

# Nano-Mechanics of Pit Initiation on Metals and Alloys

Digby D. Macdonald

Department of Materials Science and Engineering, University of California at Berkeley,  
Berkeley, CA 94720

For more than forty years, the conditions for the existence of the passive state, and hence for the existence of our metals-based civilization, which is based upon the use of the reactive metals (Al, Cr, Fe, Ni, etc) to build machines, have been described in terms of equilibrium thermodynamics in the form of Pourbaix diagrams. These diagrams plot equilibrium potential versus pH relationships for various reactions (e.g., Fe/Fe<sub>3</sub>O<sub>4</sub>, Fe/Fe<sup>2+</sup>, Fe<sub>3</sub>O<sub>4</sub>/Fe<sup>2+</sup>) to define regions of stability or predominance. However, Pourbaix diagrams provide an equilibrium view of passivity, whereas passive films are non-equilibrium structures, whose existence depends upon an appropriate relationship between the rate of formation and the rate of destruction. Accordingly, a more accurate and realistic description of the phenomena of passivity and passivity breakdown must be found in the field of electrochemical kinetics. It is this kinetic theory for depassivation (loss of passivity) that is presented in this paper. It is shown that the kinetic theory for depassivation not only accounts for transpassive dissolution, acid depassivation, flow-assisted corrosion, and fretting corrosion, but it also led to the discovery of a new form of depassivation, which is termed “resistive depassivation”. When applied to microscopic regions on a metal surface, at which cation vacancies that are generated at the film/solution interface by the absorption of chloride ion into surface oxygen vacancies condense at the metal/film interface, and hence cause cessation of the growth of the barrier layer into the metal, “depassivation” theory provides a natural account of passivity breakdown. This paper will present the theory of passivity breakdown according to the point defect model and will show that the theory accounts essentially for all that is known about this important phenomenon.

# Emergent Piezoelectricity in Mono- and Bilayers of Inorganic Two-Dimensional Crystals

Karel-Alexander N. Duerloo<sup>1</sup>, Dr. Mitchell T. Ong<sup>2</sup>, Prof. Evan J. Reed<sup>1</sup>

<sup>1</sup>Stanford University, USA

<sup>2</sup>Lawrence Livermore National Laboratory, USA

Nobel Prize-winning work on graphene has placed atomically thin two-dimensional (2D) crystals at the focus of considerable research attention. The discovery of 2D crystals was groundbreaking because these materials possess several *emergent* properties that are not present in their bulk 3D parent crystal. 2D emergent properties include: exceptional mechanical strength, graphene's exotic electronic properties, and direct band gaps in transition metal dichalcogenides.

Our modeling work has discovered that piezoelectricity is an emergent property of many 2D crystals: BN, MoS<sub>2</sub>, MoSe<sub>2</sub>, MoTe<sub>2</sub>, WS<sub>2</sub> and WSe<sub>2</sub>. These atomically thin 2D crystals are piezoelectric, whereas their bulk parent crystals are not. This radically new notion of piezoelectric monolayers being isolated from an entirely non-piezoelectric 3D crystal suggests potential for intriguing electromechanical effects in the single- and few-layer regime.

In the single-layer case, our density functional theory calculations reveal that the piezoelectric coefficients of the studied 2D crystals are on par with commonly used 3D wurtzite piezoelectrics. Piezoelectric coupling in 2D crystals could have exciting implications for nanoscale piezotronics.

Piezoelectric effects also exist in the 2-layer case: we have studied a bilayer consisting of two BN monolayers and have found that flexural electromechanical coupling is yet another emergent property that is unique to the bilayer case. A BN bilayer can be seen as a cantilever-type heterostructure where one layer's strain is opposite from that of the other. This hints at the possibility of electrically controlling or sensing the curvature of a membrane that is only ~3 Å thick. More detailed analysis reveals that such a bilayer of BN amplifies piezoelectric displacements by a factor on the order of 10<sup>3</sup>-10<sup>4</sup>.

