

Mechanics Controls Catalysis (Sometimes)

M. F. Francis^{1,2}, W. A. Curtin¹

¹École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

²Brown University, Providence, Rhode Island, United States

The control and optimization of catalytic processes is a key goal in many technologies. Here, we demonstrate via computation that the application of mechanical stress can modify chemisorption energies at stepped surfaces, and thus catalytic activity, in ways not previously envisioned. Specifically, compressive stresses can induce stronger binding of chemical species at steps, which is the opposite of the well-established trend found on close-packed surfaces. The mechanism driving this new stress effect is shown to be the mechanical relaxation of the deformed material during chemisorption, which can be larger, and of the opposite sign, than the electronic effects due to changes in the d-band structure. Application of stress can thus simultaneously shift binding energies on steps up (or down) and on terraces down (or up), and potentially increase overall catalytic activity in wide classes of systems. These trends can be rationalized using the theory of elasticity, and suggest multiscale approaches for efficiently predicting stress effects on binding energies without full quantum calculations.

Strain Effects on Defects and Diffusion in Perovskites

Dane Morgan¹, Tam Mayeshiba¹, Yueh-Lin Lee¹, Milind Gadre¹, Anh Ngo¹, Yang-Shao Horn², Stuart Adler³

¹University of Wisconsin, Madison, WI 53706, USA

²Massachusetts Institute of Technology, Cambridge, MA 02139, USA

³University of Washington, Seattle, WA 98195, USA

Oxygen active materials are capable of actively incorporating and transporting oxygen through their bulk. Such materials are of interest for a wide range of applications, from solid oxide fuel cells to gas separation membranes to chemical looping. Recent work has shown that strain can play a significant role in altering the transport of oxygen through oxygen active materials, particularly in fluorite structured compounds. However, transition metal perovskites are an important class of oxygen active materials that have received only limited attention. In this work we use ab initio methods to model the coupling of strain and defect formation and migration energetics in a range of transition metal perovskites. We explore the formation volumes of oxygen vacancies and demonstrate how their sizes arise from a combination of local bond breaking and electron donation. We further find that the oxygen transport can be enhanced by orders of magnitude through tensile strain effects. Comparison is made to recent experimental results from Kubicek, et al. on (La,Sr)CoO₃ [1] and excellent agreement is found. We demonstrate that a simple strain model can qualitatively explain the ab initio results but with significant quantitative discrepancies.

We gratefully acknowledge financial supported from the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award number DE-SC0001284, NSF Graduate Fellowship Program under Grant No. DGE-0718123, and computing support from NSF National Center for Supercomputing Applications (NCSA - DMR060007).

[1] Kubicek, M., Cai, Z., Ma, W., Yildiz, B., Hutter, H., & Fleig, J. (2013). Tensile lattice strain accelerates oxygen surface exchange and diffusion in La_{1-x}Sr_xCoO_{3-δ} thin films. *ACS Nano*, 7(4), 3276–86. doi:10.1021/nn305987x

An *ab initio* investigation of the stability of ZnO in an electrochemical environment

Mira Todorova, Jörg Neugebauer

Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str. 1, 40237 Düsseldorf,
Germany

Theoretical and modeling concepts in semiconductor defect chemistry and electrochemistry have hugely evolved over the last years and are crucial for their respective fields such as optoelectronics and semiconductor devices or corrosion and battery materials. Despite being based on the same fundamental building blocks - charged defects/ions - the underlying theoretical concepts and communities have little overlap. To bridge the gap we have recently developed a unified approach that is based on a fully grand-canonical description of both ions and electrons and that connects and “translates” the respective concepts [1].

Our method links *ab initio* calculations quite naturally to experimental observables, such as the pH-scale and the electrode potential, which determine and characterise the state of an electrochemical system. Employing this approach provides surprising new insight into apparently “old” problems such as water stability, opens new routes to construct electrochemical phase (Pourbaix) diagrams, and gives a handle to an absolute alignment of electrochemical potentials. Applying the approach to ZnO, we will discuss the impact of an electrochemical environment on the stability of native bulk point defects as well as on the stability of the polar Zn terminated ZnO(0001) surfaces.

[1] M. Todorova and J. Neugebauer, Phys. Rev. Applied. 1, 014001 (2014).

A Multi-Scale Study of the Chemo-Mechanical Behavior of Battery Materials

Feifei Fan, Ting Zhu

Georgia Institute of Technology, USA

High-capacity lithium-ion batteries are critically important for a wide range of applications, from portable electronics to electric vehicles. However, they cannot meet requirements for more demanding applications due to limitations in capacity, charging rate, and cyclability. One leading cause of such limitations is the mechanical degradation and associated capacity fading in electrodes during charging/discharging processes. In this work, we use multi-scale simulations to study the chemo-mechanical responses of electrode materials including morphological evolution and stress generation. We will show how the chemical reactions lead to mechanical failures in electrode materials from atomistic scale to continuum scale. The results provide insights into chemical-reaction-induced microstructural evolution in nanomaterial electrodes, and have implications for an optimization of electrode design in next generation lithium-ion batteries.

