



Molecular level investigation of the interaction of cerium dioxide layer on steel substrate used in refrigerating systems

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Abstract

The use of cerium coating in corrosion inhibition of refrigerating systems provides an environmentally acceptable approach than the traditional chromium coating which is restricted. However the integrity of the films produced by cerium coatings is still a matter of concern and active research. The simulations presented here are, to our knowledge, the first atomistic simulation of cerium dioxide coating on steel substrate. Although some approximations were made, this does provide a starting point that can be refined in future efforts. The interactions between the cerium dioxide molecules favor dense packed films rather than isolated molecules on Fe (111) surface.

Keywords: Molecular dynamics; Interaction energy; Cerium coating; Corrosion inhibition

1. Introduction

The coating of steel and other metals is important in the control and prevention of corrosion. The mitigation of corrosion can be achieved economically by the use of corrosion inhibitors. Chromates have been extensively used in an aqueous environment for the protection of steel. Although chromates are cheap and effective, they are not acceptable because their toxicity. Alternative inhibitors such as molybdates, organic inhibitors such as phosphonates, mixtures of phosphate, borates and silicates and surfactants like sulphonates have been used in place of chromates. Chromates are anodic inhibitors and help to form passive oxide on the metal surface. In recent years, the use of rare earth metal salts as inhibitors has been gaining attention [1].

It is well known that lanthanide ions form insoluble hydroxides [1] which enable them to be used as cathodic inhibitors. Lanthanides have a low toxicity and their ingestion or inhalation has not been considered harmful to health [2] whilst the toxic effects of them are similar to those produced by sodium chloride. [3] Furthermore, lanthanides can be considered as economically competitive products [4] because, as elements, some of them are relatively abundant in nature; [5] cerium, for instance, is as plentiful as copper. [6] Production of lanthanides has shown a continuous increase in recent years. [7] Taking all these facts into account, it is reasonable to consider the development of corrosion protection methods using this family of compounds.

At first, the lanthanide elements, principally cerium, were used in protection against corrosion at high temperatures. Using several incorporation methods, cerium and, to a lesser extent, other Rare Earth (RE) elements have been used to improve the adherence of oxide films developed during the oxidation processes of different metallic alloys.[8-15]

The nature of the film which may protect the underlying metal from corrosive attack in a given environment plays a crucial role in determining the rate of metal loss. Under passive conditions the oxide film present on the surface of the metal is naturally protective and leads to low corrosion rates.

The earliest applications of lanthanides as corrosion inhibitors were stimulated by the need to replace chromates imposed by new international environmental standards. There are several papers in the literature dealing with the use of lanthanides as corrosion inhibitors for several metals and alloys [16-38]

The use of cerium coating in corrosion inhibition of refrigerating systems provides an environmentally acceptable approach than the traditional chromium coating which is restricted. However the integrity of the films produced by cerium coatings is still a matter of concern and active research. Among all the lanthanide compounds, cerium salts have successfully been used as corrosion inhibitors on different metals and alloys [39-45].

The aim of the work presented here is two-fold: (1) to develop a technique for performing explicit molecular dynamic simulations of cerium dioxide film supported on iron substrate, and (2) to compute the interaction energy between the cerium dioxide layer and the iron substrate. The simulation methodology is presented in the computational details section and the results for interaction energy are discussed in the results and discussion section followed by our main conclusions.

2. Computational details

Steel is compositionally an alloy of iron, carbon and some trace metals. Iron is the primary ingredient in general structural steels. At temperatures $< 912^{\circ}\text{C}$, bulk-iron metal has the stable crystalline structure of body-centered cubic (bcc) [46]. In this study, the (111) surface is modeled to investigate the stable surface of iron. The carbon and the trace metals are not modeled due to their scarcity to appear in a typical atomic-scale domain. The condition of a typical ambient environment is simulated—at a temperature (298K) and under one standard atmospheric pressure (1 ATM). The atmospheric corrosion could occur at a relative humidity $> 60\%$, above which the steel surface is moist as covered with a coherent film of water [46]. In building the steel system model, 32 Fe atoms forming a thin iron sheet (with a thickness of 2 iron atoms) are included in a bulk water domain at a pH of 7 in a simulation box.

