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Electrochemical dissolution of surface alloys in acids: Thermodynamic trends from first-principles calculations

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Abstract

A simple procedure is introduced to use periodic Density Functional Theory calculations to estimate trends in the thermodynamics of surface alloy dissolution in acidic media. With this approach, the dissolution potentials for solute metal atoms embedded in the surface layer of various host metals (referenced to the dissolution potential of the solute in its pure, metallic form) are calculated. Periodic trends in the calculated potentials are found to be related to trends in surface segregation energies of the various solute/host pairs. The effects of water splitting and concomitant hydroxyl adsorption on the dissolution potentials are also considered; these effects do not change the potentials for highly oxophilic solutes embedded in less active hosts, but they do decrease the dissolution potential for more inert solutes on oxophilic hosts. Finally, the dissolution of Pt "skin" layers from Pt_3X (X = Fe, Co, and Ni) bulk alloys is analyzed; the Pt skins are found to be stabilized compared to pure Pt.

Keywords: Leaching; Dissolution; Stripping; Surface alloys; Acids; Density functional theory; Underpotential deposition; Fuel cells

1. Introduction

The dissolution of metals in acidic environments has long been a problem of significant technological and scientific importance; such phenomena are known to play an important role in corrosion processes [1] and in the destabilization and/or the deactivation of electrocatalysts [2]. In addition, the microscopically reverse phenomenon, metal adsorption on metallic surfaces, can be of significance in processes such as electroplating and underpotential deposition [3–7]. In pure metals, the electrode potentials at which dissolution and stripping occurs have been known for years and are tabulated in the electrochemical series [8]. However, for many important electrochemical processes, and in particular for catalytic electrodes, the metals of interest are actually alloys. The dissolution of alloys above the so-called "critical potential" (during which cavities form in the material) is known as dealloying and is an active field of corrosion research [9,10]. However, systematic empirical data for alloy dissolution in the absence of cavity formation (the so-called subcritical region) are scarce. Hence, the development of a theoretical understanding of trends in metal alloy dissolution potentials in the subcritical region could be of some practical importance.

Surface alloys – alloys wherein solute atoms are embedded in the surface layer of a pure host metal (note that the host can also be referred to as the "substrate") – have recently begun to attract attention for use in electrocatalytic applications [11–15]. In spite of this increasing interest in their catalytic properties, however, relatively little information exists concerning the electrochemical stability and dissolution properties of these alloys; theoretical and experimental electrochemical research has traditionally focused on the study of metal adatoms prepared by underpotential deposition (UPD) [3–5,16–18]. In general, both the trends in dissolution properties and the electrocatalytic properties of surface alloys can be quite different from those of UPD-prepared materials. For example, a recent study of the hydrogen evolution reaction (HER) demonstrated that a BiPt surface alloy has an HER current that is significantly higher than the current of the underpotentially deposited Bi on Pt [19]. To select appropriate surface alloys to catalyze given electrochemical reactions, it would clearly be useful to have an

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understanding of the dissolution and stripping properties of such alloys.

Bulk alloys are another class of materials that could benefit from an improved understanding of metal dissolution trends. These alloys have many potential electrocatalytic applications (for example, Pt–Co and Pt–Ni are state-of-the-art catalysts for the oxygen reduction reaction [20,21]), and in spite of the fact that they have a well-defined bulk structure, they routinely exhibit unusual concentration profiles in the surface region. These surface profiles resemble the structure of surface alloys, and as such, the same principles that govern the dissolution potentials of surface alloys are expected to control the dissolution of the surface layers of the bulk alloys. Such dissolution phenomena can have a profound impact on the performance of the catalyst [2,22].

In this study, we present a simple formalism for estimating the potentials at which surface alloy dissolution becomes favorable. We concentrate here on the thermodynamic limit of such processes where vacancies created during dissolution have healed, and we show how to predict trends in dissolution potentials for solute atoms embedded in the surface layers of host substrates. We analyze the resulting trends in terms of the surface segregation energies of these surface alloys, and we demonstrate how the effect of water splitting and hydroxyl adsorption can be incorporated into the dissolution analysis. We close by indicating how the formalism can be extended to bulk alloys.

