grid-based implementation of DFT with the projector-augmented wave method.

2.2. Cluster Expansion

Electronic state calculations including those in the framework of Density Functional Theory are computationally expensive and sample a limited region of the configuration space. To reasonably sample the configuration space of oxygen adsorbed on silver or incorporated into subsurface sites we employed a cluster expansion method to coarse-grain quantum-chemical energy using a lattice gas Hamiltonian model. The energy of a system is described as a combination of effective interaction potentials described by Eq. 4:

$$E(\vec{\sigma}, \vec{\delta}) = E_0 + \sum_j V_j \delta_j + \sum_i V_i \sigma_i + \sum_{i,j} V_{ij} \sigma_i \sigma_j + \sum_{i,j} V_{ij}^I \delta_i \delta_j + \sum_{i,j} V_{ij}^{II} \sigma_i \delta_j + \dots \quad (4)$$

Where V corresponds to effective cluster interactions (ECI), σ and δ correspond to occupation numbers for different species, and indices i and j correspond to a collection of sites that form a ‘cluster’ such as a single site, a pair, a triplet, etc. Completeness of the basis set of effective cluster interactions ensures accurate representation of the energy. In a feasible implementation, however, the basis set must be truncated in both distance and size (single, pair, triplet).

The ECI parameters were calculated by minimizing the square of the residual, (χ) between the DFT calculated energies (E_{DFT}) and cluster expansion prediction (E_{CE}) for each DFT calculation (i) in the DFT library of N calculations, in Eq. 5:

$$\chi^2 = \frac{1}{N} \sum_i^N (E_{DFT}^i - E_{CE}^i)^2 \quad (5)$$

We focus on oxygen on Ag and have explicitly included (i) oxygen atoms on the Ag(111) surface of silver, (ii) step sites to model catalyst surfaces that contain under-coordinated Ag sites and (iii) subsurface oxygen atoms. Atomistic lattice-gas models for oxygen adsorption on the (111) facet of an fcc metal typically involve a 2-dimensional triangular lattice with two types of three-fold surface sites; shown in Fig. 1. The (111) facet dominates the surface of many metal catalysts such as Ag and Au and is an attractive model system in its simplicity. Real nanoparticles have under-coordinated step and edge sites (see Fig. 2) that differ chemically and catalytically from this ideal model system and these sites have been known to drive the reactivity of some catalytic particles as well as facilitate undesired side reactions. To this end we have explicitly included step sites in our Cluster Expansion/Monte Carlo approach to model under-coordinated step and edge Ag atoms.

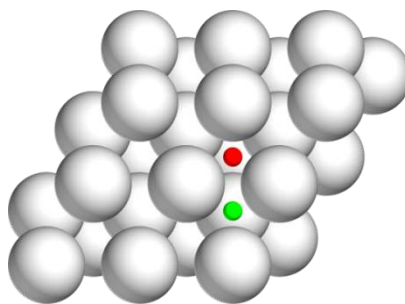


Figure 1. Metal surface depiction demonstrating fcc-type (red) and hcp-type (green) three-fold adsorption sites.

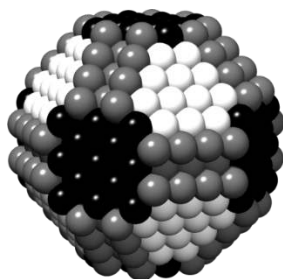


Figure 2. Sample nanoparticle depiction with (111), (110), and (100) facets; white, gray, and black, respectively.

2.3. Monte Carlo

A Grand Canonical Monte Carlo simulation using the Metropolis algorithm was employed to probe the effects of environmental conditions (T, partial pressure of gas-phase reactants)^[7]. The Metropolis algorithm determines the probability of trial Monte Carlo moves from an initial state (m) to final state (n) shown in Eq. 6:^[8]

$$\rho_{m \rightarrow n} = \min \left\{ 1, \frac{\rho_n}{\rho_m} \right\} \quad (6)$$

where the probability for each state (ρ_i) is defined from the Boltzmann distribution. These simulations incorporated particle insertion and particle removal, with a transition probability for particle insertion (Eq. 7)**Error! Reference source not found.** and particle removal (Eq. 8):

$$\rho_{insertion} = \begin{cases} 1 & \Delta E \leq 0 \\ e^{-\beta(\Delta E - \Delta\mu_0)} & \Delta E \geq 0 \end{cases} \quad (7)$$

$$\rho_{removal} = \begin{cases} 1 & \Delta E \leq 0 \\ e^{-\beta(\Delta E + \Delta\mu_0)} & \Delta E \geq 0 \end{cases} \quad (8)$$

with the chemical potential of the gas phase species $\Delta\mu_0 = f(T, P_{O_2})$ and ΔE calculated from the cluster expansion. Many trial moves (10^7) are performed until oxygen coverage and system energy are converged within the limit of statistical fluctuation.