The state of adhesion of cerium dioxide coat at the steel/solution interfaces is new approach in studying the inhibition effectiveness in corrosion science research. The semi-empirical computational methods have been used most successfully in finding correlation between theoretically calculated properties and experimentally determined inhibition efficiency for uniform corrosion [47-57]. In the present study, we are reporting on some attempts to elucidate the film properties of the cerium dioxide coating on steel substrate in aqueous solutions using semi-empirical methods as well as molecular dynamics simulation techniques. Cerium dioxide coating has been simulated as adsorbate on Fe (111) substrate to find the interaction energy between the steel surface and the cerium dioxide layer. The geometry optimization process is carried out for the studied cerium dioxide using an iterative process, in which the atomic coordinates are adjusted until the total energy of a structure is minimized, i.e., it corresponds to a local minimum in the potential energy surface. The forces on the atoms in the cerium dioxide atoms are calculated from the potential energy expression and will, therefore, depend on the force field that is selected.

Interaction between CeO_2 film and Fe (111) surface was carried out in a simulation box ($14.27 \text{ \AA} \times 14.27 \text{ \AA} \times 44.7 \text{ \AA}$) with periodic boundary conditions to model a representative part of the interface devoid of any arbitrary boundary effects. The Fe (111) was first built and relaxed by minimizing its energy using molecular mechanics, then the surface area of Fe (111) was increased and its periodicity is changed by constructing a super cell, and then a vacuum slab with 15 \AA thicknesses was built on the Fe (111) surface. The number of layers in the structure was chosen so that the depth of the surface is greater than the non-bond cutoff used in calculation. Using 2 layers of Fe (111) atoms gives a sufficient depth that the cerium dioxide coat will only be involved in non-bond interactions with Fe (111) atoms in the layers of the surface, without increasing the calculation time unreasonably. This structure then converted to have 3D periodicity. As 3D periodic boundary conditions are used, it is important that the size of the vacuum slab is great enough (15 \AA) that the non-bond calculations for the cerium coat does not interact with the periodic image of the bottom layer of atoms in the surface. After minimizing the Fe (111) surface and CeO_2 (111)

layer molecules, the corrosion system will be built by layer builder to place the CeO₂ (111) molecules on Fe (111) surface, and the behaviours of these molecules on the Fe (111) surface were simulated using the COMPASS (condensed phase optimized molecular potentials for atomistic simulation studies) force field. The Discover molecular dynamics module in Materials Studio 5.0 software from Accelrys Inc. [58] allows selecting a thermodynamic ensemble and the associated parameters, defining simulation time, temperature and pressuring and initiating a dynamics calculation. The molecular dynamics simulations procedures have been described elsewhere [59]. The interaction energy, $E_{\text{Fe-CeO}_2}$, of the Fe (111) surface with CeO₂ coating was calculated according to the following equation:

$$E_{\text{Fe-CeO}_2} = E_{\text{system}} - (E_{\text{Fe (111)}} + E_{\text{CeO}_2}) \quad (1)$$

where E_{system} is the total energy of the Fe (111) surface together with the CeO₂ coating, $E_{\text{Fe (111)}}$ and E_{CeO_2} are the total energy of the Fe (111) surface and free CeO₂ coating, respectively. The binding energy between CeO₂ coating and Fe (111) surfaces were the negative value of the interaction energy [60], as follow:

$$E_{\text{binding}} = -E_{\text{Fe-CeO}_2} \quad (2)$$

In this atomistic simulation study we use explicit atom molecular dynamics in our study of forming cerium dioxide film on iron substrate. This technique has been successfully used in the past in studies of free lipid bilayers in aqueous solution [61,62]. With this approach, we capture the bonded and non-bonded interactions between atoms at a fundamental level. Although such simulations of such systems are often computationally limited to small sizes, we can capture the dynamical behavior of these systems at the smallest end of the spectrum of length and time scales. Since macroscopic properties arise from the ensemble behavior of individual atoms, molecular dynamics allows us to extract the macroscopic interaction energy between the film and the substrate using an atomistic perspective [46].

The atomistic simulations provide a detailed view of the interaction between the cerium dioxide layer and substrate allowing us to extract the interaction energy of the cerium dioxide layer with iron substrate. Analytical calculations of the interaction energy offer a means to understand the corrosion inhibition properties of cerium dioxide coat on steel substrate.

