



# Trapping of Hydrogen Absorbed in Aluminum during Corrosion



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## ARTICLE INFO

### Article history:

Received 22 February 2015  
 Received in revised form 30 March 2015  
 Accepted 30 March 2015  
 Available online 1 April 2015

### Keywords:

aluminum  
 corrosion  
 hydrogen absorption  
 hydride  
 hydrogen trapping

## ABSTRACT

A model for hydrogen capture in aluminum during aqueous corrosion is presented, incorporating near-surface trapping of H atoms at vacancies produced by metal dissolution. Vacancy-hydrogen interactions are described by a simple non-interacting thermodynamic model incorporating binding of multiple H atoms at vacancies, with energetics derived from first-principles calculations. At large absorption rates, submicron-thickness near-surface layers containing elevated vacancy-hydrogen defects concentrations are predicted, consistent with prior experimental observations. The defect layers arise because of the high sensitivity of the vacancy-hydrogen defect concentration to hydrogen chemical potential, owing to interactions of multiple H atoms with vacancies. Vacancy-hydrogen interactions therefore lead to self-concentration of hydrogen near corroding surfaces, at levels orders of magnitude higher than the H interstitial concentration. The elevated hydrogen concentration explains observations of hydride formation during corrosion, and may be relevant to hydrogen-based microscopic degradation mechanisms. The model predictions are quantitatively consistent with results of hydrogen permeation experiments.

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## 1. Introduction

Hydrogen absorption is a leading cause of degradation of metal structures, during gas-phase exposures and aqueous corrosion processes. Hydrogen absorption and transport in the metal influence kinetics of degradation, and thus incubation periods before fracture and crack propagation rates [1]. Quantitative models of hydrogen embrittlement include descriptions of hydrogen absorption and diffusion coupled to H-induced failure mechanisms [2]. Hydrogen diffusion in metals depends critically on reversible and irreversible trapping of H atoms at defects such as dislocations, precipitates, and vacancies [3–9]. In the case of the high purity aluminum-hydrogen system of interest here, hydrogen diffusion and thermal desorption measurements both suggest the importance of trapping by vacancies and dislocations [10]. Evidence for strong hydrogen interactions with vacancies in many metals has been obtained both experimentally [11–13], and through first-principles density function theory (DFT) calculations [14–19]. The equilibrium distribution of hydrogen among traps is governed by the hydrogen chemical potential ( $\mu_H$ ) or fugacity in the metal, along with the formation energies of the various hydrogen traps.

Aqueous corrosion processes can produce much larger hydrogen fugacity compared to gas-phase exposures, as a result of the very negative electrochemical potentials of active metals during dissolution. At high absorption rates, elevated  $\mu_H$  near the corroding surface can stimulate production of vacancy defects by metal dissolution [17]. Thermodynamic calculations show that complex vacancy-hydrogen defects are favored at high hydrogen chemical potentials, consisting of multiple hydrogen atoms bound to vacancies [15,16,18,19], or vacancy-hydride phases [12]. Results from H permeation experiments show that the hydrogen chemical potential in Al during alkaline corrosion is at least 0.5 eV relative to the ideal gas reference state, equivalent to an ambient hydrogen pressure of several GPa. [20]. According to thermodynamic analysis, trapping of multiple hydrogen atoms at vacancies should become increasingly important as  $\mu_H$  approaches 0.6 eV, producing elevated concentrations of trapped hydrogen [16,17,19]. Indeed, electrochemical measurements and Secondary Ion Mass Spectrometry (SIMS) analysis demonstrate extensive formation of aluminum hydride during alkaline corrosion, suggesting high near-surface hydrogen concentrations [21–24]. Also, analytical measurements detect elevated concentrations of hydrogen near crack surfaces, after testing of Al alloys in humid environments [25,26]. Self-concentration of hydrogen near crack surfaces might be an important factor in embrittlement mechanisms.

Models of hydrogen diffusion in metals have thus far considered only interactions of individual hydrogen atoms with traps, and therefore cannot predict high concentrations of hydrogen at

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corroding surfaces. Vacancy interactions with multiple hydrogen atoms should be included to accurately represent hydrogen diffusion and trapping, at the hydrogen chemical potentials present during realistic corrosion processes. This article describes a new model for hydrogen diffusion in aluminum during corrosion. The treatment of hydrogen trapping differs from previous models in that interactions of multiple hydrogen atoms with a vacancy are considered, using energetics from the DFT calculations of Ismer et al. [16]. However, interactions between defects are not included, leading to appreciable simplification. The model is tested by comparing its predictions to various experimental observations during alkaline corrosion of aluminum, including measurements of hydrogen chemical potential and hydride during the corrosion process [20,22,27,28]. It will be seen that the model captures experimental permeation transients, and also rationalizes observations of subsurface defect formation at high corrosion rates. Since other metals such as magnesium also exhibit strong vacancy-hydrogen interactions, the model may help rationalize hydrogen absorption and hydride formation in these systems [16,29].

## 2. Model

**Model description.-** The model depicts hydrogen absorption during uniform aqueous corrosion of a planar aluminum layer, envisioned as the hydrogen-transmitting membrane of a two-compartment permeation cell. The entry side of the layer is in direct contact with the corrosive solution. At this surface, anodic dissolution of aluminum at open circuit is accompanied by hydrogen formation through the accompanying cathodic water reduction reaction. Metal dissolution occurs at a constant rate limited by solution-phase mass transport [24]. A fraction of the cathodically generated hydrogen absorbs into interstitial sites, and diffuses into the metal. On the exit side of the membrane, the hydrogen chemical potential is sensed by a palladium film in contact with a non-aggressive pH-buffered solution [20].