2.3. Core-level Shifts

Previous studies of oxygen chemistry on silver surfaces have focused on identifying the states of oxygen (electrophilic, nucleophilic, neutral) that drive activity/selectivity.^{[1][9]} These states are probed experimentally by using x-ray photoelectron spectroscopy (XPS) to determine the shift of the binding energy of the O 1s electron. The physical structure of the oxygen corresponding to each state is not well understood and we hope to match the calculated core-level shifts of stable structures presented by the Monte Carlo simulations to experimentally

measured electronic fingerprints. The binding energy of core electrons determined from XPS is calculated as Eq 9:

$$E_B = h\nu - \phi - E_K \quad (9)$$

Where E_B is the core-level binding energy, $h\nu$ is the x-ray energy, ϕ is the work function and E_K is the kinetic energy of the ejected photoelectron. In the complete screening approximation the core-level binding energy is the difference between the total energies of a system in its initial state and in the final state with a core vacancy. This can be calculated directly in GPAW by using the Δ SCF method.^[10]

3. RESULTS

3.1. Lithium/Oxygen Battery Chemistry

Twenty five different lithium/oxygen structures were sampled on a platinum surface using the Dacapo code to determine relative stabilities. Single- and multi-layer Li/O overlayers as well as Li_xO_y clusters were used, similar to some model systems in the literature.^[11] A small sample of some of the more stable species is found in Fig. 3. This phase diagram shows that under charging operating conditions (potentials above 2.96 V), small clusters of lithium and oxygen are the most stable structures on the surface of a gold catalyst.

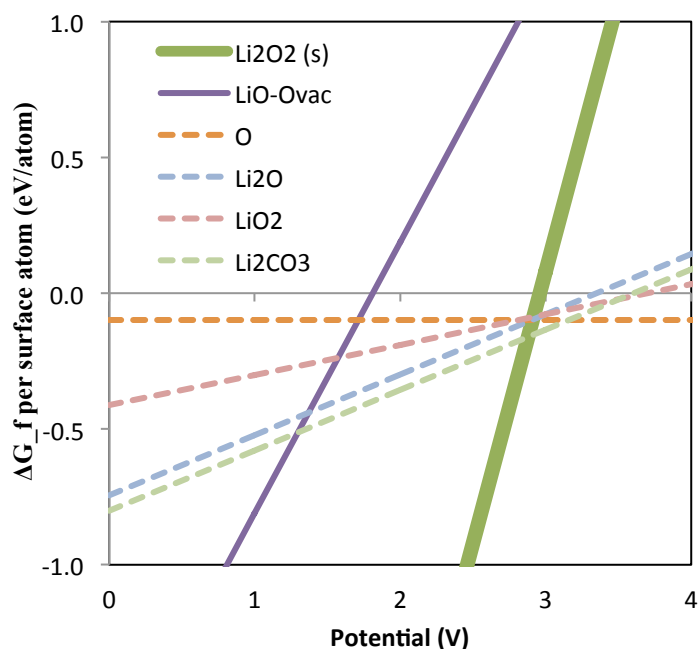


Figure 3. Li/O phase diagram

A simple system of elementary steps for modeling the oxygen evolution reaction was evaluated, with intermediates of LiO, Li_2O , and LiO_2 proposed as intermediates to this reaction that generates Li_2O_2 . The most favorable mechanism is depicted in Fig. 10. The overpotential over an Au catalyst has been experimentally determined to be around 1 eV. Using our DFT calculations in a method by Nørskov et al.^[12], the lowest overpotential proceeding through these intermediates over gold was predicted to be 2.8 V, shown in Fig. 4. This overprediction suggests that this model system is insufficient and must be improved.