To do these tasks, CASTEP which is a state-of-the-art quantum mechanics-based program designed specifically for solid-state materials science. CASTEP employs the density functional theory plane-wave pseudopotential method, which allows performing first-principles quantum mechanics calculations that explore the properties of crystals and surfaces in materials such as semiconductors, ceramics, metals, minerals, and zeolites.

3. Results and discussion

3.1 Predicting the thermodynamic properties of cerium dioxide:

Linear response, or density functional perturbation theory (DFPT), is one of the most popular methods of ab initio calculation of lattice dynamics. However, potential applications of the method extend beyond the study of vibrational properties. Linear response provides an analytical way of computing the second derivative of the total energy with respect to a given perturbation [63]. Depending on the nature of this perturbation, a number of properties can be calculated. A perturbation in ionic positions gives the dynamical matrix and phonons; in magnetic field - NMR response; in unit cell vectors - elastic constants; in an electric field - dielectric response, etc. The importance of the phonon interpretation of lattice dynamics is illustrated by the large number of physical properties that can be understood in terms of phonons: infrared, Raman, and neutron scattering spectra; specific heat, thermal expansion, and heat conduction; electron-phonon interaction and thus resistivity and superconductivity, etc. Density Functional Theory (DFT) methods can be used to predict such properties and CASTEP provides this functionality [63].