Effect of Dislocations on the oxygen ion conductivity in reduced and doped Ceria

Lixin Sun, Dario Marrocchelli, Mostafa Youssef and Bilge Yildiz

Department of Nuclear Science and Engineering, Laboratory for Electrochemical Interfaces,
Massachusetts Institute of Technology, 24-210, 77 Massachusetts Avenue, Cambridge 02139,
USA

Enhancement of ionic conductivity in thin films or multilayers of oxide materials, i.e. doped zirconia and ceria, has sparked great interest in the search for fast ion conducting structures for fuel cells. The enhancement in ionic conductivity in such structures could be attributed to elastic strain arising from the lattice mismatch at the interface. However, this assumes that the interface between two materials is perfectly coherent, while in most cases dislocations are observed, which relax the interfacial elastic strain. The strain field and the electrostatic field that arises from the dislocations can also impact the defect stability, distribution and mobility in these materials; and yet, the role of dislocation on the ionic conductivity is not consistently reported in the literature nor is it clearly understood [1-3]. The aim of our work is to quantitatively assess the dislocation's influence on the ionic conductivity, especially in fluorite oxides by computer simulations.

A $1/2\langle 110 \rangle\{100\}$ edge dislocation in reduced or doped ceria is studied by atomistic simulations with Born's model of potential. The atomistic structure is equilibrated by a hybrid algorithm combined the Monte Carlo and Molecular Dynamics simulations [5]. Starting from a uniform distribution of dopant cations and oxygen vacancies, the system is relaxed by rearranging the dopant cations and vacancies to find the most stable distribution of cations. Molecular Dynamics calculations are employed to study the transport properties of the dislocation system.

Asymmetric distribution profiles of dopant cations and oxygen vacancies were found upon after relaxation as a result of the strain field of the dislocation and also the association between dopant cations and oxygen vacancies due to elastic and electrostatic interactions. Dopant cations and oxygen vacancies enrich at the tensile strain field around the dislocation, while a depletion zone of dopants and oxygen vacancies is equilibrated on the compressive region around the dislocation. This is because the dopant cation (usually bigger than the host cation) is easier to be accommodated at the tensile region than the compressive region, and this is followed by the electrostatic attraction of vacancies to the zone enriched by aliovalently charged cations. As opposed to the speculations that regard dislocations as fast diffusion paths, the $1/2\langle 110 \rangle\{100\}$ type edge dislocation was actually found to impede oxygen transport in these doped and reducible oxides. The ionic conductivity in ceria has a non-linear dependence on the dopant concentration, with a maximum at 8-10 % concentration of dopants. Therefore, both the high concentration (>20%) of dopants in the enrichment zone and the low concentration (< 5 %) in the depletion zone around the dislocation impede oxygen transport and reduce the local ionic conductivity. Our work demonstrates that dislocations can significantly change the distribution and mobility of dopant cations and oxygen vacancies, and their effects must be considered in quantitatively interpreting the experimental results aiming to assess the effects of strain in oxide ion conductivity.

[1] M. Sillassen et al., *Adv Funct. Mater.* 20 2010

[2] C. Korte et. al., *Phys Chem Chem Phys* 10 2008

[3] I. Kosacki et al., *Solid State Ion* 176 2005

[4] H. B. Lee, F. B. Prinz and W. Cai, *Acta. Mater.* 58 (2010) 2197

First-Principles Study of Oxygen Reduction Reaction on Bulk Metallic Glasses

Zhengzheng Chen and Gang Lu

Department of Physics & Astronomy
California State University, Northridge, California 91330, USA

Pt or Pd-based bulk metallic glasses (BMGs) are promising candidates for electrocatalysts in fuel cells due to their outstanding durability and structural controllability [1]. In particular, unlike conventional metallic catalysts, BMGs can sustain high strains - without nucleation of dislocations to relax the strains - that can be used to tune their catalytic activities. However, it is very challenging to characterize the catalytic activities of BMGs and to optimize their chemical compositions experimentally. Here we report the first computational effort to study stress-dependent oxygen reduction reaction (ORR) on Pd-based BMGs from first-principles.