To study the solid/solid interface between metal catalyst surface and lithium peroxide we propose modeling the catalytic surface using a model system comprising a metal slab with Li_2O_2 nanowire, shown in Fig. 5. This explicitly includes the quantum-chemical effects of the catalyst/reactant interface in the Density Functional Theory system. Such a system has been used to describe catalytic effects of solid/solid interfaces previously.^[13]

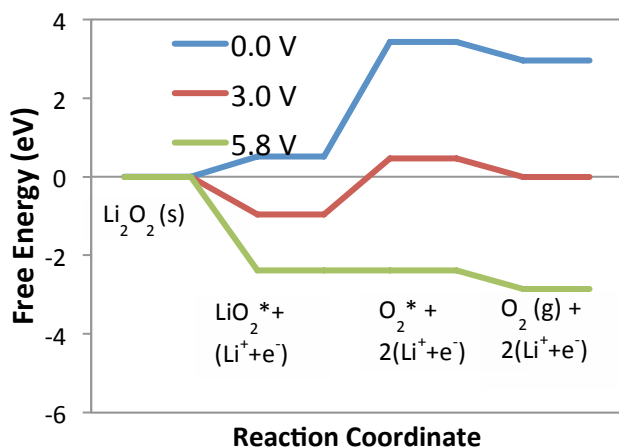


Figure 4. Prediction of the overpotential for Oxygen Evolution (charging) Reaction over Au(111) surface

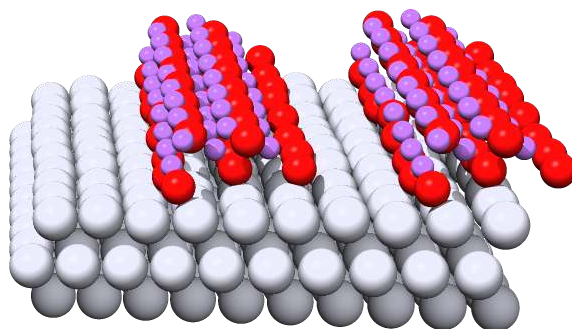


Figure 5. Proposed system for modeling solid/solid interface of metal surface and lithium peroxide. Gray, purple, and red spheres denote platinum, lithium, and oxygen atoms, respectively.

3.2. Cluster Expansion

A representative DFT model system used for the cluster expansion calculations can be found in Fig. 6 (side view and top view, Ag(322) repeated unit cell 2x2). DFT calculations were performed using Dacapo with the generalized gradient approximation. The wave functions are expanded in plane waves with an energy cutoff of 350 eV. Adsorbate atoms and the top layer of the silver slab are relaxed until the force on each atom is lower than 0.1 eV/Å. 9 irreducible Monkhorst-pack k-points are used for the Brillouin zone integration of the smallest 2x1 unit cell. Equivalent k-point sampling is used for all DFT calculations to maximize the precision when comparing the energies of structures in differently sized unit cells. Finite temperature Fermi smearing ($kT=0.1$ eV) is employed to facilitate SCF convergence, with the total energy extrapolated back to $kT=0$ eV.

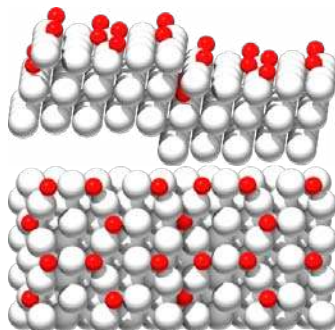


Figure 6. Top and side view of Ag(322) model system

Intra-terrace near neighbor interactions up to 6th near neighbor (Fig. 7, left) and up to equivalent 3rd near neighbor distance are included over a step (Fig. 7, right). Interactions containing subsurface oxygen species interactions up to 4th near neighbor were included.

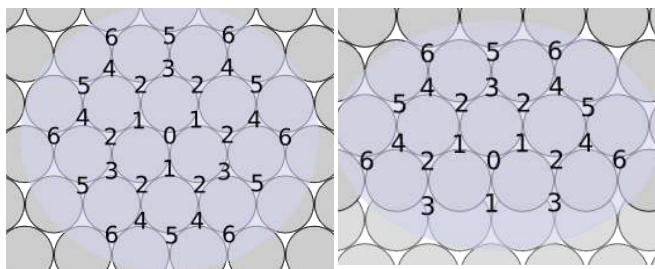


Figure 7. Near neighbor stencils for terrace (left) and step sites (right)

Based on a limited number of DFT calculations (~161) we have calculated a set of terrace and step-site oxygen interaction parameters. The correlation between Cluster Expansion-calculated and DFT-calculated energy for each DFT calculation can be found in Fig. 5. The ECI parameters yielded a cross-validation score of ~0.2 eV. The CV score is a quantization of the error of the predictive model and can be improved by introducing additional calculations. The correlation of DFT calculated energy and the fitted Cluster Expansion energies can be found in Fig. 8. The interaction potentials give us the ability to predict adsorbate geometric structures under catalytically relevant conditions. Ideally the cross-validation score will be brought down below 0.1 eV by running additional calculations to increase the frequency of each interaction parameter in the library. It can also be improved by including more expansion terms such as three-body terms.