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## **Chemistry in the double layer: Implications for developing better microkinetic models in electrochemistry, corrosion research, and alloy design**

Santanu Chaudhuri, Aslihan Summer, Jie Xiao, Martin Losada

University of Illinois at Urbana-Champaign, Illinois Applied Research Institute, College of Engineering, Champaign, IL 61820

Intermetallic phases which are cathodic with respect to the alloy matrix are known to induce localized corrosion. Our research in search for a microkinetic model based first-principles guided multiscale modeling will be presented. Current computational approach at different length scales is somewhat segmented and remain unclear about connections to experimental work performed using rotating disk electrodes (RDEs) for unmodified electrodes and inhibited reaction kinetics. Need for a corrosion model that couples transport of ions through the electrochemical double layer (EDL) is an important input to the localized corrosion reaction on the cathodic precipitates. As a multiscale framework, progress in first-principles density functional theory (DFT) based calculations of the cathodic reactions on Cu surface and transport calculations using molecular dynamics simulations of the electrolyte adjacent to electrode surface will be discussed. A coupling between reaction kinetics on solvated electrodes and transport of reactive species such oxygen, hydroxyl and peroxy ions forms the basis for our microkinetic model. Moreover, alloy surfaces undergo segregation and morphological changes which alters electrode surface area and active site densities. Our ongoing effort in understanding energetic preference for segregation in binary and ternary cathodic precipitates will be briefly presented for underscoring the challenges for obtaining microstructures based kinetic insights on corrosion in metal alloys using a multiscale model. Finally, for understanding RDE experiments, analyzing the electrochemical reactions under solvent flow (basis for Levich Equation) is important. Our microscale model can incorporate solvent flow and the effects on the ionic equilibria. However, polarization of the double layer and changes in the ordering in the electrolyte layers which changes transport is poorly understood. Especially, classical force fields need polarizable framework to obtain reasonable agreements with experimental data for transport coefficients. A comparison with Cu RDE experiments will be presented to explain the current state-of-the-art in force field development and challenges in modeling reactions in the double layer under potentiodynamic conditions.

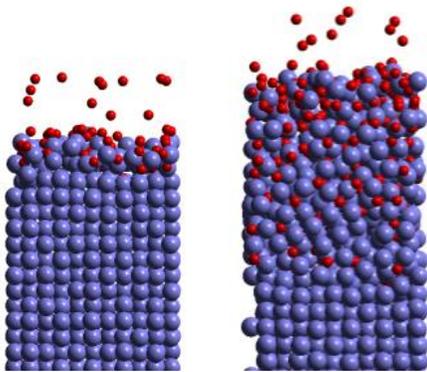
# Ionic motion during field-assisted oxidation of aluminium studied by molecular dynamics simulations

Astrid Gubbels-Elzas, Barend J. Thijsse

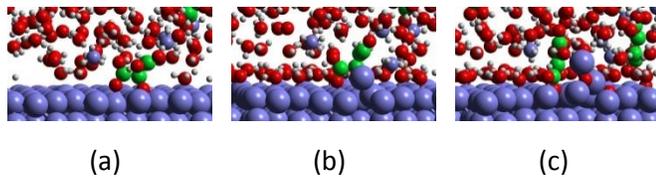
Department of Materials Science and Engineering, Delft University of Technology,  
The Netherlands

Molecular dynamics simulations with the REAX force field were performed to model the growth of an oxide layer on (100)-oriented aluminium in three different oxidation environments: atomic oxygen gas, liquid water, and an aqueous ammonium tartrate solution. The anodizing behaviour was studied at two different temperatures (300 K and 600 K), in the absence of an external electric field and with field strengths of 0.5 to 2.0 V/Å applied over the growing oxide. Figs. 1 and 2 show representative snapshots. The aim of this study is to determine how the ion motion in the oxide layer is affected by such an applied anodizing potential and by the oxidizing medium.

The principal findings are: (1) O and Al ions move through the oxide via interrupted sequences of short replacement steps rather than as a continuous motion across the oxide, (2) dissociation of H<sub>2</sub>O molecules at the surface is crucial, and (3) the dependence of the ion motion on the electric field strength exhibits steps in the growth behaviour.