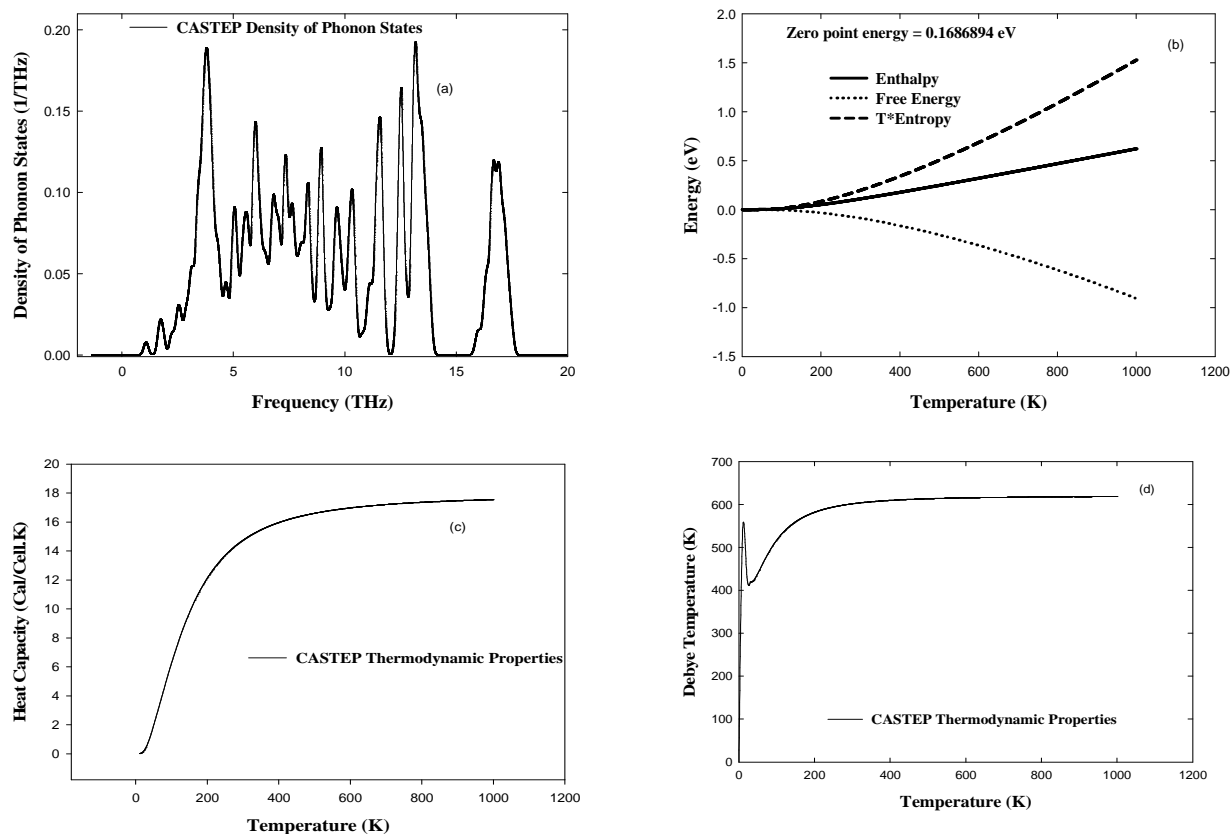


Fig. 1: CASTEP thermodynamic properties for CeO_2

Phonon calculations in CASTEP [64–65] (Fig. 1a) can be used to evaluate the temperature dependence of the enthalpy, entropy, free energy, and lattice heat capacity of a cerium dioxide crystal in a quasi-harmonic approximation. These results can be compared with experimental data (for example heat capacity measurements) or used to predict phase stability of different structural modifications or phase transitions. All energy-related properties Fig. 1b,c,d are plotted on one graph Fig. 1, and the calculated value of the zero-point energy is included, Fig. 1b. The heat capacity is presented in Fig. 1d. It should be noted that the quasi-harmonic approximation, on which the phonon calculation is based, becomes inefficient at temperatures higher than one third of the Debye temperature (Fig. 1d). As a result, at temperatures higher than the Debye temperature, anharmonic effects appear that cannot be explained by a change of volume alone. Fig. 1b shows that the CeO_2 layer is thermodynamically stable which according to CASTEP calculations.

3.2 Calculation of packing energy for cerium dioxide film

The water/metal interface is critical to the performance of a number of chemical and materials systems including electrocatalysts for fuel cells, corrosion resistant metal alloys, and electrochemically-deposited electronic and magnetic films. The reactivity and electrochemical behaviour of the metal/solution interface is dictated by the explicit atomic and electronic structure that forms at the interface as a response to environmental conditions such as an applied potential [66]. Elucidating the structure and chemistry at this interface, however, is a considerable challenge due to the large number of molecular configurations that result from different water molecule orientations in the hydrogen bonded network, the presence or formation of ions and their positions within the interface and the potential reactions that can occur between these species [67].

Prior to molecular dynamics calculations, geometry optimization has been performed for CeO_2 (111) as indicated in Fig. 2.

Figure 3 shows cerium dioxide layer, iron layer, cerium dioxide layer on iron layer and a snap shot of the whole solvated system undergo molecular dynamic experiments. From the molecular dynamic simulations studies, the calculated packing energy for cerium dioxide film on iron substrate (111) is presented in Fig. 4.

Figure 4 shows the calculated packing energy as a function of area per molecule for the cerium dioxide coating on Fe (111) surfaces. For the Fe(111) surface a minimum of -31.7 kJ mol⁻¹ is found at a packing of 61 Å² per molecule. In Fig. 4, as the film density increases at high area per molecule the interaction energy decreases smoothly. This indicates that there is a driving force for film formation through favourable interactions between cerium dioxide molecules and iron substrate.