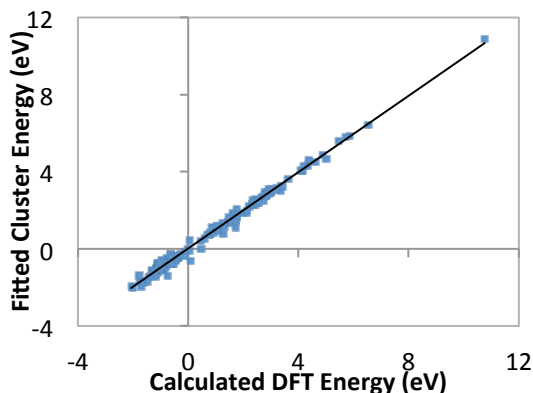


Figure 8. Correlation between DFT library and fitted cluster-calculated energies

3.3. Monte Carlo Simulations

The important question we are addressing is determining the relative partitioning between various oxygen species on a metal surface. Many have argued that the existence of sub-surface oxygen is important for catalytic performance. Using Grand Canonical Monte Carlo simulations, we investigated the partitioning of on- and sub-surface oxygen, focusing on step, terrace, and subsurface oxygen under different oxidation conditions. The energy difference associated with each Monte Carlo step is calculated using the Cluster Expansion interaction potentials procedure, outlined above. Results from this simulation are found in Fig. 9 where the amount of various oxygen species at an O_2 partial pressure of $1.0e-8$ atm is determined as a function of temperature. Snapshots of relevant structures can be found in Fig. 10. We found that subsurface oxygen exists only at low temperatures, $<350K$. A strong interaction between oxygen and undercoordinated Ag atoms allows for oxygen to remain adsorbed at higher temperatures. The structures identified in this simulation will be used with Core-level shift calculations in the future.

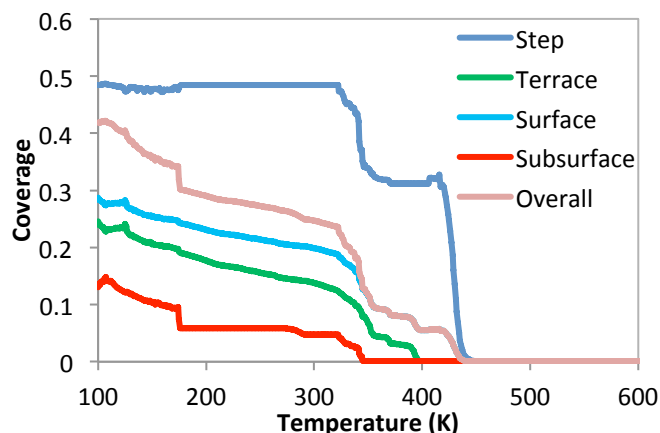


Figure 9. Oxygen coverage at varying temperature predicted by Monte Carlo simulations

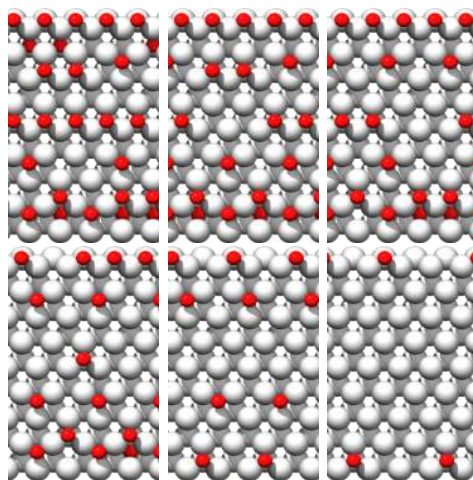


Figure 10. From top left to bottom right, snapshots at 150K, 250K, 300K, 330K, 350K, and 400K