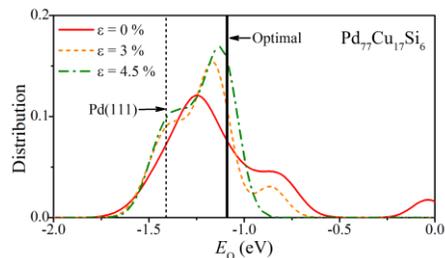


Figure 1: Distribution of binding energy (E_O) of Pd₇₇Cu₁₇Si₆ BMG under different biaxial strains

Two chemical compositions of BMGs - Pd₇₇Cu₁₇Si₆ and Pd₇₇Cu₆Si₁₇ are examined in this work. The oxygen binding energy (E_O) on the surface is used as the descriptor for the ORR activity [2]. Owing to the amorphous nature of BMGs, a statistical analysis is necessary to characterize the ORR performance of BMGs. For example, the distribution of E_O exhibits a finite broadening, and is sensitive to the local chemical environments on the surface. It is found that local Si-rich environment is detrimental to ORR activity whereas local Cu-rich environment is beneficial to ORR performance. Detailed analysis on

E_O distributions reveals that there is an optimal Si content for superior ORR activity. The effect of stress on ORR activity is examined as well and compression stresses are found to enhance ORR activity.

This work was sponsored by the Army Research Office – Multidisciplinary University Research Initiative under Contract W911NF-11-1-0353. We acknowledge Sharvan Kumar and Yiyi Yang for fruitful discussions.

[1] M. Carmo et al, ACS Nano **5**, 2979 (2011).

[2] J. K. Nørskov et al, J. Phys. Chem. B **108**, 17886 (2004).

Role of solvation dynamics in influencing nanoscale corrosion and passive oxide breakdown

Subramanian K.R.S. Sankaranarayanan¹, Sanket A. Deshmukh¹ and Shriram Ramanathan²

¹Center for Nanoscale Materials, Argonne National Laboratory, Argonne IL-60439

²School of Engineering and Applied Sciences, Harvard University, Cambridge MA-02138

Pitting corrosion, a common form of electrochemical corrosion, occurs due to halide ion interaction with metal surfaces and is typically initiated at a lattice defect site. Although continuum theories have looked at possible pathways for pitting initiation in the metal/oxide environment, atomistic understanding of the role of solvent condition and solvation dynamics on electrochemical corrosion phenomena could advance our understanding further of this important problem. We perform an all atom reactive molecular dynamics simulation to probe the influence of chloride ion concentration on the local structure and dynamics of interfacial water near a passive oxide surface. Using representative example of MgO-Cl-water and FeO-Cl-water system, these simulations are being utilized to study electrolyte adsorption, solvation behavior and surface speciation on the passive oxide surfaces in the presence of aqueous media. Na⁺ and Cl⁻ ions with varying concentration are incorporated into the simulation cell to examine the ionic distribution in the near surface region of the oxide film and evaluate the role of solvation dynamics on Cl⁻ adsorption. Proximity effects on water molecules (H₂O) near a passive oxide surface at room temperature are evaluated based on various structural and dynamical correlation functions. In an aqueous environment without any chloride ions, we find significant ordering of water molecules in the two layers close to the oxide interface. The extent of ordering decreases with increasing distance from the oxide-water interface. Our simulations suggest that interfacial ordering is strongly correlated to the Cl⁻ concentration; a non-monotonic variation is observed with the extent of ordering decreasing strongly above a threshold Cl⁻ concentration. Subsequent studies will aim at correlating solvation dynamics with near-surface oxide layer stoichiometry, point defect concentration, passive oxide density and composition. The findings could provide insights into the role of solvation dynamics in influencing aqueous corrosion phenomena.

Acknowledgement: Use of the Center for Nanoscale Materials was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357

Diagnosis of the Mechanism of Anodic Oxide Film Growth on Platinum in H₂SO₄

Feixiong Mao^{1,2}, Samin Sharifi-Asl², Digby D. Macdonald²

¹ School of Materials and Metallurgy, Northeastern University, Shenyang 110819, China

² Department of Materials Science and Engineering, The University of California at Berkeley, Berkeley, CA 94720

Diagnostic criteria for the growth of the anodic oxide film on platinum in H₂SO₄ are reported. The criteria apply to the generalized High Field Model, which postulates that the electric field within the film is dependent upon the applied voltage and film thickness, and the Point Defect Model, which describes the electric field as being constant during film growth. The constancy of the electric field in the passive film on platinum, as demonstrated in this work, is attributed to band-to-band Esaki tunneling, which buffers the electric field against changes in the applied voltage and film thickness. In this paper, we apply an analytical analysis of the oxide film growth transient on platinum in H₂SO₄ and demonstrate, unequivocally, that the PDM provides a superior theoretical framework than does the HFM for interpreting oxide film growth on platinum. Importantly, the criteria have been shown theoretically to apply to metal interstitial conduction, which is the mechanism of conduction in the HFM and in the PtO oxide film on platinum, rather than being restricted to oxygen vacancy conductors, as originally derived.