**Figure 1:** Configuration at 1000 ps for oxidation of Al in atomic oxygen gas at 300 K without an electric field (left) and at 600 K with a field of 2V/Å (right).



**Figure 2:** Tartrate ion (green) pulling Al atoms out of the surface and thereby assisting the growth of oxide.

**Colours:** blue=Al, red=O, grey=H, green=C, small blue=N.

# The Volcano of Hydrogen Pickup in Zirconium Alloys Explained by p-type Doping of the Passive Oxide Layer

Mostafa Youssef, Bilge Yildiz

Massachusetts Institute of Technology, Massachusetts 02139, USA

Hydrogen pickup in zirconium alloys is a prominent challenge in front of the design of these alloys for fuel cladding in nuclear reactors. In 1960 a volcano-like relationship was identified between the fraction of hydrogen picked up in zirconium alloys and the 3d transition metals that are typically used to alloy zirconium. The peak of the volcano was found to be coincident with Nickel [1]. This empirical observation was used subsequently in the design of zirconium alloys without a physical understanding of its origin. Here we establish using a combination of density functional theory (DFT) calculations and thermodynamic analysis that the origin of this volcano is the variation in the ability of the 3d transition metals to p-type dope  $ZrO_2$ . The latter is the passive the layer that grows natively on zirconium alloys.

By modelling the defect equilibria in  $ZrO_2$  co-doped with hydrogen and a transition metal, one at a time, we computed two metrics related to hydrogen pickup. The first is the solubility of hydrogen in  $ZrO_2$  as a function of the transition metals. This metric exhibits a volcano-like relationship with the 3d metals similar to the one identified experimentally but the peak is coincident with Co. The second metric is the equilibrium chemical potential of electrons (Fermi level) in the co-doped  $ZrO_2$  as a function of the transition metals. We found out that this metric exhibits a mirror image of the volcano with the minimum at Co as well. That is, Co is the element that achieves the most p-type doping of  $ZrO_2$  among the 3d metals. It turns out that p-type doping lowers the formation energy of interstitial proton which, in turn, increases the solubility of hydrogen in  $ZrO_2$  giving rise to the volcano of hydrogen solubility.

Beyond the above thermodynamic picture, there is a kinetic incarnation for these results. Lowering the chemical potential of electrons (p-type doping), increases the activation barrier for the electron transfer from  $ZrO_2$  to the protons adsorbed on its surface. These protons are byproduct of water splitting. This electron transfer is needed to reduce the protons, form  $H_2$  molecules, and avoid picking up hydrogen. Thus, p-type doping both increases the solubility of hydrogen in the bulk of  $ZrO_2$  and obstructs the reduction of protons on the surface of  $ZrO_2$ . The two effects synergistically lead to picking up hydrogen into  $ZrO_2$  and the underlying zirconium alloy.

This physical understanding opens the route for physics-based design of hydrogen pickup-resistant zirconium alloys.

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## **Multiscale Corrosion Modeling and Computational Design of Aerospace Coatings Systems**

E. Sapper<sup>1</sup>, I.S.Cole<sup>2</sup>, M. Breedon<sup>2</sup>, C. Chu<sup>2</sup>, F. Chen<sup>2</sup>, M. Chen<sup>2</sup>, J. Osborne<sup>1</sup>

<sup>1</sup>BOEING RESEARCH & TECHNOLOGY

<sup>1</sup>PO Box 3707, Seattle, WA, USA, 98124

<sup>2</sup>CSIRO

<sup>2</sup>Private Bag 33, Clayton South, Victoria 3169

A multiscale model is being developed which connects aspects of aerospace material corrosion and performance at all relevant length scales, from atomistic corrosion mechanisms and metallic microstructures to in-flight exposure conditions determined by flight path, global wind patterns, and ocean currents releasing aerosolized electrolyte into the environment.