3.4. Core-level Shifts

As stated above, the main objective of the project is to relate the geometric structure of oxygen atoms on silver to their electronic structure. This will allow experimentalists to properly assign their measured electronic structure to geometry and ultimately it will shed light on the critical physical and electronic factors governing the functionality of specific oxygen species. An experimental technique often used to measure the electronic structure of oxygen in Ag catalysis is x-ray absorption spectroscopy. We have started to simulate the core-level shift (CLS) (i.e., XPS spectra) associated with the molecular structure of the various states of oxygen atom on Ag. These calculations were performed using a real-space grid-based implementation of DFT with the projector-augmented wave method. A revised Perdew-Burke-Ernzerhof (RPBE) functional was used to approximate exchange-correlation interactions. In our initial studies we focused on Ag(111) surfaces using a $2 \times 2 \times 3$ slab with 10 Å of vacuum space. We used 18 irreducible k -points and a grid spacing of 0.2 Å. Oxygen atoms were adsorbed on different sites of the surface and subsurface. The O adsorbate and top two layers of the slab were allowed to relax until the force on all atoms was converged to less than 0.1 eV/Å. The finite temperature Fermi function ($k_B T = 0.1$ eV) is utilized to facilitate the SCF convergence by smearing the band occupation around the Fermi level, and the total energy of the system is extrapolated back to $k_B T = 0$ eV. The complete screening model is used as an approximation to evaluate the core-level binding energies of the O1s electron. The main assumption of the complete screening model is that the conduction electrons are fully relaxed in the presence of a core-hole. The core-level shifts can then be directly calculated with respect to a particular reference state. We used the bulk of Ag_2O as the reference state. The calculated CLSs for atomic oxygen on Ag(111) surfaces with varying coverage of subsurface oxygen with respect to Ag_2O bulk are shown in Fig. 8. The calculated CLS for experimentally identified Ag_{12}O_6 surface oxide agrees with measurement very well, showing that the O1s electron has lower binding energy, i.e., nucleophilic character. We also observed that the atomic oxygen with the existence of subsurface oxygen has higher binding energy, indicating their electrophilic character. We have just begun these calculations, and we will continue them in future studies.

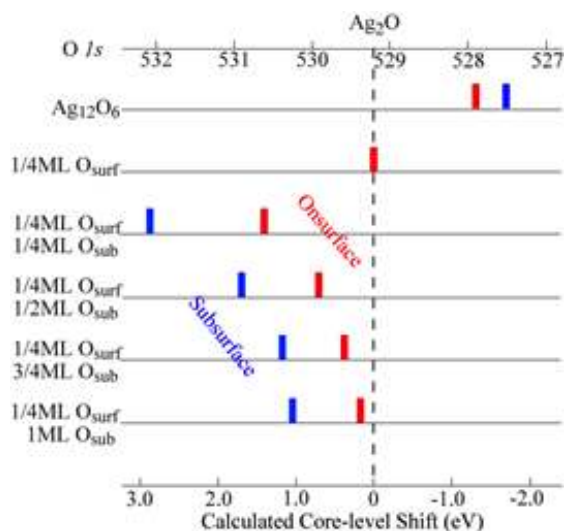


Figure 11. CLSs of oxygen species on Ag(111) surface calculated using the complete screening approximation.

4. SUMMARY

This report describes work done in computational heterogeneous catalysis for two test cases involving multi-phase interfaces; lithium/oxygen batteries and oxygen chemistry on silver surfaces under relevant reaction conditions.

The lithium/oxygen battery test case was evaluated using DFT calculations showing the thermodynamically favorable surface conditions to have relatively low coverage of lithium/oxygen clusters. A few elementary-step reactions tested using DFT showed little agreement with experimental results. The next step in this research is evaluating a solid/solid interface between discharge product (Li_2O_2) and catalytic surface, which has been outlined in Section 3.1.

The oxygen/Ag test case was evaluated by coarse-graining DFT calculations through the Cluster Expansion method. The results of the calculation of interaction parameters are presented; the cross-validation score remains higher than desired and can be improved by adding more DFT calculations to the library or by adding more interaction potentials such as three-body. This information was used in Monte Carlo simulations to produce a phase diagram showing partitions of oxygen over a wide range of temperatures. Some predictions of oxygen/Ag core-level shifts have also been made by Density Functional Theory with the results agreeing with experimental results.

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