2. Methods

The DACAPO code [23] is used for all total energy calculations in this study. A four-layer slab, periodically repeated in a super cell geometry with six equivalent layers of vacuum between any two successive metal slabs, is used. A (2 × 2) unit cell is employed. All slabs are treated in their most stable crystal systems (fcc or hcp) with the exception of Fe, which is treated in an fcc system. Only the close-packed surfaces of the various metals are considered. The top two layers of the slab are allowed to relax until the total force on all atoms is less than 0.05 eV/Å in any Cartesian direction.

When adsorbed species are present, adsorption is allowed on only one of the two exposed surfaces of the metal slabs, and the electrostatic potential is adjusted accordingly [24]. Ionic cores are described by ultrasoft pseudopotentials [25], and the Kohn–Sham one-electron valence states are expanded in a basis of plane waves with kinetic energy below 340 eV; a density cutoff of 500 eV is used. The surface Brillouin zone is sampled with a 162(1 × 1) Chadi–Cohen **k** point grid. The convergence of the total energy with respect to the cutoff energies and the **k** point set is confirmed. The exchange-correlation energy and potential are described by the generalized gradient approximation (GGA-RPBE) [23]. The self-consistent RPBE density is determined by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi population of the Kohn–Sham states ($k_BT = 0.1$ eV), and Pulay mixing of the resulting electronic density [26]. All total energies have been extrapolated to $k_BT = 0$ eV. Spin polarization effects are included in the reported results for alloys in which naturally magnetized metals (Ni, Co, Fe) are present.

The binary transition metal surface alloys considered in this study consist of one solute atom alloyed into the surface unit cell of a substrate (a "host"). For solute "A" alloyed into the surface layer of host "B," the notation A/B is used to denote the surface alloy. All Group VIII and Group IB metals are included in the analysis. The solute coverage on these alloys is 0.25 ML. Although solute coverages in surface alloys can vary significantly from one system to the next [27], we do not expect calculated trends in alloy dissolution potentials to be a strong function of coverage. We have repeated the dissolution calculations for a subset of the considered systems at a solute coverage of 0.33 ML (all alloys except those containing metals from Group 8-VIII were repeated), and we found an average change of 0.03 eV in the magnitudes of the dissolution potentials compared to the 0.25 ML case.

The bulk alloy dissolution calculations are also done with 2 × 2 unit cells; in these calculations, both three and four atomic layers are used. The lattice constants of the slabs are optimized for the bulk alloy composition (see also description below), and all atoms of the slab are then fixed in their bulk-truncated positions. An 18(1 × 1) Chadi–Cohen **k**-point grid is employed, and planewave and density cutoffs of 340 and 500 eV are used, respectively. All calculations are performed spin polarized.

To determine cohesive energies for the pure metals, all lattice constants are optimized for a four-atom unit cell with the RPBE functional. A 10 × 10 × 10 Monkhort–Pack **k**-point grid is used for these calculations.

Adsorption energies for hydroxyl (OH) are estimated based on a simple database of oxygen (O) adsorption energies. The oxygen adsorption energies are evaluated on three-layer surface alloys at a solute coverage of 1/3 ML in the surface layer (for details, see, e.g., [28]). The oxygen adsorption energy is calculated on all top and bridge sites on each surface alloy of interest, and simple correlations (determined by computing both the hydroxyl and the oxygen adsorption energies on pure Cu, Ag, Pd, Ir, Rh, Au, Fe, Pt, and Ni at 1/3 ML coverage) are then used to estimate the hydroxyl adsorption energy. Correlations of $BE_{OH} = 0.51BE_O - 0.15$ and $BE_{OH} = 0.45BE_O - 0.28$ are used for the bridge and top sites; these correlations have average error magnitudes of 0.12 and 0.05 eV, respectively. To test the validity of these correlations for alloys, we calculated the hydroxyl binding energies on X–Rh surface alloys with Rh substrates using the same unit cell as was used for the atomic O calculations (X refers to the 11 elements, other than Rh, that were used in the present study). We considered OH adsorption at the X top sites in each alloy, together with adsorption at the X–Rh bridge sites. The average magnitude of the error of the correlations was 0.07 eV. Our neglect of threefold sites will introduce some additional errors into our analysis; although top and bridge sites are favored by OH on a number of metals, threefold sites can be favored in some cases [29,30]. On Cu(1 1 1), for example, we calculate that OH adsorbed at a threefold site is ∼0.05 eV more stable than is OH adsorbed at a bridge site. However, we do not expect errors of this magnitude to change our conclusions regarding the effect of hydroxyl on qualitative trends in dissolution potentials; the understanding of such trends is the primary purpose of this work.