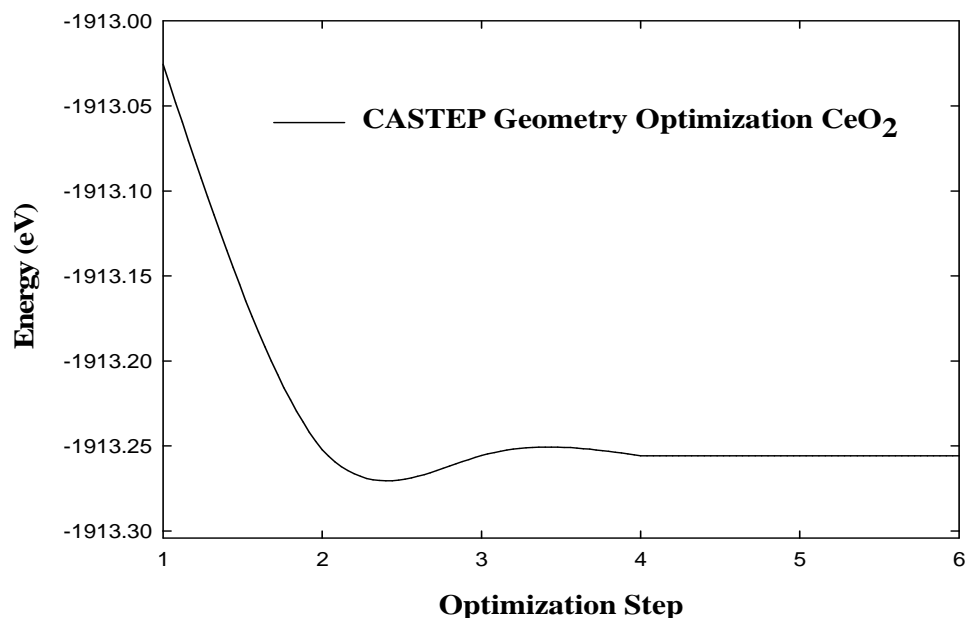
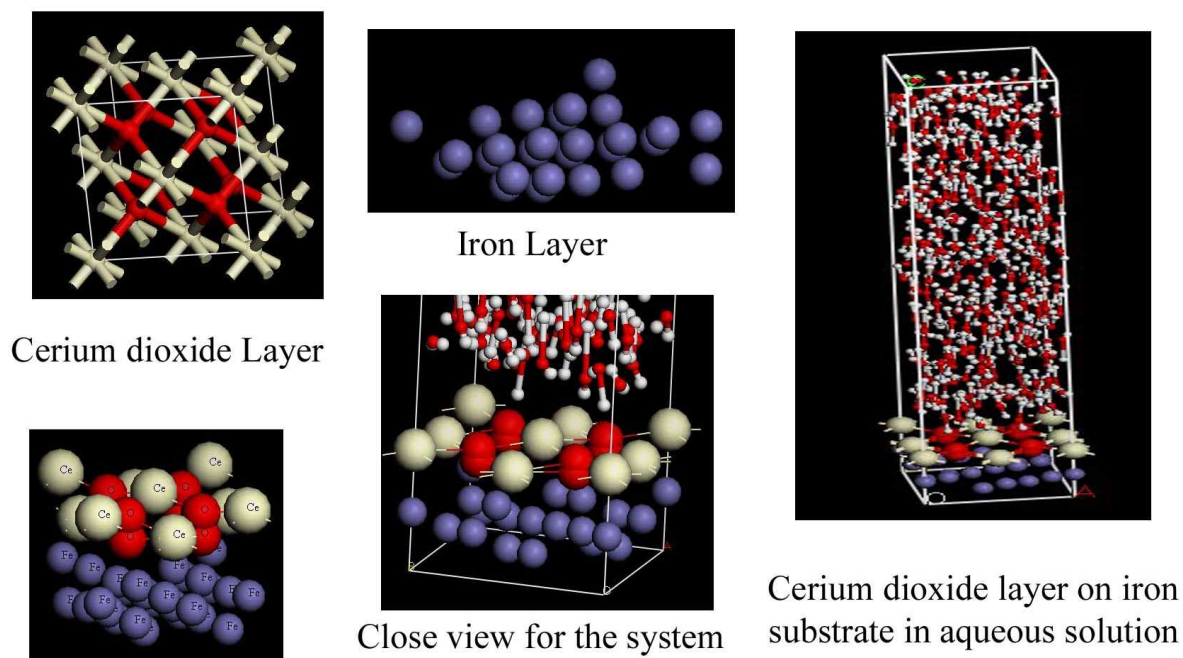


Fig. 2: Geometry optimization for CeO₂ (111) layer



Cerium dioxide Layer on iron (111)

Fig. 3: Snap shots of the molecular dynamics simulations for CeO₂, Fe (111) and the solvated corrosion system

