DFT study of the interaction of chloride with hydroxylated NiO(111) surfaces

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Localized interactions of chloride ions with passivated surfaces can cause the breakdown of passivity and the localized attack of the substrate, leading to localized corrosion (pitting). One of the proposed mechanisms for the initiation of localized corrosion involves the adsorption of Cl^- on the passive film surface followed by penetration of Cl^- into the oxide layer. On Ni(111), it has been shown that the passive film consists of an ultra-thin film (1nm) of NiO(111) with a surface layer of hydroxyls[1,2].

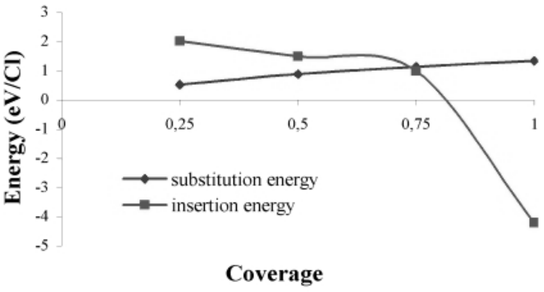
Theoretical chemistry can provide useful atomic scale information on the interaction of chlorides with hydroxylated oxide surfaces. The recent advances in the atomic scale modeling of periodic systems offer new possibilities of applications to surface chemistry. The objective of this work was a Density Functional Theory (DFT) investigation of the substitution of surface hydroxyls by chlorides on hydroxylated NiO(111) surfaces and the insertion of Cl^- into the oxide lattice, two processes that form the basis of the penetration mechanism of the initiation of localized corrosion.

The calculations were performed using the Vienna *ab initio* simulation package (VASP)[3,4]. VASP performs an iterative solution of the Kohn-Sham equations of density functional theory using residuum-minimization techniques and an optimized charge-density mixing routine. The surfaces were modeled by periodically repeated slabs. For anhydrous NiO(111), the slab consisted of three NiO layers forming seven atomic layers: 3 Ni layers and 4 O layers, the two outmost O layers being half layers so that the overall stoichiometry of the slab was respected. Vacuum was inserted using a cell vector perpendicular to the surface plane of 1.5 nm. The atomic positions of the first atomic layers (three for the calculations involving chloride ions, four for all other cases) were frozen using bulk parameters. Relaxation of the atomic positions in the remaining layers was only allowed along the direction perpendicular to the surface. Brillouin zone integrations have been performed using grids which sizes were adapted to the size of the unit cell used.

The results show that the dissociative adsorption of water (hydroxylation) is more favorable than the molecular adsorption and that it stabilizes the NiO(111) surface. The most stable configuration was obtained with 100% coverage of hydroxyl groups perpendicular to the surface plane. The reconstruction of the NiO lattice observed in the absence of adsorbed water was lifted with the Ni and O atoms very near their bulk positions. The adsorption energy is –0.25 eV per water molecule.

The adsorption of Cl^- was considered by replacing the surface hydroxyl ions (OH^-), and their insertion by exchanging the adsorbed Cl^- with the lattice O^{2-} ions. Different surface concentrations were modeled: 25%, 50%, 75% and 100%. The results show that the local structure of the oxide layer is strongly related to the coverage with Cl^- ions. While reconstruction for the pure hydroxylated surface was negligible, that with a low Cl^- coverage leads to a significant surface reconstruction. The atoms at the surface tend to separate from the bulk atoms isolating a stoichiometric buckled layer. Such a separation is much less crucial for high Cl^- coverage: only few bonds tend to disappear. Not surprisingly considering the ionic radius of a Cl^- ion, a disordering of the oxide layer is observed when considering the insertion of a chloride ion in the inner atomic layers.

For each Cl^- coverage, the substitution and insertion energies were calculated from the surface energies after substitution and after insertion. The graph below shows the variation of the substitution and insertion energies per chloride ion with increasing Cl^- coverage.



The substitution energy is positive (unfavorable process) and increases linearly with the Cl^- coverage. This trend is mainly due to the unfavorable repulsive electrostatic interaction between chloride ions; chloride ions being larger than hydroxyl ions. Thus substitution is not energetically favored on a perfect hydroxylated NiO(111) surface, and further substitutions are less likely to occur. This trend does not support a mechanism where high local concentrations of chloride ions initiate the corrosion process on perfect hydroxylated oxide surfaces, except if the potential is high enough to force Cl^- onto the surface.

For Cl^- coverages up to 0.75, the insertion process is energetically unfavorable, yielding a value of about 1eV per Cl^- inserted. For high concentrations of chloride ions on the surface, the substitution energy decreases rapidly, favoring the insertion process ($\Delta E_{insertion} \approx -4.1$eV for the full surface coverage of Cl^-). This severe drop in energy is attributed to the repulsive electrostatic interactions between the surface Cl^- ions: the repulsion is strong enough at the surface to make the insertion of an ion in the inner oxide layer favorable. These results show that in the event where high concentrations of chloride ions can be forced onto the NiO(111) surface, they set up appropriate conditions for the insertion of chlorides in the oxide lattice.

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