Investigation of Localized Corrosion and the Role of Transport in Lightweight Alloys using Microkinetic Models with First-principles Link

Jie Xiao[2], Aslihan Sumer[1], Martin Losada[1], and Santanu Chaudhuri[*]

[1]ISP/Applied Sciences Laboratory, Washington State University, Spokane Technology Center
120 N. Pine St. Spokane, WA 99202

[2]College of Chemistry, Chemical Engineering and Materials Science, Soochow University
199 Ren-Ai Rd., Suzhou Industrial Park, Suzhou, Jiangsu 215123, China

Intermetallic phases which are cathodic with respect to the alloy matric are known to induce localized corrosion. Our research in search of a microkinetic model is dependent on a number of important processes that have been identified in recent experimental work. 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. The interrelationship between them, however, is still poorly understood. Attempts at calculating the transport and the reaction in a coupled framework is complex. The main objective of this work is to identify theories that can scale from atomistic to continuum models for the corrosion. In addition, a microkinetic model such as the one that will be discussed considered the cathodic coupling with alloy matrix and incorporates different cathodic precipitates. We will discuss a hierarchical model where values calculated are scaled from atomistic calculations to a coupled corrosion kinetics model to elucidate the role of corrosion. For reactions at the surface, we use first-principles density functional theory (DFT). For transport, we use nanoscale molecular dynamics simulations, and couple the calculated rate constants in microscale using Nerst-Planck electrodiffusion at the alloy interface including explicit g arbitrary Lagrangian Eulerian (ALE) treatment of localized corrosion/dissolution that leads to pitting.

The first order of modeling is a coupled model of cathodic kinetics at the alloy interface. It included the transport of species in dilute electrolyte and more ordered EDL where dissolution-diffusion are coupled during the corrosion process. For example, the S-phase surface in Al-2024 alloys undergoes Mg-dissolution and Cu de-alloying. As a result, the cathodic reactions are closely coupled to the diffusion process where loss of Mg^{2+} in NaCl electrolyte in related to the mechanism and energetics of possible chemical reactions between dissolved oxygen and other surface adsorbates such as H_2O, OH, OOH, etc. The situation is slightly different for the so-called θ-phase (Al_2Cu) in Al-2024 an related alloys. In this case, the Cu de-alloying makes the surface stable and Cu-like. We calculated the relative kinetics of S- and θ-phase as cathode, and found the root cause as to why S-phase is more cathodic in comparison to the θ-phase (Figure 1a). Calculation of all reaction rates and diffusion constants in such a complex microkinetic model for localized corrosion is difficult. So, we have only calculated some key reactions and diffusion constants. Some key relations between transport and reactions during localized corrosion are be experimentally verified. Thus, the microkinetic model of localized corrosion

proposed has validation abilities with corrosion under immersion condition in dilute NaCl solution.

However, beyond the free corrosion condition, potentiodynamic conditions can change the assumptions of such models for corrosion kinetics significantly. The electrode polarization leads to the polarization of the EDL. In addition, the reactions from solvated electrons can only be treated using more computationally expensive time-dependent theories such as TD-DFT. We will briefly discuss the challenges of such higher-level theories providing feedback to our current model and what needs to be resolved to calculate the role of EDL in modifying transport at the polarized cathodic/anodic interface. One important governing relationship between the potential of metal M at zero charge and chemically polarized solvent molecules is follows:

$$E_{\sigma=0}^{M} = \phi_{hkl}^{M} + \delta_{\chi}^{M} - g^{S}(dip)_0 + const$$

where $g^{S}(dip)_0$ is the potential drop due to any preferentially oriented and chemically polarized solvent molecules, δ_x^{M} is a dipole term accounting for the polarization of the metal surface in the presence of the solvent and const is a constant term depending on the reference electrode. We have calculated the polarization of oxygen molecule on a surface (Figure 1b) in presence of a solvation sphere and in presence of electrolytes. The significance of applied electrode potential and adsorbate density will be discussed. Overall, the challenges of modeling transport near electrode surface shows some important advances with positive implications for corrosion and battery research.
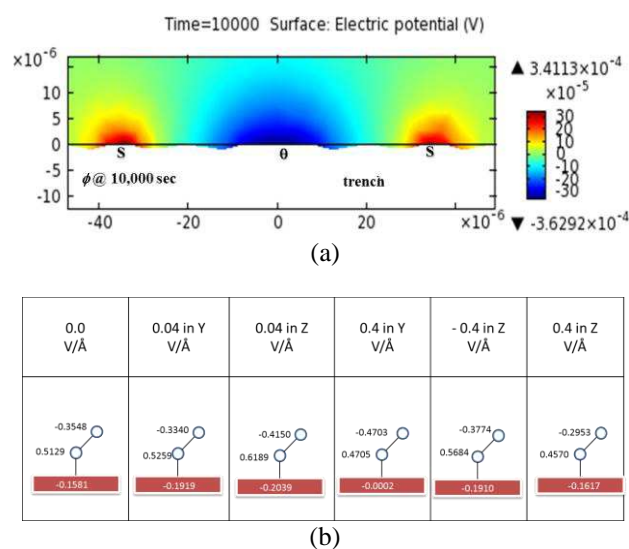

(a)

(b)

Figure 1: (a) The calculated relative cathodic nature of θ- and S-phase calculated using our model, and (b) the charge on an O_2 molecule adsorbed on a dealloyed cathodic precipitate.

References

1. Xiao, J.; Chaudhuri, S. Predictive modeling of localized corrosion: An application to aluminum alloys Electrochimica Acta **2011**, 56, 5630.