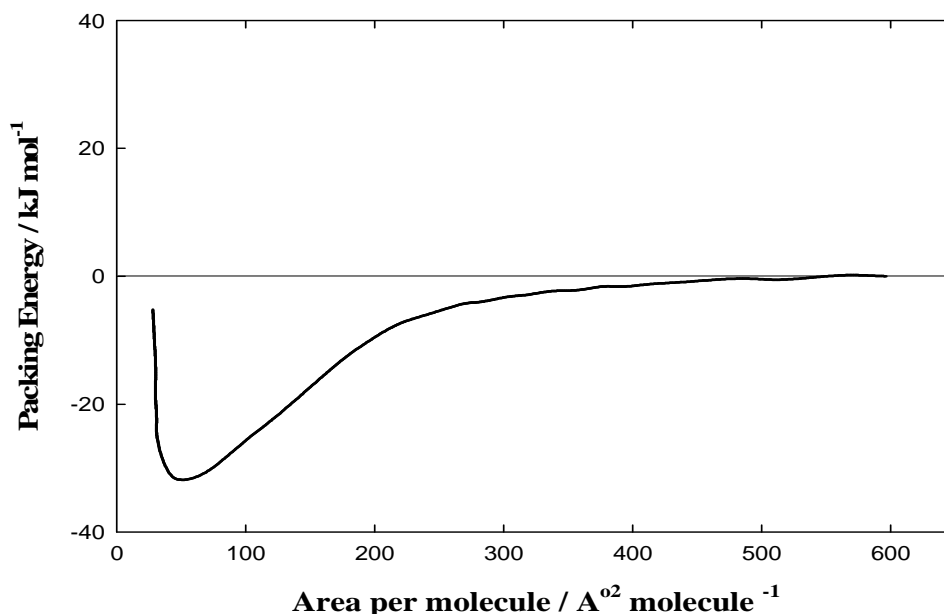


Fig. 4: calculated packing energy as a function of area per molecule for the cerium dioxide coating on Fe (111) surfaces

The formation of a rare earth metal oxide on the metal surface impedes the cathodic reduction of oxygen and thus cathodic inhibition achieved by the addition of a rare earth metal salt to a system. The surface atom concentration ratio, [Ce/Ce+Fe] [68]. The metal surface is covered with cerium dioxide and the thickness of the film increases with time. Deposition and growth of islands of rare earth oxide have been observed [46]. The islands may be associated with anodic and cathodic sites located in the microstructure of the steel surface.

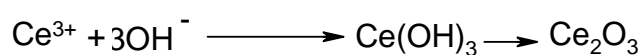
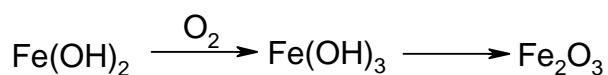
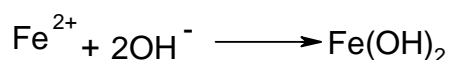
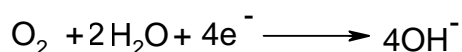
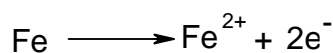
The interaction of cerium dioxide layer with Fe (111) surface was investigated with molecular dynamics (MD) simulation as seen in Fig. 3. An adsorption model containing one cerium layer and metallic surface was built using Discover module in Materials Studio 5.0 software. During simulations, all the bulk atoms in the Fe (111) systems were kept “frozen”, and the cerium layer were allowed to interact with the metal surface freely. The simulation system was optimized with COMPASS force field [69]. The canonical ensemble MD simulation was performed with Discover module in Materials Studio 5.0. The simulation temperature was set at 298 K, and the temperature was controlled by Andersen thermostat [70].

The cutoff radius was 1.2 nm, and the intermolecular interaction energy beyond cutoff radius was revised with average density approximation. The time step was 1 fs, the simulation time was 1000 ps, and a frame was recorded every 2500 steps during simulation [71].

The values of the interaction energy and the binding energy of the studied cerium dioxide layer on Fe (111) surface equals -563.8 and 563.8 kJ mole⁻¹, respectively. The higher the binding energy, the more easily the adhesion of cerium layer to iron substrate, the higher is the inhibition efficiency [72].

3.3 Mechanism of inhibition

Based on the electrochemical polarization and surface analytical data available in the literature, it is possible to surmise the following mechanism for inhibition by rare metal salts [73]:



Conclusion

The simulations presented here are, to our knowledge, the first atomistic simulation of cerium dioxide coating on steel substrate. Although some approximations were made, this does provide a starting point that can be refined in future efforts. The interactions between the cerium dioxide molecules favour dense packed films rather than isolated molecules on Fe (111) surface.

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