Within the metal, hydrogen atoms dissolved at interstitial sites trap at lattice vacancies and dislocations. The equilibrium vacancy concentration is very small in the absence of dissolved hydrogen, but increases dramatically at high hydrogen chemical potential. It is envisioned that vacancies are introduced by metal dissolution, and then diffuse into the near-surface region, where they accumulate until the vacancy and hydrogen concentrations approach equilibrium. Equilibration of vacancies and hydrogen produces a highly defective region near the corroding surface, consistent with our earlier electron microscopy and positron annihilation spectroscopy findings [27,28]. Rather than attempting to model the details of metal atom diffusion in this defective layer, we simply assume that the vacancy concentration remains close to equilibrium at the local hydrogen concentration.

The interstitial and vacancy defects produced by hydrogen absorption would expand the metal lattice, and thus generate biaxial compressive stress along with elastic or plastic deformation [30]. The stress field can influence transport by altering the driving force for diffusion [6]. However, stress effects on diffusion are not included at the present exploratory stage of modeling. The stress field is largely determined by the volume changes accompanying the dominant trapping processes, which have not yet been resolved.

**Defect thermodynamics.-** Equilibrium concentrations of vacancy-hydrogen defects are calculated using the thermodynamic model of Ismer et al. [16]. The defect formation energies in this model are derived from DFT calculations in the Al-H system. The equilibrium concentrations of hydrogen interstitials and vacancy-hydrogen defects are calculated neglecting defect-defect

interactions. This non-interacting defect model is strictly valid in very dilute concentrations. However, in the present calculations it will also be applied to higher concentrations, in order to semi-quantitatively explore the implications of vacancy trapping at the elevated hydrogen chemical potentials that may characterize corrosion processes. Fully realistic calculations for high hydrogen chemical potentials would require new models accounting for aggregation of vacancy-hydrogen defects and hydride phases, as are found experimentally in many metal-hydrogen systems [12].

In the framework of the non-interacting defect assumption, concentrations of hydrogen interstitial and vacancy-hydrogen defects are related to the hydrogen chemical potential  $\mu_H$ . The hydrogen concentration at normal interstitial sites is

$$C_H = \frac{2}{\Omega} \exp\left(-\frac{E_{fH} - \mu_H + E_{zp}}{RT}\right) \quad (1)$$

where  $\mu_H$  is referenced to an isolated  $H_2$  molecule at 0 K. In Eq. (1),  $C_H$  is molar concentration,  $E_{fH}$  is the H interstitial formation energy,  $\Omega$  is the molar volume of metal atoms, and  $E_{zp}$  is the difference of zero-point vibrational energy between H atoms in Al and  $H_2$  molecules [16]. While the implied energy units in equilibria such as Eq. (1) are J/mol, defect energies and chemical potentials through this article are cited in the typical eV units. First-principles calculations suggest that vacancy-hydrogen defects in aluminum may be populated with as many as 12 hydrogen atoms, i. e. one in each of the tetrahedral interstitial sites neighboring the vacancy in the face-centered cubic lattice [15,16,19]. The concentration of vacancy-hydrogen defects containing  $n$  hydrogen atoms ( $V+nH$ ) is

$$C_{VH}(n) = \frac{S(n)}{\Omega} \exp\left[-\frac{E_{fV}(n) - n(\mu_H - E_{zp})}{RT}\right] \quad (2)$$

where  $S(n)$  is the number of configurations of the defect and  $E_{fV}$  is the defect formation energy. From Eqs. (1) and (2), the equilibrium constant for trapping of lattice hydrogen in the vacancy complex is

$$K_{VH}(n) = \frac{C_{VH}(n)}{C_H^n} = \frac{S(n)}{2^n} \exp\left(-\frac{E_{fV}(n) - nE_{fH}}{RT}\right) \quad (3)$$

The present calculations included  $V+nH$  defects with up to seven H atoms. Increasing  $n$  above 7 did not significantly change the predicted defect concentrations over the experimentally relevant  $\mu_H$  range. Table 1 lists values of defect trapping equilibrium constants determined from the defect formation energies of Ismer et al. [16]. Although the internal  $V+nH$  defects in Eq. (3) originate as surface vacancies produced by dissolution, surface vacancies are not considered explicitly because they are assumed to be in equilibrium with internal vacancies.

In addition to vacancy trapping, the model also includes first-order binding of H to dislocations, which significantly influence hydrogen diffusion in Al [10]. The concentration of H trapped at dislocations is taken as  $C_{HD} = K_{DH}C_H$ . Here, the dislocation trapping equilibrium constant is  $K_{DH} = \exp(-E_{bD}/RT)$ , where  $E_{bD}$  is the binding energy of H to a dislocation. This formulation does

**Table 1**  
Defect formation energies and equilibrium constants.

	$E_f$ (eV)	$K_{VH}(n)$ or $K_{DH}$
V+H	0.94	$2.01 \times 10^{-4}$
V+2H	1.30	116
V+3H	1.66	$3.98 \times 10^7$
V+4H	2.03	$6.05 \times 10^{12}$
V+5H	2.43	$1.96 \times 10^{17}$
V+6H	2.81	$9.64 \times 10^{21}$
V+7H	3.25	$3.14 \times 10^{25}$
Dislocation+H	0.189	1560

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