The complete multiscale model links a wide range of individual modules together, each residing in different length and time scale regimes. The model provides a means of assessing the impact of atomistic and molecular mechanisms such as species transport and adsorption, as well as component surface morphology, on the predicted service lifetime of an aerospace material, and will have significant impact in the design of protection systems for future aircraft. This presentation will focus on the design and decision-making aspects of the work, including exercising the model for existing and novel system for corrosion prevention.

# Prediction of Crack Growth Rate in Type 304 Stainless Steel Using Artificial Neural Networks and the Coupled Environment Fracture Model

Jiangbo Shi<sup>1,2</sup>, Jihui Wang<sup>1</sup>, Digby D. Macdonald<sup>2</sup>

<sup>1</sup>School of Materials Science and Engineering, Tianjin University, Tianjin 300072, P. R. China;

<sup>2</sup>Department of Nuclear Engineering, University of California at Berkeley, Berkeley, CA 94720, USA

It has long been recognized that intergranular stress corrosion cracking (IGSCC) in sensitized stainless steels reflects complex interactions between stress, material properties, and environmental parameters. This complexity can lead to significant scatter in the crack growth rate (CGR) that, in turn, leads to difficulties in predicting CGR with the desired engineering accuracy under any given set of conditions. In the present work, a crack growth rate database has been established from data reported in the literature and an artificial neural network (ANN) was developed having linear and sigmoid transfer functions. The ANN aims at predicting the CGR in sensitized Type 304 stainless steel and to delineate the dependencies of the CGR on each of the principal independent variables of the system (i.e. temperature, conductivity, stress intensity, degree of sensitization, electrochemical potential, and pH) using back propagation error minimization. The ANN revealed the underlying relationships that map the dependencies of the dependent variable (CGR) on the various input independent variables. A sensitivity analysis using the trained ANN establishes that IGSCC in sensitized Type 304SS in high temperature (288°C) aqueous environments is primarily electrochemical in character. The coupled-environment fracture model (CEFM), which is a deterministic, physico-electrochemical model for predicting crack growth rate, was customized to take into consideration the impact of the degree of sensitization on crack propagation rate and was then used to predict IGSCC CGR in Type 304 stainless in simulated Boiling Water Reactor (BWR) primary coolant circuits. Comparison of the ANN-predicted CGR and the CGR predicted by the CEFM as a function of the independent variables reveals good agreement between these two approaches.

## Growth and breakdown of iron sulfide passivating corrosion films: Towards a mechanistic, multiscale model

Aravind Krishnamoorthy<sup>1</sup>, F. William Herbert<sup>1</sup>, Bilge Yildiz<sup>2</sup>

<sup>1</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge MA 02139

<sup>2</sup>Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge MA 02139

In sour (H<sub>2</sub>S-containing) environments relevant to the oil & gas industry, the corrosion of steel components is partially inhibited by the formation of passivating, iron sulfide-containing films. Acting as a barrier layer, these films control metal loss but are susceptible to localized breakdown which can lead to catastrophic failure through pitting corrosion. Due to challenges in the characterization of these sulfide films, even fundamental mechanistic information such as the nature of the rate controlling unit process is not conclusively known [1]. Therefore, susceptibility of materials to failure in these critical systems is quantified largely using empirical formulae that have little basis in the mechanism of sulfide corrosion [2].

In this study, we present a multiscale model for the growth and breakdown of iron sulfide passive films based on the elementary unit processes of electron- and ion transfer reactions. The relative kinetic rates of these processes depends on a host of factors including system temperature, activity of sulfur and film thickness, necessitating the use of a multiscale model that can span all the requisite time scales. Our model couples activation barriers for surface reactivity calculated *ab initio* using Density Functional Theory (DFT) simulations and mesoscale diffusivity of Fe<sup>2+</sup> ions in the iron sulfide film calculated using kinetic Monte Carlo (kMC). The calculated activation barriers are validated with experimental results from the authors' work and literature. We also provide a mechanistic pit initiation model adapted from the well-known Point Defect Model [3]. Taken together, these two results lead to a more deterministic description of the growth and degradation kinetics of sulfidic passive films on iron.

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